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Canada
DINERIE, BIS(DIPHENTYLPHOSPHINO) METHANE COMPLEXES
OF RHODIUM

by

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A Thesis
Submitted to the Faculty of Graduate Studies in Partial
Fulfillment of the Requirements for the Degree of

DOCTOR OF PHILOSOPHY

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March 1984
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ABSTRACT

Bis[(diphenyl)phosphino)methane (dpbm) has proven to be an extremely versatile ligand, capable of holding two metal centres in close proximity under various conditions. As a result of the inherent flexibility of dpbm, a number of unique chemical reactions involving both metals has been observed.

This thesis deals with the synthesis of a variety of binuclear, dpbm bridged complexes of the general formula, 

$$[\text{Rh}_2(\mu-X)(\text{CO})_2(\mu-dppm)]^{n+} \ [X = \text{OH, Cl} \ (n=0), \text{OCH}_3, \text{OC}_2\text{H}_5, \text{OH, Br, I, NCS, N}_3, \text{NCO}, \text{O}_2\text{CR} \ (R = \text{H, CH}_3, \text{CH}_2\text{Cl}, \text{CHCl}_2, \text{CCl}_3 \text{and CF}_3) \ (n=1)]$$

and their reactions with small molecules. Two members of this series, $X = \text{OH, Cl}$ and $\text{O}_2\text{CCF}_3$ have been structurally characterized.

Reactions of the complexes possessing A-frame geometry ($X = \text{OH, Cl, OCH}_3, \text{OC}_2\text{H}_5, \text{OH, Br, I, NCS, N}_3, \text{NCO}$) with carbon monoxide and sulphur dioxide have been examined and, except in the case of $X = \text{Br}$ and $I$ those reactions that occurred involved the bridgehead ligand. As an example, the reaction of $[\text{Rh}_2(\mu-NCS)(\text{CO})_2(\mu-dppm)]^{2+}$ with carbon monoxide gave a bridging cyanide complex, $[\text{Rh}_2(\mu-CN)(\mu-\text{CO})(\text{CO})_2(\mu-dppm)]^{2+}$-CIO$_4$. This complex proved to be fluxional and to possess an unusual $\sigma-\pi$ bridging cyanide ligand which undergoes "wind shield wiper" type motion in solution even down to $-80^\circ \text{C}$.

The reaction of $[\text{Rh}_2(\mu-\text{OR})(\text{CO})_2(\mu-dppm)]^{2+}$ (R = H, CH$_3$ and C$_2$H$_5$) with carbon monoxide gave an unsaturated 46 electron cluster, $[\text{Rh}_3(\mu-\text{CO})_3(\mu-1,2-dppm)]^{2+}$CIO$_4$.CH$_2$Cl$_2$ whose structure resembles that of a doubly bridged A-frame complex, with Rh(CO)$_3$ as the bridgehead ligand. The terminal carbonyl on the bridging rhodium was substitutionally labile.
and could be replaced by a wide variety of phosphines (PPh₃, PMePh₂, PEt₃ and η₁-dppm). A rationale is proposed for the stability of this cluster by comparison to the expected 48 electron species [Rh₃(CO)₇(µ-1,2-dppm)₂]ClO₄.

The reactions of the carboxylate bridged complexes, [Rh₂(µ-O₂CR)(CO)₂(µ-dppm)₂]ClO₄ with carbon monoxide, dihydrogen/carbon monoxide (1:1), halogens and terminal acetylenes have also been examined. Reactions with carbon monoxide, dihydrogen/carbon monoxide (1:1) and halogens yielded complexes, [Rh₂(µ-CO)(µ-O₂CR)(CO)₂(µ-dppm)₂]ClO₄ (R = CH₂Cl, CHCl₂, CCl₃, CF₃), [Rh₂(µ-H)(µ-CO)(CO)₂(µ-dppm)₂]ClO₄ and [Rh₂(µ-O₂CR)X₂(CO)₂(µ-dppm)₂]ClO₄ (R = H, CH₃, CF₃; X = Cl, Br, I) respectively. [Rh₂(µ-CO)-(µ-O₂CCF₃)(CO)₂(µ-dppm)₂]ClO₄ has been structurally characterized. Reacting the carboxylate complexes, [Rh₂(µ-O₂CR)(CO)₂(µ-dppm)₂]ClO₄ (R = CH₂, CF₃) with terminal acetylenes, R'C₆H₂(R' = H, Ph and tBu (R = CF₃ only)) resulted in the formation of the σ-τ bridging acetylide complexes, [Rh₂(µ₂-η²-C₂R')(CO)₂(µ-dppm)₂]ClO₄. One member of this series, R' = tBu has been structurally characterized to confirm this bridging mode. Reactions of the acetylide complexes with carbon monoxide, sulphur dioxide, hydride, phosphines and dihydrogen/carbon monoxide (1:1) have been investigated.
LIST OF ABBREVIATIONS AND SYMBOLS

Anal. - Analysis
acac - acetylacetonate anion
Calc. - Calculated
COD - 1,5-cyclooctadiene
Cy - cyclohexyl
dm - doublet of multiplets
DMAD - dimethyl acetylene dicarboxylate
dpam - bis(diphenylarsino)methane
dppm - bis(diphenylphosphino)methane
( unless otherwise stated)
d - doublet
deg - degree
Esd - estimated standard deviation
Et - ethyl
HFB - hexafluoro-2-butyne
HOMO - highest occupied molecular orbital
IR - infrared
LUMO - lowest occupied molecular orbital
Me - methyl
m - medium
mw - medium to weak
NMR - nuclear magnetic resonance
OAc - acetate
Ph - phenyl
q - quartet
qt - quintet
s - strong in IR; singlet in NMR
sh - shoulder
t - triplet
Bu - tertiary butyl
ttq - triplet of triplet of quintets
vs - very strong
UV - ultraviolet
w - weak
< - angle
µ - denotes bridging ligands
νas - antisymmetric stretch
νs - symmetric stretch
δ - bending mode in IR; chemical shift in NMR
DMA - N,N-dimethylacetamide
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CHAPTER 1

INTRODUCTION

1.1. General Introduction

Homogeneous catalysis by mononuclear and polynuclear transition metal complexes has received considerable attention in the last two decades and the outcome has been extremely impressive. Homogeneous catalysis has many great virtues, one of which is that the mechanistic details of the reactions can, in principle, be understood at the molecular level. On the other hand, much less mechanistic detail is available for heterogeneously catalyzed reactions as a result of the difficulties associated with comprehending the molecular processes taking place on surfaces, even with modern instrumentation.

During the past few years, a number of articles has appeared in the literature suggesting that molecular fragments bonded to transition metal clusters may serve as simple models for chemisorbed and catalytic intermediates occurring during reactions catalyzed by metal surfaces.
This proposition has stimulated several research groups to focus their attention on the synthesis and reactivity of binuclear complexes in which the metal centres are held in close proximity to one another. Although binuclear complexes can only be considered as cluster prototypes, the cluster-surface analogy has relevance to the chemistry of binuclear complexes since the interaction of certain small molecules with only two metal centres can be sufficient to characterize certain chemisorption and catalytic processes. A detailed study of these binuclear systems has therefore been undertaken in the hope of not only mimicking catalytic steps on metal surfaces but also providing a greater understanding of the more sophisticated multicentred systems. Furthermore, these binuclear complexes possess the potential to activate substrates and also effect catalytic and stoichiometric transformations as a result of cooperative interactions between the two metal centres. In particular, the activation of substrates such as carbon monoxide and hydrogen has attracted considerable world wide attention as the search goes on to find alternatives to costly and dwindling petrochemical feedstocks currently used in the production of liquid fuels and organic chemicals.

The use of bidentate phosphine ligands has proved to be an effective approach in accomplishing the synthesis of binuclear complexes in which the metal centres are held
close to one another. Balch and coworkers\textsuperscript{14} have shown that in binuclear complexes with bridging diphosphine ligands, the metals can act in a cooperative fashion or as two monomeric units, depending upon the separation between the metal centres, which in turn is determined by the bite size of the diphosphine ligand. Bis(diphenylphosphino)methane (dppm), and to a lesser extent its arsine analogue (dpam), have been the most widely used because of their demonstrated flexibility in bridging the two metals under various conditions. Complexes of these ligands include examples with metals joined by single\textsuperscript{15,16} and multiple bonds,\textsuperscript{17,18} one or two bridging ligands,\textsuperscript{19,20} and cases where there are neither bridging ligands nor metal-metal bonds (\textit{vide infra})\textsuperscript{21,22}

The wide range of metal-metal distances spanned by these ligands also illustrates their flexibility. For complexes with bridging dppm ligands, the metal-metal separation varies from 2.46 to 3.38 Å whereas for dpam the range is 2.52 to 3.81 Å.\textsuperscript{23} The dppm ligand not only can act as a bridging ligand but also as either a chelating\textsuperscript{24,25} or monodentate\textsuperscript{26,27} ligand. No attempt will be made, however, to discuss complexes with such coordination modes of the dppm ligand in this introduction.

In the past, many binuclear dppm complexes of rhodium,\textsuperscript{28-30} iridium,\textsuperscript{31} palladium,\textsuperscript{32-35} and platinum,\textsuperscript{16,36-40} in which each metal atom possesses four
coordinate square planar geometry have been synthesized. These include structural types such as the molecular A-frame (1), the face to face dimer (2) and side by side dimer (3) all of which are known to exhibit very rich and interesting chemistry involving the making and breaking of metal-metal bonds.

A-frame complexes are characterized by two approximately square planar metal centres held together by two trans dppm ligands and further joined by a bridgehead ligand X. Since the square planes are inclined to each other, typically at an angle of ca. 80°, the metal out of plane orbitals overlap between the metal atoms opposite the bridgehead ligand to define the endo pocket of the A-frame.
complex in which the binding of small molecules has been observed.\textsuperscript{31, 41} In face to face dimers, the coordination planes are parallel to each other whereas in side by side dimers, the metals are connected with a metal-metal bond rather than bridgehead ligand and the coordination planes are usually drawn in such a manner that they appear to be coplanar. In practice, however, one of the coordination planes of the side by side dimer is twisted about the metal-metal vector by an angle of ca. 40°.\textsuperscript{16} In addition to these four coordinate structural forms, there is a number of equally well characterized binuclear complexes with coordination numbers five and six, as exemplified by the molecular A-frames with metal-metal bonds (4)\textsuperscript{42-44} and the doubly bridged A-frames (5).\textsuperscript{20, 45, 46}

Binuclear complexes with symmetric ligands related to dpdm and dpam are also known. These ligands include

\begin{itemize}
\item $\text{Ph}_2\text{PCHMePPPh}_2$, \textsuperscript{47}
\item $\text{Ph}_2\text{PC(Me)}_2\text{PPPh}_2$, \textsuperscript{48}
\item $\text{Ph}_2\text{SbCH}_2\text{SbPh}_2$, \textsuperscript{49}
\end{itemize}
Their chemistry, however, has not yet been fully investigated. Examples are also known of binuclear complexes with unsymmetrical bridging ligands such as (diphenylarsino)(diphenylphosphino)methane, and 2-(diphenylphosphino)pyridine and 2-(bis(diphenylphosphino)methyl)pyridine. Both dppm and 2-(diphenylphosphino)pyridine have been used to bridge two different metal centres and the study of such heterobimetallic complexes is an area that has begun to blossom recently. One reason for the interest in heterobimetallic complexes is the belief that they may exhibit exciting chemistry as a result of the differing chemical properties of the adjacent metals enabling separate, unique functions to be utilized.

1.2. A Survey of Dimeric, Bis(diphenylphosphino)methane Complexes of Rhodium

This survey, although not comprehensive, covers the literature up to the end of 1983 derived mainly from the major North American and European journals and, wherever possible, the rhodium-dppm complexes will be compared briefly to their iridium, palladium and platinum counterparts.
1.2.1. Face to Face Dimers

The reaction of the rhodium dicarbonyl dimer, Rh<sub>2</sub>Cl<sub>2</sub>(CO)<sub>4</sub> with dppm gave the first rhodium-dppm complex, to which a polymeric formulation \( \text{[RhCl(CO)(\mu-dppm)Rh(CO)Cl]} \) was assigned. Subsequently, Mague and Mitchener reinvestigated this complex and its arsine analogue and reformulated them as the face to face dimers, \( \text{trans-Rh}_2\text{Cl}_2(\text{CO})_2(\mu-L)_2 \) (L = dppm (6), dpam) by the structural characterization of the arsine analogue. This structure was also subsequently demonstrated for the dppm analogue.

Unlike most other dppm bridged complexes in which the dppm methylene groups are cis folded, the methylene groups of dppm in \( \text{trans-Rh}_2\text{Cl}_2(\text{CO})_2(\mu-dppm)_2 \) are found to be folded in trans fashion. Either type of folding is thought to occur in order to minimize interactions between the phenyl rings and the equatorial ligands. The structural parameters of both \( \text{Rh}_2\text{Cl}_2(\text{CO})_2(\mu-L)_2 \) (L = dppm, dpam)
indicate the absence of a rhodium-rhodium single bond
(L = dppm, Rh-Rh = 3.2386(5) Å; L = dpam,
Rh-Rh = 3.396(1) Å). Although no formal metal-metal bond
is present in these and the related dimers, [Rh₂(CNR)₄-
(μ-dppm)₂](BPh₄)₂ (R = CH₃, n-C₄H₉, C₆H₁₁, t-C₄H₉) pre-
pared by the reaction of [Rh(CNR)₄](BPh₄)₂ with dppm, the
electronic spectra of these complexes show the presence of
proximity shifted charge transfer bands, indicating the
presence of a weak metal-metal interaction.⁷²,⁷³

In square planar complexes, the lowest energy elec-
tronic transition arises from metal to ligand charge trans-
fer absorptions.⁷⁴ When such metal centres are brought
close together, as in a face to face dimer, there is consid-
erable overlap of both the filled metal orbitals and the
empty ligand orbitals on each centre. This overlap lowers
the energy gap between the HOMO and the LUMO. As a result,
the lowest energy absorption of a single metal centre
shifts to lower energies when two such metal centres are
in close proximity. Such a shift to lower energies gives
rise to the term proximity shifted charge transfer
absorptions.¹⁴

The iridium counterpart of trans-Rh₂Cl₂(CO)₂-
(μ-dppm)₂ has also been synthesized by the reaction of
Ir₂Cl₂(COD)₂ (COD = 1,5-cyclooctadiene) with dppm in an
atmosphere of carbon monoxide, using benzene as the solvent.
The face to face dimers trans-\( \text{Rh}_2\text{Cl}_2(\text{CO})_2(\mu\text{-dppm})_2 \) and [\( \text{Rh}_2(\text{CNR})_4(\mu\text{-dppm})_2 \)](\( \text{BPh}_4 \))_2 (\( R = \text{CH}_3, \text{n-C}_4\text{H}_9, \text{c-C}_6\text{H}_{11} \)) very readily undergo 1,2-oxidative addition reactions with iodine to give the Rh(II) species, \( \text{Rh}_2\text{I}_2\text{Cl}_2(\text{CO})_2(\mu\text{-dppm})_2 \) (7) and [\( \text{Rh}_2\text{I}_2(\text{CNR})_4(\mu\text{-dppm})_2 \)](\( \text{BPh}_4 \))_2 (8) which contain rhodium-rhodium single bonds.\(^{71,72}\) Similar complexes have also been obtained for the dpam analogue. trans-\( \text{Rh}_2\text{Cl}_2(\text{CO})_2(\mu\text{-L})_2 \) (\( L = \text{dppm}, \text{dpam} \)) and [\( \text{Rh}_2(\text{CNR})_4(\mu\text{-dppm})_2 \)](\( \text{BPh}_4 \))_2 (\( R = \text{t-C}_4\text{H}_9 \)) also both undergo reactions with small molecules such as carbon monoxide,\(^{75,76}\) sulphur dioxide\(^{42,76}\) and acetylenes,\(^{77-79}\) the details of which will be discussed in section 1.2.2(i). A face to face dimeric structure with square pyramidal geometry for each rhodium atom has been postulated for \( \text{Rh}_2(\text{CN})_2(\text{CO})_4(\mu\text{-dppm})_2 \), which has been synthesized by the reaction of \( \text{Rh}_2\text{Cl}_2(\text{COD})_2 \) with potassium cyanide and dppm in an atmosphere of carbon monoxide.\(^{80}\)
Rh$_2$(CN)$_2$(CO)$_4$(u-dppm)$_2$ (9) loses two moles of carbon monoxide in solution under a dinitrogen purge to give the face to face dimer, Rh$_2$(CN)$_2$(CO)$_2$(u-dppm)$_2$ (10) via the carbonyl bridged complex, Rh$_2$(u-CO)(CO)$_2$(CN)$_2$(u-dppm)$_2$ (11) (equation 1). The structure 9 has been proposed on the basis of Analytical, IR and $^{31}$P spectroscopy data. This structure is somewhat questionable since the analogous thiocyanate complex with a similar proposed structure has been proven to be incorrect (Chapter 2).

Similar behaviour has also been observed for the diarsine analogue, Rh$_2$(CN)$_2$(CO)$_4$(u-dpam)$_2$. Both complexes Rh$_2$(CN)$_2$(CO)$_4$(u-L)$_2$ (L = dppm, dpam) function as homogeneous catalysts for the hydrogenation of phenyl-
acetylene to styrene, with the complex having \( L = \text{dppm} \) exhibiting a rate ten times faster than that with \( L = \text{dpam} \). \(^{81}\)

Unlike rhodium and iridium, face to face dimers of palladium and platinum complexes are extremely rare. The complexes \( \text{Pt}_2(\text{C} = \text{CR})_4(\mu-\text{dppm})_2 \) (\( R = \text{Ph} \) and \( p\)-tolyl) represent the only known platinum face to face dimers,\(^ {82}\) whereas no well characterized examples for palladium have been isolated, although they are found to occur in solution and as intermediates.\(^ {83-85}\) As an example, the reaction of \( \text{Pd}_2X_2(\mu-\text{dppm})_2 \) (12) (\( X = \text{Cl}, \text{Br}, \text{I} \)) with the corresponding halogen (\( X_2 \)) gives \( \text{Pd}X_2(\text{dppm}) \) (13) via the intermediate \( \text{Pd}_2X_4(\mu-\text{dppm})_2 \) (14) (equation 2).\(^ {83}\)

\[ \text{Pd}_2X_2(\mu-\text{dppm})_2 + X_2 \rightarrow \text{Pd}X_2(\text{dppm}) + \text{Pd}_2X_4(\mu-\text{dppm})_2 \]

\[ \text{equation 2} \]
1.2.2. A-frame Complexes

1.2.2(i). A-frame Complexes without Metal-Metal Bonds

The face to face dimers have the ability to form A-frame type complexes under various conditions. This has been demonstrated, for example, by the reaction of trans-Rh₂Cl₂(CO)₂(μ-dppm)₂ with sodium sulphide in methanol suspension to form the sulphide bridged A-frame complex Rh₂(μ-S)(CO)₂(μ-dppm)₂ (15). This was reported by Eisenberg in 1977 and represented the first structurally characterized binuclear complex possessing the A-frame geometry. The geometry around each metal centre in this complex is found to be approximately square planar and the coordination planes are inclined at a dihedral angle of 83.3(3)° to one another. The absence of a rhodium-rhodium single bond is evident from the separation of the two metal centres (3.154(2) Å), in keeping with the prediction
based on conventional electron counting techniques. An unusual feature of this complex is the rather high degree of twisting of the Rh$_2$P$_2$C$_2$ ring that causes two of the phenyl groups of the trans dppm ligands to be placed close to the endo pocket. Although Rh$_2$($\mu$-S)(CO)$_2$(μ-dppm)$_2$ does not react with carbon monoxide, the reaction with sulphur dioxide gives a symmetrical 1:1 adduct identified as Rh$_2$($\mu$-S)(μ-SO$_2$)(CO)$_2$(μ-dppm)$_2$ (16) in which the sulphur dioxide occupies the endo pocket of the A-frame. The reaction of Rh$_2$($\mu$-S)(CO)$_2$(μ-dppm)$_2$ with methyl isocyanide gives Rh$_2$($\mu$-S)(CNMe)$_2$(μ-dppm)$_2$, with substitution of both terminal carbonyl ligands. No evidence has been presented for the formation of bridging isocyanide adducts.

In addition to the reactions with sulphur dioxide and methyl isocyanide, both of which are known to take place at the metal centres, Rh$_2$($\mu$-S)(CO)$_2$(μ-dppm)$_2$ also shows considerable reactivity at the sulphur bridge. This is demonstrated by the ready protonation and
alkylation of the bridgehead sulphur atom of \( \text{Rh}_2(\mu-\text{S})(\text{CO})_2(\mu-\text{dppm})_2 \) when treated with electrophilic reagents such as \((\text{Et}_2\text{OR})\text{PF}_6\) \((R = \text{H}, \text{Et})\), to yield the cationic A-frame complexes \([\text{Rh}_2(\mu-\text{SR})(\text{CO})_2(\mu-\text{dppm})_2]\text{PF}_6\) \((R = \text{H}, \text{Et})\).

Furthermore, benzyl bromide also brings about S-alkylation to give \([\text{Rh}_2(\mu-\text{SCH}_2\text{Ph})(\text{CO})_2(\mu-\text{dppm})_2]\text{Br}^+\) which has been isolated as the hexafluorophosphate (\(\text{PF}_6^-\)) salt. These experimental observations are in good agreement with the theoretical results obtained by Hoffman and Hoffmann, which predict an increase in nucleophilicity of the bridgehead ligand on going from \([\text{Rh}_2(\mu-\text{Cl})(\text{CO})_2(\mu-\text{dppm})_2]^+\) to \(\text{Rh}_2(\mu-\text{S})(\text{CO})_2(\mu-\text{dppm})_2\). The same authors presented a detailed description of the electronic structure of various A-frames, a discussion which is considered beyond the scope of this introduction. Although no reaction between hydrogen and \(\text{Rh}_2(\mu-\text{S})(\text{CO})_2(\mu-\text{dppm})_2\) has been detected, \(\text{Rh}_2(\mu-\text{S})(\text{CO})_2(\mu-\text{dppm})_2^-\) has the ability to catalyze the hydrogenation of ethylene very slowly at room temperature.

The A-frame complex \(\text{Rh}_2(\mu-\text{Se})(\text{CO})_2(\mu-\text{dppm})_2\) has also been synthesized from \(\text{trans-Rh}_2\text{Cl}_2(\mu-\text{dppm})_2\) in an analogous manner using potassium selenide. Although its reactions with small molecules and its catalytic activity have not been reported, the behaviour towards electrophilic reagents was found to be similar to that of the sulphur bridged complex. Thus, the treatment of \(\text{Rh}_2(\mu-\text{Se})(\text{CO})_2(\mu-\text{dppm})_2\) with \(\text{R}^+\) \((R = \text{H}, \text{CH}_3)\) gives the cations
T [Rh$_2$(μ-SeR)(CO)$_2$(μ-dppm)$_2$]$^+$ which have been isolated as their perchlorate salts.

The A-frame complex, [Rh$_2$(μ-PHCy)(CO)$_2$(μ-dppm)$_2$]PF$_6$, which contains a cyclohexyl phosphide bridge is also known.$^{29}$ The synthesis of this complex is achieved by the reaction of trans-Rh$_2$Cl$_2$(CO)$_2$(μ-dppm)$_2$ with cyclohexylphosphine and n-butyllithium, followed by the addition of sodium hexafluorophosphate. Attempts to extend this procedure to bulkier phosphines such as diphenylphosphine and dicyclohexylphosphine were unsuccessful, presumably as a result of extreme steric pressure between the dppm methylene groups and the bulky substituents on the phosphide bridge.

Complexes electronically similar to Rh$_2$(μ-S)(CO)$_2$(μ-dppm)$_2$ have been prepared for the metals iridium,$^{31}$ palladium$^{33}$ and platinum.$^{37}$ Ir$_2$(μ-S)(CO)$_2$(μ-dppm)$_2$ was the first binuclear complex of iridium to be identified as possessing the A-frame geometry. The synthesis of Ir$_2$(μ-S)(CO)$_2$(μ-dppm)$_2$ can be accomplished by the treatment of [Ir$_2$Cl(CO)$_4$(μ-dppm)$_2$]PF$_6$ with sodium sulphide in methanol. The synthesis of [Ir$_2$Cl(CO)$_4$(μ-dppm)$_2$]PF$_6$ can be achieved by the reaction of Ir$_2$Cl$_2$(COD)$_2$ with carbon monoxide and dppm, and the former complex has been shown to have the asymmetric structure 17 shown below. This compound, however, has been reformulated and shown to possess a similar structure proposed for the diarsine analogue.$^{76,154}$ The solution chemistry of Ir$_2$(μ-S)(CO)$_2$(μ-dppm)$_2$ differs
significantly from that of the rhodium analogue. This is evident from the reactions with carbon monoxide and dihydrogen. The reaction of \( \text{Ir}_2(\mu-S)(\text{CO})_2(\mu\text{-dppm})_2 \) with carbon monoxide yields \( \text{Ir}_2(\mu-S)(\mu\text{-CO})(\text{CO})_2(\mu\text{-dppm})_2 \). An X-ray study of this complex has confirmed \(^{31} \) that the molecule possesses an A-frame type structure with carbon monoxide bridging the two metals. The two iridium centres of \( \text{Ir}_2(\mu-S)(\mu\text{-CO})(\text{CO})_2(\mu\text{-dppm})_2 \) exhibit square pyramidal coordination with an iridium-iridium distance of 2.843(2) Å, which is consistent with the presence of an iridium-iridium single bond. \( \text{Ir}_2(\mu-S)(\text{CO})_2(\mu\text{-dppm})_2 \) is so far the only A-frame complex reported to undergo the oxidative addition of dihydrogen. This reaction yields two hydrido iridium(II) complexes of stoichiometry \( \text{Ir}_2(\mu-S)\text{H}_2(\text{CO})_2(\mu\text{-dppm})_2 \); possible structures for which are shown by 18 to 20. It has not proved possible to distinguish by
$^1$H NMR spectroscopy which of these structures can be attributed to the two hydride complexes formed in the reaction. It has been proposed, however, that the $^1$H NMR results can be explained in terms of a mixture of (18) and rapidly equilibrating mixture of (19) and (20). $\text{Ir}_2(\mu-S)(\text{CO})_2(\mu\text{-dppm})_2$ is an active catalyst for the hydrogenation of acetylene, ethylene and propylene to their corresponding alkanes, in contrast to its rhodium counterpart which is a very poor catalyst. Despite the reactivity of $\text{Ir}_2(\mu-S)(\text{CO})_2(\mu\text{-dppm})_2$ it does not act as a catalyst either
for the hydroformylation of alkenes or for carbon monoxide reduction.

The complexes \( M_2(\mu-X)Cl_2(\mu\text{-dppm})_2 \) (21) \((M = \text{Pd, Pt, } X = \text{S}; M = \text{Pt, } X = \text{Se})\) have been synthesized by the addition of sulphur or selenium across the metal-metal bond of the side by side dimer \( M_2Cl_2(\mu\text{-dppm})_2 \) \((M = \text{Pd (12); } M = \text{Pt (22)})\) (equation 3).\(^{33,37}\) This is the most versatile method of synthesizing A-frame complexes of palladium and platinum and a number of small molecules such as carbon monoxide,\(^{32,36}\) sulphur dioxide,\(^{33}\) methylene,\(^{37,40}\) isocyanides,\(^{32,88}\) acetylenes\(^{34}\) and carbon disulphide\(^{89}\) can also be added across the metal-metal bond. Unlike the rhodium and iridium analogues, no examples are known where A-frame complexes of palladium and platinum bind small molecules in the endo pocket.
The complexes $\text{Rh}_2(\mu-X)\text{Cl}_2(\mu-$dppm$)_2$ ($X = S, Se$) behave towards electrophiles in a similar fashion to $\text{Rh}_2(\mu-S)(\text{CO})_2(\mu-$dppm$)_2$. For example, treatment of $\text{Pt}_2(\mu-X)\text{Cl}_2(\mu-$dppm$)_2$ ($X = S, Se$) with methyl triflate gives the cations $[\text{Pt}_2(\mu-X\text{CH}_3)\text{Cl}_2(\mu-$dppm$)_2]^+$ ($X = S, Se$) which can be isolated as their perchlorate salts. $\text{Pd}_2(\mu-S)\text{Cl}_2$-$\text{(dppm)}_2$ has been structurally characterized$^{33}$ and the structural parameters are comparable to those of $\text{Rh}_2(\mu-S)(\text{CO})_2(\mu-$dppm$)_2$. The significant difference between these structures, however, is that the twisting of the $\text{Pd}_2\text{P}_4\text{C}_2$ ring is considerably less than that seen in $\text{Rh}_2(\mu-S)(\text{CO})_2(\mu-$dppm$)_2$. Although no electrophilic addition to the sulphur bridge of $\text{Pd}_2(\mu-S)\text{Cl}_2(\mu-$dppm$)_2$ has been reported, its oxidation with meta-chloroperbenzoic acid converts the bridgehead sulphur to sulphur dioxide giving $\text{Pd}_2(\mu-$SO$_2$)$\text{Cl}_2(\mu-$dppm$)_2$. This can also be obtained by the (reversible) addition of sulphur dioxide across the palladium-palladium single bond of $\text{Pd}_2\text{Cl}_2(\mu-$dppm$)_2$. $\text{Pd}_2(\mu-$SO$_2$)$\text{Cl}_2(\mu-$dppm$)_2$ has also been structurally characterized$^{33}$ and shown to contain two pairs of crystallographically non-equivalent molecules in the unit cell with palladium-palladium distances of 3.220(4) and 3.383(4) Å indicating the absence of palladium-palladium single bonds. In all three A-frame complexes, $M_2(\mu-Y)X_2(\mu-$dppm$)_2$ ($M = \text{Rh}, X = \text{CO}, Y = S; M = \text{Pd}, X = \text{Cl}, Y = S, \text{SO}_2$), the methylene
groups of the dppm ligands are cis and are bent towards the bridgehead ligand.

The A-frame complex \([\text{Rh}_2(\mu-\text{Cl})(\text{CO})_2(\mu-\text{dppm})_2]\text{BPh}_4\) (23) has also been studied extensively. The synthesis of this complex was originally achieved by a two-step procedure. The first step involved the treatment of \([\text{Rh(\text{CO})}_2\text{Cl}_2]^-\), formed from the reaction of rhodium trichloride hydrate with carbon monoxide in refluxing aqueous ethanol, with dppm and sodium tetraphenylborate (NaBPh₄) under an atmosphere of carbon monoxide. The resultant \([\text{Rh}_2(\mu-\text{Cl})(\mu-\text{CO})(\text{CO})_2(\mu-\text{dppm})_2]\text{BPh}_4\) (24) when purged by dinitrogen in acetone or dichloromethane solution gave the A-frame complex \([\text{Rh}_2(\mu-\text{Cl})(\text{CO})_2(\mu-\text{dppm})_2]\text{BPh}_4\). The latter reaction could be reversed by passing carbon monoxide through a dichloromethane or acetone solution of \([\text{Rh}_2(\mu-\text{Cl})(\text{CO})_2(\mu-\text{dppm})_2]\text{BPh}_4\) (equation 4).
The $[\text{Rh}_2(\mu-\text{Cl})(\text{CO})_2(\mu-\text{dppm})_2]^+$ cation has been structurally characterized as the tetrafluoroborate salt whereas its carbon monoxide adduct, $[\text{Rh}_2(\mu-\text{Cl})(\mu-\text{CO})(\text{CO})_2(\mu-\text{dppm})_2]^+$, has been characterized as the tetraphenylborate and $[\text{Rh}(\text{CO})_2\text{Cl}_2]^-$ salts. $[\text{Rh}_2(\mu-\text{Cl})(\mu-\text{CO})(\text{CO})_2(\mu-\text{dppm})_2]_2\text{BPh}_4$ represents the first structurally characterized A-frame complex possessing a small molecule in the endo pocket of the parent A-frame, $[\text{Rh}_2(\mu-\text{Cl})(\text{CO})_2(\mu-\text{dppm})_2]_2\text{BPh}_4$. The rhodium-rhodium separation of 2.8415(7) Å confirms the presence of a rhodium-rhodium single bond in $[\text{Rh}_2(\mu-\text{Cl})(\mu-\text{CO})(\text{CO})_2(\mu-\text{dppm})_2]_2\text{BPh}_4$. If the rhodium-rhodium single bond is excluded, the geometry around each of the metal centres is that of a distorted trigonal bipyramid. The structure determination of $[\text{Rh}_2(\mu-\text{Cl})(\text{CO})_2(\mu-\text{dppm})_2]_2\text{BF}_4$ has shown that the molecule has an A-frame geometry with the metal centres exhibiting distorted square planar geometry. The rhodium-rhodium distance of 3.1520(8) Å confirms the absence of a rhodium-rhodium single bond which is also predicted by conventional electron counting techniques. Unlike in $\text{Rh}_2(\mu-\text{S})(\text{CO})_2(\mu-\text{dppm})_2$, no significant twisting of the dppm ligands is found in $[\text{Rh}_2(\mu-\text{Cl})(\text{CO})_2(\mu-\text{dppm})_2]_2\text{BF}_4$. As found in $\text{Rh}_2(\mu-\text{S})(\text{CO})_2(\mu-\text{dppm})_2$ and $\text{Pd}_2(\mu-\text{X})\text{Cl}_2(\mu-\text{dppm})_2$ ($\text{X} = \text{S, SO}_2$), the methylene groups of the dppm ligands of $[\text{Rh}_2(\mu-\text{Cl})(\text{CO})_2(\mu-\text{dppm})_2]_2\text{BF}_4$ and $[\text{Rh}_2(\mu-\text{Cl})(\mu-\text{CO})(\text{CO})_2(\mu-\text{dppm})_2]_2\text{BPh}_4$ are cis and bent towards the bridging chloride. The diarsine analogues of the latter two...
compounds are also known.

Experiments using labelled carbon monoxide ($^{13}$CO) have shown that the formation of $[\text{Rh}_2(\mu-\text{Cl})(\mu-\text{CO})(\text{CO})_2(\mu-\text{dppm})_2]^+$ from $[\text{Rh}_2(\mu-\text{Cl})(\text{CO})_2(\mu-\text{dppm})_2]^+$ involves the initial attack of 13-carbon monoxide at a terminal site followed by the original terminal carbonyl group moving to the bridging position (equation 5). \[41\]

\begin{align*}
[\text{Rh}_2(\mu-\text{Cl})(\mu-\text{CO})(\text{CO})_2(\mu-\text{dppm})_2]\text{BPh}_4 \text{ does not lose carbon monoxide in the solid state but does so under vacuum.}
\end{align*}
Similar behaviour has been observed for the dpam analogue. Of these complexes, however, when prepared as the hexafluorophosphate salts, only the dpam analogue loses carbon monoxide in the solid state. This behaviour has been attributed to the large bite size of the dpam analogue as well as to the stability of the dicarbonyl cation when associated with the hexafluorophosphate counter anion.\(^{76}\)

Trans-Rh\(_2\)Cl\(_2\)(CO)\(_2\)(\(\mu\)-dppm)\(_2\) also reacts rapidly with carbon monoxide in methanol to give [Rh\(_2\)(\(\mu\)-Cl)(\(\mu\)-CO)(CO)\(_2\)(\(\mu\)-dppm)\(_2\)]Cl.\(^{75}\) This complex, however, slowly loses carbon monoxide in the solid state with reversion to the neutral dimer, trans-Rh\(_2\)Cl\(_2\)(CO)\(_2\)(\(\mu\)-dppm)\(_2\). By contrast, [Rh\(_2\)(\(\mu\)-Cl)(\(\mu\)-CO)(CO)\(_2\)(\(\mu\)-dpam)\(_2\)]Cl could not be isolated under these conditions.

\(^{31}\)P\(\{^1\)H\} NMR spectroscopy is a useful technique for the characterization of rhodium A-frame complexes. The \(^{31}\)P\(\{^1\)H\} NMR spectra of symmetrical A-frame complexes are second order, of the spin system AA'A''XX'. Such spectra consist of two major lines which accounts for half of the total intensity, in addition to a number of minor peaks. These minor peaks, especially those between the major absorptions, are usually considered diagnostic of whether or not the complex contains a metal-metal bond. Figure 2.2 (page 84) shows the \(^{31}\)P\(\{^1\)H\} NMR spectrum of a typical symmetrical cationic A-frame complex without a metal-metal
bond. The lack of minor peaks occurring close to the midpoint of the two principal lines is characteristic of an A-frame complex without a metal-metal bond. The chemical shifts for these complexes are represented by the midpoints of the two major lines and the separation between these two peaks is equal to the absolute value of the sum of all Rh-P coupling constants, denoted by $|J_{\text{Rh-P}} + XJ_{\text{Rh-P}}|$ in Hz. Figure 3.5(b) (page 163) shows the $^{31}\text{P}[^{1}\text{H}]$ spectrum of a doubly bridged cationic A-frame complex with a metal-metal bond. The presence of minor peaks close to the centre of the pattern is characteristic of an A-frame complex of this type. The chemical shifts and coupling constants are also somewhat characteristic of whether or not an A-frame complex possesses a metal-metal bond. For example, $[\text{Rh}_2(\mu-\text{Cl})(\text{CO})_2(\mu-\text{dppm})_2]_{\text{BPh}_4}$ has a chemical shift of 16.1 ppm and a coupling constant of 113.3 Hz whereas for $[\text{Rh}_2(\mu-\text{Cl})(\mu-\text{CO})(\text{CO})_2(\mu-\text{dppm})_2]_{\text{BPh}_4}$ these values change to 26.0 ppm and 94.2 Hz respectively. Hence the formation of a second bridge along with a metal-metal bond appears to increase the chemical shift while decreasing $|J_{\text{Rh-P}} + XJ_{\text{Rh-P}}|$.

$[\text{Rh}_2(\mu-\text{Cl})(\text{CO})_2(\mu-\text{dppm})_2]^{+}$ also reacts with sulphur dioxide in a reversible fashion to form $[\text{Rh}_2(\mu-\text{Cl})(\mu-\text{SO}_2)(\text{CO})_2(\mu-\text{dppm})_2]^{+}$ in which the sulphur dioxide is coordinated in the endo pocket between the metal centres.
Spectroscopic studies have shown that the sulphur dioxide attacks directly at the endo pocket, unlike carbon monoxide wherein the initial attack is terminal. The reason for the different selection of sites remains yet unanswered. Direct attack of nitric oxide and aryldiazonium ion (PhN$_2^+$)$^{30}$ has also been observed for [Rh$_2$(μ-Cl)(CO)$_2$(μ-dppm)$_2$]$^+$ but the details have not yet appeared in the literature. Prolonged treatment of [Rh$_2$(μ-Cl)(CO)$_2$(μ-dppm)$_2$]$^+$ with sulphur dioxide in the presence of chloride gives a novel A-frame complex Rh$_2$Cl$_2$(μ-SO$_2$)(μ-dppm)$_2$ (25) which contains a rhodium-rhodium single bond (2.7838(8) Å). Unlike the thirty-two electron A-frame complexes [Rh$_2$(μ-Cl)(CO)$_2$(μ-dppm)$_2$]BPh$_4$ and Rh$_2$(μ-S)(CO)$_2$(μ-dppm)$_2$, this complex possesses anionic terminal ligands and a neutral π-acceptor ligand occupying the bridgehead position. This ligand arrangement results in a thirty-electron count for the complex requiring the presence of a formal rhodium-rhodium single bond.
Rh$_2$(μ-SO$_2$)Cl$_2$(μ-dppm)$_2$ can also be prepared by the reaction of trans-Rh$_2$Cl$_2$(CO)$_2$(μ-dppm)$_2$ with sulphur dioxide, for a period of two hours. The stepwise addition of small quantities of sulphur dioxide to trans-Rh$_2$Cl$_2$(CO)$_2$(μ-dppm)$_2$ (6) has shown that the initial product of this reaction is an asymmetric complex to which the structure Rh$_2$(μ-Cl)(μ-CO)(Cl)(CO)(SO$_2$)(μ-dppm)$_2$ (26) has been proposed. This asymmetric species then rearranges to [Rh$_2$(μ-Cl)(μ-SO$_2$)-(CO)$_2$(μ-dppm)$_2$]Cl (27) and finally, after prolonged treatment with sulphur dioxide, to give Rh$_2$(μ-SO$_2$)Cl$_2$(μ-dppm)$_2$ (25) with coordination of chloride and loss of carbon monoxide (equation 6).
The stepwise addition of tert-butyl isocyanide to $[\text{Rh}_2(\mu-\text{Cl})(\text{CO})_2(\mu-\text{dppm})_2]^+$ (scheme 1) and its arsine analogue (scheme 2) has also been studied extensively. The treatment of $[\text{Rh}_2(\mu-\text{Cl})(\text{CO})_2(\mu-\text{dppm})_2]^+$ (23) with one equivalent of tert-butyl isocyanide ($\text{BuNC}$) results in the formation of an asymmetric complex $[\text{Rh}_2(\mu-\text{Cl})(\mu-\text{CO})(\text{CO})_2(\text{CN}^\text{Bu})(\mu-\text{dppm})_2]^+$ (28) in which the incoming ligand attacks a terminal site of the A-frame and the terminal carbonyl group moves to the bridging site. Hence the reaction of $[\text{Rh}_2(\mu-\text{Cl})(\text{CO})_2(\mu-\text{dppm})_2]^+$ with one equivalent of tert-butyl isocyanide provides further support for the proposed mechanism for the formation of $[\text{Rh}_2(\mu-\text{Cl})(\mu-\text{CO})(\text{CO})_2(\mu-\text{dppm})_2]^+$ from $[\text{Rh}_2(\mu-\text{Cl})(\text{CO})_2(\mu-\text{dppm})_2]^+$. The symmetric bis(isocyanide) complex, $[\text{Rh}_2(\mu-\text{Cl})(\mu-\text{CO})(\text{CN}^\text{Bu})_2(\mu-\text{dppm})_2]^+$ (29) is obtained when $[\text{Rh}_2(\mu-\text{Cl})(\mu-\text{CO})(\text{CO})_2(\mu-\text{dppm})_2]^+$ is treated with two equivalents of tert-butyl isocyanide whereas the addition of three equivalents gives a mixture of products, one of which has been identified as $[\text{Rh}_2(\text{CN}^\text{Bu})_4(\mu-\text{dppm})_2]^{2+}$ (30). This latter complex can also be obtained by the reaction of $[\text{Rh}_2(\text{CN}^\text{Bu})_4]^{2+}$ with two equivalents of dppm.

Contrasting behaviour has been observed for the reaction of the chloro-bridged arsine analogue, $[\text{Rh}_2(\mu-\text{Cl})(\text{CO})_2(\mu-\text{dpam})_2]^+$ (31) with tert-butyl isocyanide. Thus, the reaction of $[\text{Rh}_2(\mu-\text{Cl})(\text{CO})_2(\mu-\text{dpam})_2]^+$ with one equivalent of tert-butyl isocyanide gives the face to face
Scheme 1

[Diagram showing a reaction scheme involving Rh complexes and t-BuNC]
Scheme 2
dimer \( [\text{Rh}_2(\text{CO})_2(\text{Cl})(\text{CN}^\text{Bu})(\mu-\text{dpam})_2]^+ \) (32). This observation demonstrates the instability of the bridging carbonyl group as a result of the large bite size of dpam by comparison to that of the dppm ligand. The reaction of two equivalents of tert-butyl isocyanide with \( [\text{Rh}_2(\mu-\text{Cl})(\text{CO})_2(\mu-\text{dpam})_2]^+ \) leads to \( [\text{Rh}_2(\text{CO})(\text{Cl})(\text{CN}^\text{Bu})_2(\mu-\text{dpam})_2]^+ \) (33) in which the isocyanide ligands are both attached to the same rhodium atom. The addition of three equivalents, however, did not yield the anticipated tris(isocyanide) complex and only the bis(isocyanide) complex could be isolated. Treatment of \( [\text{Rh}_2(\mu-\text{Cl})(\text{CO})_2(\mu-\text{dpam})_2]^+ \) with four equivalents or more of the isocyanide gave \( [\text{Rh}_2(\text{CN}^\text{Bu})_4(\mu-\text{dpam})_2]^{2+} \) (34) which could not be synthesized by the reaction of dpam on \( [\text{Rh}_2(\text{CN}^\text{Bu})_4]^2+ \), as observed for the dppm analogue.

The presence of four tert-butyl groups in \( [\text{Rh}_2(\text{CN}^\text{Bu})_4(\mu-\text{dppm})_2]^{2+} \) might have been expected to severely hinder the attachment of small molecules between the metal centres. Despite this crowding, however, both carbon monoxide and sulphur dioxide are found to bridge the metal centres of \( [\text{Rh}_2(\text{CN}^\text{Bu})_4(\mu-\text{dppm})_2]^{2+} \) to give \( [\text{Rh}_2(\mu-L)-(\text{CN}^\text{Bu})_4(\mu-\text{dppm})_2]^+ \) (35) \( (L = \text{CO, SO}_2) \). Similar behaviour has been observed for the diarsine analogue, \( [\text{Rh}_2(\text{CN}^\text{Bu})_4(\mu-\text{dpam})_2]^{2+} \), although in this case, the carbon monoxide adduct appears to be too unstable to be isolated in the solid state.
[Rh$_2$(CN$^t$Bu)$_4$(μ-dppm)$_2$]$^{2+}$ also binds activated acetylenes between the metal centres to yield the symmetrical complexes, [Rh$_2$(μ-Acet)(CN$^t$Bu)$_4$(μ-dppm)$_2$]$^{2+}$ (Acet = C$_2$(CF$_3$)$_2$. C$_2$(CO$_2$Me)$_2$). An X-ray structural determination of [Rh$_2$(μ-C$_4$F$_8$)(tBuNC)$_4$(μ-dppm)$_2$](PF$_6$)$_2$ (36) has shown that the acetylene is bound as a cis-dimetalated olefin ($r$(C=C) = 1.318(9) Å; <Rh−C=C = 111.8(3)°) and, as expected from the thirty-four electron count, for the dimer,
the rhodium-rhodium distance of 2.9653(6) Å indicates the presence of a weak rhodium-rhodium single bond.\textsuperscript{90}

Two distinct bridging modes are known for coordinated acetylenes. Of the two, the more common is the quasi tetrahedral geometry (37)\textsuperscript{91-106} with the less common being the cis-dimetallated olefinic geometry (38).\textsuperscript{34,78,107-109}

In the quasi tetrahedral geometry, the acetylene molecule lies perpendicular and above the metal-metal axis, whereas in the cis-dimetallated case the acetylene lies parallel to the metal-metal axis. When an acetylene adopts a cis-dimetallated olefinic geometry, each carbon of the acetylene is joined to only one metal atom and the acetylene as a whole acts as a two-electron donor to the dimer by donating only one electron to each metal centre. In the tetrahedral geometry, the acetylene donates four electrons overall; two electrons to each metal. The characteristic structural features of the cis-dimetallated olefin are as
follows. The substituents of the acetylene assume a cis geometry and the angles around the acetylenic carbons are close to 120°. Therefore, each carbon can be considered to be sp² hybridized as found in organic alkenes. The coordination of the acetylene to the metal centres in this fashion causes a considerable increase in the carbon-carbon distance of the acetylenic function. The observed distances range approximately from 1.27-1.37 Å,¹¹¹ which compares favourably with that for a normal carbon-carbon double bond (1.34 Å). Although a wide range is observed, most carbon-carbon distances for this type of bonding are in the range 1.31-1.34 Å.

In the pseudo tetrahedral bridging mode, the two acetylenic carbons and the two metal centres are directed approximately towards the corners of a tetrahedron. The acetylenic carbon-carbon distances range from 1.32 to 1.42 Å and the C-C-R angles from 130°-150°.¹¹¹ All acetylenic complexes structurally characterized so far in binuclear dppm chemistry are found to possess the less common cis-dimetalalted olefinic geometry.³⁴,⁴⁴,⁴⁵,¹¹² Hoffman and Hoffmann have performed a detailed theoretical study of these acetylenic bridging dppm complexes in order to identify the possible reasons for this observation. This study has clearly demonstrated that in the perpendicular orientation, as a result of the mismatch of low-lying empty orbitals with the HOMO of the acetylene, the latter interacts with low-lying filled metal orbitals causing the HOMO of the
acetylene complex to go up in energy considerably. Also, the stabilization gained by the parallel configuration as a result of the interaction of one particular acetylenic orbital with the appropriate empty metal orbital is partially lost in the perpendicular configuration as a result of poor overlap.

Much less is known about the chemistry of the bromo and iodo analogues of \([\text{Rh}_2(\mu-\text{Cl})(\text{CO})_2(\mu-\text{dppm})_2]B\text{Ph}_4\). The synthesis of \([\text{Rh}_2(\mu-\text{Br})(\text{CO})_2(\mu-\text{dppm})_2]B\text{Ph}_4\) has been achieved as follows: the first step is the reaction of \(\text{Rh}_2\text{Cl}_2(\text{COD})_2\) with dppm and sodium bromide in an acetone-methanol solution, under an atmosphere of carbon monoxide, to give \([\text{Rh}_2(\mu-\text{Br})(\mu-\text{CO})(\text{CO})_2(\mu-\text{dppm})_2]B\text{Ph}_4\). Purging dinitrogen through a dichloromethane solution of this complex yields \([\text{Rh}_2(\mu-\text{Br})(\text{CO})_2(\mu-\text{dppm})_2]B\text{Ph}_4\). The synthesis of the iodo analogue, \([\text{Rh}_2(\mu-\text{I})(\text{CO})_2(\mu-\text{dppm})_2]^+\) has not yet appeared in the literature. \([\text{Rh}_2(\mu-\text{X})(\text{CO})_2L_2]^+\) (\(X = \text{Cl, Br, L} = \text{dppm, dpam}\)) do not form adducts with hydrogen. They are, however, found to be catalysts for the hydrogenation of alkynes and alkenes to the corresponding alkanes under mild conditions.\(^{81}\)

The iridium counterpart of \([\text{Rh}_2(\mu-\text{Cl})(\mu-\text{CO})(\text{CO})_2(\mu-\text{dppm})_2]^+\) is known\(^{75}\) but very little is yet known about its chemistry.\(^{76}\) Some symmetrical, electronically similar halide bridged dppm complexes of palladium and platinum are
also known including \([\text{Pd}_2(\mu-X)(\text{CH}_3)_2(\mu-\text{dppm})_2]X\) \(^{39}\) (\(X = \text{Br}, \text{I}\)) \(^{84}\) and \([\text{Pt}_2(\mu-\text{Cl})(\text{CH}_3)_2(\mu-\text{dppm})_2]X\) \((X = \text{Cl}, \text{PF}_6)\) \(^{38}\).

The synthesis of the series \([\text{Pd}_2(\mu-X)(\text{CH}_3)_2(\mu-\text{dppm})_2]X\) \((X = \text{Br}, \text{I})\) was achieved by the reaction of \(\text{Pd}_2(\text{dppm})_3\) with the appropriate methyl halide \((\text{CH}_3X: X = \text{Br}, \text{I})\).

Spectroscopic data of these palladium A-frames indicate that they are in equilibrium with their corresponding face to face dimers, \(\text{Pd}_2X_2(\text{CH}_3)_2(\mu-\text{dppm})_2\) \((\text{equation 7})\) \(^{84,85}\).

\[\text{Pd}_2(\mu-X)(\text{CH}_3)_2(\mu-\text{dppm})_2]X^{-} (X = \text{Br}, \text{I})\] react with carbon monoxide at elevated pressures to produce the diacetyl derivatives \([\text{Pd}_2(\mu-X)(\text{COCH}_3)_2(\mu-\text{dppm})_2]X\) \((X = \text{Br}, \text{I})\). \(^{85}\) This reaction, however, does not take place when the counter ion is a non-coordinating anion such as hexafluorophosphate.

This may indicate that carbonylation takes place via the initial attack of carbon monoxide on the face to face dimer or else the iodide and bromide promotes insertion of carbon monoxide in a manner which is not clearly understood. The
complex \([\text{Pd}_2(\mu-\text{I})(\text{COCH}_3)_2(\mu-\text{dppm})_2]\text{I}\) reacts with a variety of substrates such as oxygen, iodine, bromine and diphenyl disulphide to give acetic anhydride, acetyl iodide, acetyl bromide and phenyl thioacetate respectively. In all cases, the palladium complex is converted to \(\text{Pd}_2\text{I}_2(\mu-\text{dppm})_2\).

\([\text{Pt}_2(\mu-\text{Cl})(\text{CH}_3)_2(\mu-\text{dppm})_2]\text{Cl}\) has been prepared by the reaction of \(\text{Pt}(\text{CH}_3)_2(\text{dppm})\), with \(\text{HCl}\) in benzene.

The synthesis of rhodium A-frame complexes by a method analogous to that used in the synthesis of many palladium and platinum A-frames (page 18) has been reported.\(^{45,46}\) This involves the direct addition of small molecules across the rhodium-rhodium single bond of \(\text{Rh}_2(\text{CO})_2(\mu-\text{dppm})_2\), a complex that is electronically similar to \(\text{M}_2\text{X}_2(\mu-\text{dppm})_2\) (\(\text{M} = \text{Pd, Pt; X} = \text{Cl, Br, I}\)). The synthesis of \(\text{Rh}_2(\text{CO})_2(\mu-\text{dppm})_2\) has been achieved by the reduction of \(\text{trans-Rh}_2\text{Cl}_2(\text{CO})_2(\mu-\text{dppm})_2\) with sodium borohydride in ethanol suspension. \(\text{Rh}_2(\text{CO})_2(\mu-\text{dppm})_2\) (41) is extremely reactive and adds a variety of ligands such as acids (\(\text{H}^+\)), carbon monoxide, acetylenes, carbon dioxide and isocyanide across the rhodium-rhodium single bond to give \(\text{Rh}_2(\mu-\text{X})(\text{CO})_2(\mu-\text{dppm})_2\) (42) (equation 8). With \(\text{X} = \text{CH}_3\text{NC}\), it proved necessary to add one equivalent only of the ligand in order to obtain \(\text{Rh}_2(\mu-\text{CNCH}_3)(\text{CO})_2(\mu-\text{dppm})_2\) since the addition of excess resulted in the isolation of \(\text{Rh}_2(\mu-\text{CNCH}_3)(\text{CNCH}_3)_2(\mu-\text{dppm})_2\). This behaviour is analogous to the reaction of
isostructural $\text{Pd}_2X_2(\mu\text{-dppm})_2$ ($X = \text{Cl}, \text{Br}$) with excess methyl isocyanide. The first step of this reaction also involves the insertion of one molecule of methyl isocyanide into the palladium-palladium single bond to give $[\text{Pd}_2(\mu\text{-CNCH}_3)(X)\text{H}]_2(\mu\text{-dppm})_2$ which can further react with excess methyl isocyanide to give $[\text{Pd}_2(\mu\text{-CNCH}_3)(\text{CNCH}_3)_2(\mu\text{-dppm})_2]^{2+}$. This complex has been structurally characterized as the hexafluorophosphate salt and shown to be devoid of a palladium-palladium single bond (3.215(2) Å), as expected. $\text{Rh}_2(\text{CO})_2(\mu\text{-dppm})_2$ not only adds acetylenes across the rhodium-rhodium bond but also acts as a catalyst for the hydrogenation of both ethylene and acetylene to ethane at 80 °C, with the rate of acetylene hydrogenation being greater than that for ethylene hydrogenation. This suggests that two different mechanisms are operative for these hydrogenation reactions.
Since acetylenes are known to add across the rhodium-rhodium single bond of \( \text{Rh}_2(\text{CO})_2(\mu\text{-dppm})_2 \), the hydrogenation of acetylenes may well involve activation of the substrate by both metals prior to its hydrogenation whereas the reaction with ethylene most probably involves attachment of the substrate only to one single metal centre prior to hydrogenation.

The successive addition of acid(H⁺) and carbon monoxide to \( \text{Rh}_2(\text{CO})_2(\mu\text{-dppm})_2 \) in either order produces the \([\text{Rh}_2(\mu\text{-H})(\mu\text{-CO})(\text{CO})_2(\mu\text{-dppm})_2]^+\) cation which has been structurally characterized as the p-toluene sulphonate salt.46 The geometry at each metal centre of \([\text{Rh}_2(\mu\text{-H})(\mu\text{-CO})(\text{CO})_2(\mu\text{-dppm})_2]^+\) (p-CH₃C₆H₄SO₃).THF can best be described as a distorted square pyramid and the rhodium-rhodium distance of 2.731(2) Å indicates the presence of a rhodium-rhodium single bond. The presence of a metal-metal bond is somewhat surprising in this instance since conventional electron counting does not impute a rhodium-rhodium single bond in \([\text{Rh}_2(\mu\text{-H})(\mu\text{-CO})(\text{CO})_2(\mu\text{-dppm})_2]^+\). The presence of single bond indicates that despite a thirty-two electron count this molecule resembles the A-frame carbon monoxide adducts, \([\text{Rh}_2(\mu\text{-Cl})(\mu\text{-CO})(\text{CO})_2(\mu\text{-dppm})_2]\text{BPh}_4\) and \([\text{Ir}_2(\mu\text{-S})(\mu\text{-CO})(\text{CO})_2(\mu\text{-dppm})_2]\text{BPh}_4\), both of which have metal-metal bonds as a result of their thirty-four electron configurations. This notion has been supported by the theoretical work of Hoffman and
Hoffmann which revealed that the molecular orbital pictures of $[\text{Rh}_2(\mu-\text{H})(\mu-\text{CO})(\text{CO})_2(\mu-\text{dppm})_2]^+$ and $[\text{Rh}_2(\mu-\text{Cl})(\mu-\text{CO})(\text{CO})_2(\mu-\text{dppm})_2]^+$ are in fact very similar.

The bridging carbonyl group of $[\text{Rh}_2(\mu-\text{H})(\mu-\text{CO})(\text{CO})_2(\mu-\text{dppm})_2]^+$ can be removed by heating the complex to 60 °C in tetrahydrofuran solution yielding the cationic A-frame, $[\text{Rh}_2(\mu-\text{H})(\text{CO})_2(\mu-\text{dppm})_2]^+$. From this complex, the Rh(0) starting material $\text{Rh}_2(\text{CO})_2(\mu-\text{dppm})_2$ can be obtained by treatment with one mole of sodium trimethoxyborohydride. Conversion of $\text{Rh}_2(\mu-\text{CO})(\text{CO})_2(\mu-\text{dppm})_2$ to $\text{Rh}_2(\text{CO})_2(\mu-\text{dppm})_2$, however, does not appear to be possible. This behaviour is in contrast to the palladium and platinum analogues $\text{M}_2(\mu-\text{CO})\text{Cl}_2(\mu-\text{dppm})_2$ ($\text{M} = \text{Pd, Pt}$) in which facile removal of the bridging carbonyl group has been observed. $[\text{Rh}_2(\mu-\text{H})(\mu-\text{CO})(\text{CO})_2(\mu-\text{dppm})_2]^+$ is found to be a very efficient homogeneous catalyst for the water-gas shift reaction $(\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2)$. Furthermore, this complex is found to catalyze the hydroformylation and hydrogenation of ethylene to propanal and ethane respectively with $\text{CO} + \text{H}_2\text{O}$ as the source of hydrogen.

Alkynitrosoureas are known to act as sources of carbenes and nitrosylating agents in the presence of transition metal complexes. Somewhat different behaviour, however, has been observed in the presence of the Rh(0) complex, $\text{Rh}_2(\text{CO})_2(\mu-\text{dppm})_2$. This complex promotes the
decomposition of alkylnitrosoureas, eventually leading to the face to face dimer, \( \text{Rh}_2(\text{NCO})_2(\text{CO})_2(\mu-\text{dppm})_2 \) which has also been prepared by Sanger\(^80\) from the reaction of \( \text{Rh}_2\text{Cl}_2(\text{COD})_2 \) with potassium cyanate and dppm in an atmosphere of carbon monoxide. When \( [\text{Rh}_2(\mu-\text{H})(\mu-\text{CO})(\text{CO})_2(\mu-\text{dppm})_2]^+ \) is used, however, the cationic A-frame \( [\text{Rh}_2(\mu-\text{NCO})(\text{CO})_2(\mu-\text{dppm})_2]^+ \) is formed. These reactions have been studied by monitoring the gaseous by-products formed and plausible reaction pathways have been proposed.

Although no hydrido dppm complexes of palladium are known, the following dimeric, electron-deficient bridging platinum hydrido complexes have been reported: \( [\text{Pt}_2(\mu-\text{H})\text{H}_2(\mu-\text{dppm})_2]^+ \)\(^{115,116}\), \( [\text{Pt}_2(\mu-\text{H})\text{Cl}_2(\mu-\text{dppm})_2]^+ \)\(^{115,116}\) and \( [\text{Pt}_2(\mu-\text{H})(\text{CH}_3)_2(\mu-\text{dppm})_2]^+ \)\(^{117,118}\). Of these complexes, \( [\text{Pt}_2(\mu-\text{H})\text{H}_2(\mu-\text{dppm})_2]^+ \) has been examined extensively and shown to exhibit a rich chemistry.\(^{119-122}\) The most interesting reaction undergone by this complex is the reversible addition-elimination reaction with carbon monoxide to give hydrogen and \( [\text{Pt}_2(\mu-\text{H})(\text{CO})(\mu-\text{dppm})_2]^+ \)\(^{(44)}\) (equation 9).\(^{120,122}\) This reaction is noteworthy since it appears to be the first example of a reversible reductive elimination of dihydrogen from a binuclear complex mitigated by carbon monoxide. The reversible displacement of carbon monoxide by dihydrogen in transition metal complexes is rare but has been observed in two situations as shown in equations 10 and 11.\(^{123,124}\)
Ir(CO)$_3$(PPh$_3$)$_2$ + H$_2$ $\rightleftharpoons$ IrH$_2$(CO)$_2$(PPh$_3$)$_2$ + CO  \hfill (10)

Os$_3$(CO)$_{12}$ + H$_2$ $\rightleftharpoons$ Os$_3$H$_2$(CO)$_{10}$ + 2 CO  \hfill (11)

Similar behaviour has been observed when [Pt$_2(\mu$-$\text{H})H_2(\mu$-dppm)$_2$]$^+$ is treated with monophosphines such as methyldiphenylphosphine, triphenylphosphine and diphosphines such as dppm. The reactions with phosphines are found to be rapid by comparison to that with carbon monoxide.

Studies have shown that [Pt$_2(\mu$-$\text{H})H_2(\mu$-dppm)$_2$]$^+$ acts as a catalyst for the water-gas shift reaction at 100 °C in methanol and equation 9 is an important step in the proposed catalytic cycle.
1.2.2(ii). A-frame Complexes with Metal-Metal Bonds

$\text{Rh}_2(\mu$-SO$_2$)Cl$_2(\mu$-dppm)$_2$ prepared by the reaction of $[\text{Rh}_2(\mu$-Cl)(CO)$_2(\mu$-dppm)$_2]^+$ with sulphur dioxide in the presence of chloride ions (vide infra), was the first structurally characterized rhodium A-frame complex shown to contain a metal-metal bond. The sulphur dioxide molecule was found to bridge the metal centres through sulphur in a symmetrical fashion with approximate tetrahedral geometry around the sulphur. This is the most commonly observed coordination mode for sulphur dioxide in polynuclear complexes when bridging two metal atoms. The sulphur dioxide bridges found in polynuclear complexes are either supported by a metal-metal bond, as in $[\text{Fe(CO)}_4]_2\text{SO}_2$ and/or by other ligands, or they can be unsupported as, for example, in $[\text{Pd}_2(\mu$-SO$_2$)Cl$_2(\mu$-dppm)$_2]$. Although polynuclear complexes with unsupported sulphur dioxide bridges are less common, those few that have been structurally characterized all show large M-S-M angles (91.2(2)-118.0(2)°). $\text{Pd}_2(\mu$-SO$_2$)Cl$_2(\mu$-dppm)$_2$, for example, exhibits a Pd-S-Pd angle of 95.2° (av.). Bridging sulphur dioxide complexes with metal-metal bonds, on the other hand, show more typical M-S-M angles of ca. 80°. Although exhibiting a normal Rh-S-Rh angle of 79.84(7)°, $\text{Rh}_2(\mu$-SO$_2$)Cl$_2(\mu$-dppm)$_2$ displays some rather unusual structural parameters. For example, both Rh-S distances were found to be significantly shorter than other metal-sulphur distances for second row and third row
platinum metals in structurally related complexes.\textsuperscript{33,126} This seems to be attributable to the extensive back donation of electrons from both metals to the sulphur \(\pi^*\) unoccupied orbitals. This can be supported by the S-O stretching frequencies which are relatively low by comparison with those found in similar complexes.

In dichloromethane, \(\text{Rh}_2(\mu-\text{SO}_2)\text{Cl}_2(\mu-\text{dppm})_2\) reacts with carbon monoxide with the displacement of sulphur dioxide to give \([\text{Rh}_2(\mu-\text{Cl})(\mu-\text{CO})(\text{CO})_2(\mu-\text{dppm})_2]\text{Cl}\) which, on isolation either by evaporation or precipitation with diethyl-ether, gives trans-Rh\(_2\)Cl\(_2\)(CO)\(_2\)(\mu-dppm)\(_2\).

Other metal-metal bonded A-frame complexes have resulted from attempts, to synthesize face to face dimers trans-Rh\(_2\)Br\(_2\)(CO)\(_2\)(\mu-dppm)\(_2\) and trans-Rh\(_2\)I\(_2\)(CO)\(_2\)(\mu-dppm)\(_2\) by metathetical exchange of the chloride in trans-Rh\(_2\)Cl\(_2\)(CO)\(_2\)(\mu-dppm)\(_2\).\textsuperscript{22} The reaction of sodium bromide with trans-Rh\(_2\)(\mu-\text{CO})(\text{CO})\(_2\)(\mu-dppm)\(_2\) gives initially an asymmetric species, [Rh\(_2\)(\mu-\text{CO})(\text{CO})\(_2\)(\mu-dppm)\(_2\)]Br\(_2\) (45) which slowly rearranges in solution to give the symmetric A-frame complex, Rh\(_2\)(\mu-\text{CO})-\text{Br} \(_2\)(\mu-dppm)\(_2\) (46). An X-ray structure determination of this complex has revealed the presence of a rhodium-rhodium single bond (2.7566(9) Å) and a normal bridging carbonyl group (Rh-C(O)-Rh = 89.4(4)°).\textsuperscript{43} The IR spectrum for this complex, however, indicates an unusually low bridging carbonyl stretching frequency (\(\nu(\text{CO}) = 1745 \text{ cm}^{-1}\)) similar to that observed for a ketonic type bridging carbonyl group.
A well-established dogma proposed by Cotton in metal carbonyl chemistry is as follows: "Carbonyl bridges are always accompanied by a metal-metal bond." These carbonyl groups are referred to as normal bridging carbonyl groups and the $\text{MCM}$ angle varies from about $70^\circ$-$90^\circ$. Furthermore, these normal bridging carbonyl groups have carbonyl stretching frequencies typically in the range 1900-1800 cm$^{-1}$. The bonding of normal bridging carbonyl groups can be considered as involving two electron three centre, molecular orbitals extending over one carbon and two metals.

Recently, four complexes have been structurally characterized and shown to violate the generalization proposed by Cotton. The first structurally characterized bridging carbonyl group without the benefit of a
formal metal-metal bond was found in \( \text{Pd}_2(\mu-\text{CO})\text{Cl}_2(\mu-\text{dpam})_2 \). The main structure difference between the normal bridging carbonyl group and the bridging carbonyl of \( \text{Pd}_2(\mu-\text{CO})\text{Cl}_2(\mu-\text{dpam})_2 \) is the large MCM angle of 119(3)° observed for the latter. This value is very close to that of an sp\(^2\) hybridized carbon atom in organic carbonyl groups. The bridging carbonyl stretching frequency of \( \text{Pd}_2(\mu-\text{CO})\text{Cl}_2(\mu-\text{dpam})_2 \) which appears at 1720 cm\(^{-1}\) in the IR spectrum is also comparable to values obtained for organic carbonyl groups. These physical parameters characterize what are now commonly referred to as ketonic type bridging carbonyl groups or dimetallated ketones. In short, these terms refer to bridging carbonyl groups which are not accompanied by a metal-metal bond. The MCM angle is the main criterion used to distinguish ketonic bridging carbonyls from normal bridging carbonyls. The bonding of the ketonic carbonyl groups to two metal centres can be visualized as the formation of two localized Rh-C sigma bonds as known in organic carbonyl groups. \(^{131}\) Although the position of the bridging carbonyl stretching frequency in the IR spectrum can be used to distinguish between ketonic carbonyls and normal carbonyl groups, this criterion is not always reliable and should be applied with caution. As an example, structurally characterized \( \text{Rh}_2(\mu-\text{CO})\text{Br}_2(\mu-\text{dppm})_2 \) has a normal bridging carbonyl group; nevertheless the carbonyl group stretch appears at 1745 cm\(^{-1}\). The low bridging carbonyl frequency observed for
this compound seems to result from extensive back donation of electron density from both metals to the \( \pi^* \) orbitals of the carbonyl group. This is supported by the short Rh-C distances and the unusually low field\(^\text{13}\)C chemical shift of the bridging carbonyl resonance (227.5 ppm). The usual chemical shift values for normal carbonyl bridges when attached to two centres are generally in the range 200-210 ppm.\(^\text{75}\) The chloro analogue, \( \text{Rh}_2(\mu\text{-CO})\text{Cl}_2(\mu\text{-dppm})_2 \) can be prepared by refluxing \( \text{trans-Rh}_2\text{Cl}_2(\text{CO})_2(\mu\text{-dppm})_2 \) in either benzene or toluene solution whereas \( \text{Rh}_2(\mu\text{-CO})\text{I}_2(\mu\text{-dppm})_2 \) can only be made from the metathetical exchange of chloride with potassium iodide in \( \text{Rh}_2(\mu\text{-CO})\text{Cl}_2(\mu\text{-dppm})_2 \).

Both the dichloro and diiodo complexes, \( \text{Rh}_2(\mu\text{-CO})X_2(\mu\text{-dppm})_2 \) (\( X = \text{Cl, I} \)) also exhibit low carbonyl stretching frequencies.

The reaction of \( \text{trans-Rh}_2\text{Cl}_2(\text{CO})_2(\mu\text{-dppm})_2 \) with potassium iodide also gives an asymmetric species \[ \text{[Rh}_2(\mu\text{-CO})(\text{CO})\text{I}(\mu\text{-dppm})_2]I \] similar to that obtained when sodium bromide is used (\textit{vide supra}). Unlike the bromo analogue, however, \( \text{[Rh}_2(\mu\text{-CO})(\text{CO})\text{I}(\mu\text{-dppm})_2]I \) does not lose carbon monoxide to give the symmetric species \( \text{Rh}_2(\mu\text{-CO})\text{I}_2(\mu\text{-dppm})_2 \). These observations are thought to be related to the bulky nature of the halide ligand. Although the simultaneous coordination of two chlorides and two carbonyls is possible in \( \text{trans-Rh}_2\text{Cl}_2(\text{CO})_2(\mu\text{-dppm})_2 \), the increased steric bulk of bromide compared to chloride does not appear to
permit the formation of trans-Rh₂Br₂(CO)₂(μ-dppm)₂. As a result, an asymmetric species [Rh₂(μ-CO)(CO)Br(μ-dppm)₂]Br results. When recoordination of the bromide takes place, however, the reaction is accompanied by the loss of carbon monoxide, presumably because of steric strain, resulting in the formation of Rh₂(μ-CO)Br₂(μ-dppm)₂. The iodo species [Rh₂(μ-CO)(CO)I(μ-dppm)₂]I does not undergo recombination of iodide even with loss of carbon monoxide and hence [Rh₂(μ-CO)(CO)I(μ-dppm)₂]I appears to be the stable species. This steric argument has been further supported by considering the dpam analogues. Although trans-Rh₂Br₂(CO)₂(μ-dppm)₂ is not known, the corresponding arsine analogue, trans-Rh₂Br₂(CO)₂(μ-dpam)₂ is found to exist and this has been attributed to the larger bite size of the dpam ligands allowing more room to accommodate both bromides and carbonyls without considerable steric interaction. The reaction of potassium iodide with trans-Rh₂Br₂(CO)₂(μ-dppm)₂ is known to give a mixture consisting of an asymmetric species [Rh₂(μ-CO)(CO)I(μ-dppm)₂]I and the diiodo dicarbonyl dimer, trans-Rh₂I₂(CO)₂(μ-dpam)₂, with the former complex as the major product. Hence, even with dpam as the bridging ligand, the formation of the asymmetric product [Rh₂(μ-CO)(CO)I(μ-dpam)₂]I as the major product stresses the fact that there is considerable steric interaction in these face to face dimers.
The asymmetric species \([\text{Rh}_2(\mu-\text{CO})(\text{CO})X(\mu-\text{dpdm})_2]X\) \((X = I, \text{Br})\) react with carbon monoxide to give the fully symmetric tricarbonyl complexes \([\text{Rh}_2(\mu-X)(\mu-\text{CO})(\text{CO})_2(\mu-\text{dpdm})_2]X\) \((X = \text{Br}, I)\). The ease of decarbonylation of these complexes shows an interesting trend. \([\text{Rh}_2(\mu-\text{Cl})-(\text{CO})_2(\mu-\text{dpdm})_2]\text{Cl}\) loses carbon monoxide rapidly in solution under a dinitrogen purge or more slowly in the solid state to give \(\text{trans-Rh}_2\text{Cl}_2(\text{CO})_2(\mu-\text{dpdm})_2\). When the anion is a non-coordinating one such as tetraphenylborate \((\text{BPh}_4^-)\), carbon monoxide is lost in the solid state only in vacuo. On the other hand, \([\text{Rh}_2(\mu-\text{Br})(\mu-\text{CO})(\text{CO})_2(\mu-\text{dpdm})_2]\text{Br}\) does not lose carbon monoxide under vacuum in the solid state but does so very slowly in solution to give \(\text{Rh}_2(\mu-\text{CO})\text{Br}_2(\mu-\text{dpdm})_2\). The removal of the bridging carbonyl group from \([\text{Rh}_2(\mu-\text{Br})(\mu-\text{CO})(\text{CO})_2(\mu-\text{dpdm})_2]\text{BPh}_4\) can only be achieved by bubbling nitrogen through its solution for about twenty-four hours. The complexes \([\text{Rh}_2(\mu-I)(\mu-\text{CO})(\text{CO})_2(\mu-\text{dpdm})_2]Y\) \((Y = I, \text{BPh}_4^-)\) do not lose carbon monoxide under any circumstances. The reaction of \([\text{Rh}_2(\mu-\text{CO})(\text{CO})X(\mu-\text{dpdm})_2]X\) \((X = \text{Br}, I)\) with sulphur dioxide also gives the symmetrical species \([\text{Rh}_2(\mu-X)(\mu-\text{SO}_2)(\text{CO})_2(\mu-\text{dpdm})_2]X\). \([\text{Rh}_2(\mu-\text{Br})-(\mu-\text{SO}_2)(\text{CO})_2(\mu-\text{dpdm})_2]\text{Br}\) on prolonged exposure to sulphur dioxide, however, gives \(\text{Rh}_2(\mu-\text{SO}_2)\text{Br}_2(\mu-\text{dpdm})_2\).

The reactions of \(\text{Rh}_2(\mu-\text{CO})X_2(\mu-\text{dpdm})_2\) \((X = \text{Cl}, \text{Br})\) with carbon monoxide,\(^{22}\) sulphur dioxide,\(^{22}\) activated
Acetylenes \((X = \text{Cl, Br, I})\)\(^{78,79}\) and carbon disulphide \((X = \text{Cl})\)\(^{132,133}\) have been studied. The reaction of carbon monoxide with \(\text{Rh}_2(\mu-\text{CO})_X(\mu-\text{dppm})_2\) \((X = \text{Cl})\) \((47)\); \(X = \text{Br}\) \((46)\) are depicted in scheme 3. With excess carbon monoxide, the tricarbonyl species, \([\text{Rh}_2(\mu-X)(\mu-\text{CO})(\text{CO})_2(\mu-\text{dppm})_2]X\) \((X = \text{Cl}\) \((48)\); \(X = \text{Br}\) \((49)\)) are obtained. The stepwise addition of carbon monoxide to \(\text{Rh}_2(\mu-\text{CO})\text{Br}_2(\mu-\text{dppm})_2\) at least has revealed that the formation of the tricarbonyl species occurs via \([\text{Rh}_2(\mu-\text{CO})(\text{CO})X(\mu-\text{dppm})_2]X\) \((X = \text{Cl} \(50)\); \(X = \text{Br}\) \((45)\)) \(\text{trans-Rh}_2\text{Cl}_2(\text{CO})_2(\mu-\text{dppm})_2\). The treatment of \(\text{Rh}_2(\mu-\text{CO})\text{Cl}_2(\mu-\text{dppm})_2\) with carbon monoxide very slowly causes the precipitation of \(\text{trans-Rh}_2\text{Cl}_2(\text{CO})_2(\mu-\text{dppm})_2\). This observed dependence on the rate of carbon monoxide addition has been explained as follows: carbon monoxide is added slowly, free chloride attacks the site between the bridging and terminal carbonyl groups of the intermediate, \([\text{Rh}_2(\mu-\text{CO})\text{Cl}(\text{CO})(\mu-\text{dppm})_2]Cl\) \((50)\) to give \(\text{trans-Rh}_2\text{Cl}_2(\text{CO})_2(\mu-\text{dppm})_2\) \((6)\) whereas in the presence of excess carbon monoxide, carbon monoxide attacks the site between the terminal chloride and bridging carbon monoxide with the terminal chloride moving into the bridging position to give \([\text{Rh}_2(\mu-\text{Cl})(\mu-\text{CO})(\text{CO})_2(\mu-\text{dppm})_2]Cl\) \((48)\).

The treatment of \(\text{Rh}_2(\mu-\text{CO})X_2(\mu-\text{dppm})_2\) \((X = \text{Cl, Br})\) with sulphur dioxide yields \(\text{Rh}_2(\mu-\text{SO}_2)X_2(\mu-\text{dppm})_2\) and \([\text{Rh}_2(\mu-X)(\mu-\text{SO}_2)(\text{CO})_2(\mu-\text{dppm})_2]X\) \((X = \text{Cl, Br})\). For \(X = \text{Br}\) \((46)\), the formation of three symmetric species
Scheme 3
Scheme 4
([(49), (51) and (52)] and two asymmetric species [(45) and (53)] has been observed during the course of this reaction. The structures proposed for these species have been derived mainly from $^{31}P{^1H}$ spectroscopy. A plausible reaction sequence for the formation of these products is shown in scheme 4. The intermediate [Rh$_2$(μ-SO$_2$)Br(CO)(μ-dppm)$_2$]Br (53) is analogous to that observed in the reaction of Rh$_2$(μ-CO)X$_2$(μ-dppm)$_2$ (X = Cl, Br) with carbon monoxide. The reaction of Rh$_2$(μ-CO)Cl$_2$(μ-dppm)$_2$ with sulphur dioxide appears to be much simpler and species analogous to 45 and 49 have not been observed, despite the fact that the final products are Rh$_2$(μ-SO$_2$)Cl$_2$(μ-dppm)$_2$ and [Rh$_2$(μ-Cl)(μ-SO$_2$)-(CO)$_2$(μ-dppm)$_2$]Cl.

Activated acetylenes such as hexafluoro-2-butyne (HFB) and dimethyl acetylenedicarboxylate (DMAD) can be added across the metal-metal bond of Rh$_2$(μ-CO)X$_2$(μ-dppm)$_2$ (X = Cl, Br and I) to give the complexes [Rh$_2$(μ-CO)(μ-Acet)-X$_2$(μ-dppm)$_2$] (X = Cl, Br and I; Acet = DMAD, HFB). The structure determination of Rh$_2$(μ-CO)(μ-DMAD)Cl$_2$-(μ-dppm)$_2$ (54) revealed that the acetylene molecule is coordinated as cis-dimetallated olefin (r(C=C) = 1.32(1) Å, <Rh-C-C = 120.3(2)°) whereas the bridging carbonyl group is of the dimetallated ketone type (<Rh-C(O)-Rh = 116.0(4)°). The rhodium-rhodium separation of 3.3542(9) Å suggests the absence of rhodium-rhodium single bond, in keeping with the
thirty-two electron count. The reaction of trans-$\text{Rh}_2\text{Cl}_2(\text{CO})_2(\mu$-$\text{dppm})_2$ with hexafluoro-2-butyne and dimethyl acetylenedicarboxylate also gives $\text{Rh}_2(\mu$-$\text{CO})(\mu$-$\text{Acet})\text{Cl}_2(\mu$-$\text{dppm})_2$ (Acet = HFB and DMAD). $\text{Rh}_2(\mu$-$\text{CO})\text{Cl}_2(\mu$-$\text{dppm})_2$ acts as a catalyst or catalyst precursor for the cyclo-trimerization of dimethyl acetylenedicarboxylate to hexamethyl mellitate at room temperature in methanol. It has been established by Maitlis that cyclo-trimerization of dimethylacetylene dicarboxylate by Pd(II) halide complexes involves the insertion of acetylene into the palladium-halide bond. A similar mechanism would appear to be involved here since the reaction takes place only in methanol where chloride dissociation can take place. Accordingly, no catalytic activity was observed in dichloromethane. $\text{Rh}_2(\mu$-$\text{CO})\text{Cl}_2(\mu$-$\text{dppm})_2$ is also capable of acting as a catalyst or catalyst precursor for the hydrogenation of styrene.
to ethyl benzene in methanol.

The ketonic bridging carbonyl group of \( \text{Rh}_2(\mu-\text{HFB})(\mu-\text{CO})\text{Cl}_2(\mu-\text{dppm})_2 \) can be removed by heating with excess trimethyl amine-oxide in chloroform solution, yielding the A-frame complex \( \text{Rh}_2(\mu-\text{HFB})\text{Cl}_2(\mu-\text{dppm})_2 \) (55). An X-ray structural determination of this complex revealed that the acetylene is bound as a cis-dimetallated olefin (\( \text{r(C=C)} = 1.31(1) \, \text{Å}, < \text{Rh-C-C} = 110.0(7)° \)). The rhodium-rhodium distance of 2.7447(9) Å indicates the presence of rhodium-rhodium single bond which is also expected from conventional electron counting techniques. As a result of the strain imposed on the acetylene by the short rhodium-rhodium single bond, the Rh-C-C angles are found to deviate from idealized \( sp^2 \) hybridization. Similar distortions are seen to occur in complexes \( (\text{n}^5-\text{C}_5\text{H}_5)_2\text{Rh}_2(\text{CO})_2(\mu-\text{HFB}) \)\(^{106}\) and \( \text{Pt}_2(\text{CO})_2(\text{PPh}_3)_2(\text{C}_2(\text{CO}_2\text{CH}_3)_2) \)\(^{107}\) having the acetylene bound as a cis-dimetallated olefin accompanied by a metal-metal bond. By way of contrast, when no metal-metal bond is present
the acetylene ligand approaches very closely the geometry of an olefin. For example, Rh$_2$(μ-CO)(μ-DMAD)Cl$_2$(μ-dppm)$_2$ and Pd$_2$(μ-HFB)Cl$_2$(μ-dppm)$_2$ have M-C-C angles of 120.3(2)° and 122.5(1)° (av.) respectively. The acetylenic carbon-carbon distances found in Rh$_2$(μ-HFB)Cl$_2$(μ-dppm)$_2$ (1.31(1) Å) and Rh$_2$(μ-CO)(μ-DMAD)Cl$_2$(μ-dppm)$_2$ (1.32(1) Å) are comparable with normal carbon-carbon double bonds (1.34 Å). This suggests that there is significant activation of the acetylene molecule when coordinated between the two metals in this fashion.

The reaction of carbon monoxide with Rh$_2$(μ-HFB)Cl$_2$(μ-dppm)$_2$ regenerates Rh$_2$(μ-CO)(μ-HFB)Cl$_2$(μ-dppm)$_2$ with the direct addition of carbon monoxide across the rhodium-rhodium single bond. Similarly with diazomethane, the insertion of a methylene group across the rhodium-rhodium single bond occurs to give the methylene bridged complex Rh$_2$(μ-CH$_2$)(μ-HFB)Cl$_2$(μ-dppm)$_2$ (56). An X-ray structural
determination of this complex shows hexafluoro-2-butyne
coordinated as a cis-dimetallated olefin (r(C=C) = 1.34(1) Å;
< Rh-C-C = 119.9(9)° and 124(1)°) and the absence of a metal-
metal bond (3.464(1) Å). The most conspicuous feature of
this structure is the angle of 114.5(5)° which is consider-
ably larger than the typical angle observed for methylene
groups bridging bonded metal atoms (74 - 88°). This is
principally due only to the large metal-metal separation
caused by the mode of acetylene bonding. In A-frame chemis-
try two other examples are known of methylene insertion
across a metal-metal bond to give bridging methylene com-
plexes. These include the reactions of either Pt₂Cl₂-
(μ-dppm)₂ 37 or [Pt₂H(PPh₃)(μ-dppm)₂]PF₆ 137 with diazomethane
to give Pt₂(μ-Th₂)Cl₂(μ-dppm)₂ and [Pt₂(μ-Th₂)(CH₂PPh₃)Cl-
(μ-dppm)₂]PF₆ respectively. Both these complexes have been
structurally characterized and shown to possess large Pt-C-Pt
angles in keeping with their observed lack of metal-metal
bonds. 137,138 Although not structurally characterized
bridging methylene complex and substituted methylene com-
plexes [Pd₂(μ-CHR)I₂(μ-dppm)₂] (R = H, CH₃) without metal-
metal bonds are known in palladium-dppm chemistry. 84 These
complexes have been synthesized from the reaction of
Pd₂(dppm)₃ with organic dihalides' (CHR₂: R = H, CH₃) which
is an example of a two centre, three fragment oxidative
addition reaction (equation 47, chapter 5). These com-
plexes, Pd₂(μ-CHR)I₂(μ-dppm)₂ react with acids such as
aqueous fluoroboric acid to bring about the protonation of the bridging ligand to form \( \text{Pd}_2(\mu-I)(\text{CH}_2\text{R})\text{I}(\mu-\text{dppm})_2 \) (\( \text{R} = \text{H, CH}_3 \)). The complex, \([\text{Pd}_2(\mu-I)(\text{CH}_3)\text{I}(\mu-\text{dppm})_2]\text{BF}_4\) represents the first structurally characterized example of an A-frame complex with an asymmetric geometry.\(^{139}\) The attempts to insert carbon monoxide, sulphur dioxide and isocyanides across the palladium-carbon bond in \( \text{Pd}_2(\mu-\text{CH}_2)\text{I}_2(\mu-\text{dppm})_2 \) have met with failure. No attempts to perform similar insertion reactions on the bridging methylene complexes of platinum, however, have been reported. Recent interest in transition metal methylene complexes stems largely from their relevance as proposed catalytic intermediates in the Fischer-Tropsch synthesis.\(^{140, 141}\) Unfortunately, no reaction that would mimic a catalytic step in the Fischer-Tropsch reaction has yet been observed in these methylene bridged A-frame complexes and, in fact, their general lack of reactivity has proven rather disappointing.

The complexes \( \text{Rh}_2(\mu-\text{SO}_2)\text{X}_2(\mu-\text{dppm})_2 \) (\( \text{X} = \text{Cl, Br} \)), \( \text{Rh}_2(\mu-\text{CO})\text{X}_2(\mu-\text{dppm})_2 \) (\( \text{X} = \text{Cl, Br, I} \)) and \( \text{Rh}_2(\mu-\text{HFB})\text{Cl}_2(\mu-\text{dppm})_2 \) are analogous to a series of palladium complexes \( \text{Pd}_2(\mu-\text{CO})\text{X}_2(\mu-\text{dppm})_2 \) (\( \text{X} = \text{Cl, Br} \))\(^{32} \) \( \text{Pd}_2(\mu-\text{SO}_2)\text{X}_2(\mu-\text{dppm})_2 \) (\( \text{X} = \text{Cl, Br} \))\(^{33} \) and \( \text{Pd}_2(\mu-\text{HFB})\text{Cl}_2(\mu-\text{dppm})_2 \)\(^{37} \) These palladium complexes have been prepared by direct addition of the appropriate small molecule across the palladium-palladium single bond of the side by side dimer, \( \text{Pd}_2\text{Cl}_2(\mu-\text{dppm})_2 \).
The main difference between the rhodium and palladium analogues is that the latter do not contain metal-metal bonds. The reaction of Pd$_2$X$_2$(μ-dppm)$_2$ (X = Cl, Br) with carbon monoxide to produce Pd$_2$(μ-CO)Cl$_2$(μ-dppm)$_2$ represented the first example of the reversible addition of carbon monoxide across a metal-metal bond. This can be considered as a simple model for the adsorption and desorption of carbon monoxide on a metal surface. Similar behaviour has been observed for sulphur dioxide whereas the addition of acetylenes (DMAD, HFB) across the palladium-palladium bond is found to be irreversible. The structure of Pd$_2$(μ-HFB)-Cl$_2$(μ-dppm)$_2$ has been determined and found to possess the acetylene bound to the metal centres as a cis-dimetallated olefin (r(C=C) = 1.338(16) Å; <Pd-C-C = 123.5(9)° and 121.5(9)°) without a palladium-palladium bond. Like their rhodium analogue, both Pd$_2$(μ-DMAD)X$_2$(μ-dppm)$_2$ (X = Cl, I) are found to act as catalysts or catalyst precursors for the cyclotrimerization of dimethyl acetylenedicarboxylate to hexamethyl mellitate.

The reaction of Rh$_2$(μ-CO)Cl$_2$(μ-dppm)$_2$ with carbon disulphide yields an asymmetric species Rh$_2$Cl$_2$(CO)(C$_2$S$_4$)- (μ-dppm)$_2$ (57) in which two carbon disulphide molecules have condensed to form a heterometallocycle.$^{132,133}$ This species can also be obtained by the reaction of trans-Rh$_2$Cl$_2$(CO)$_2$- (μ-dppm)$_2$ with carbon disulphide. The structure of
\[ \text{Rh}_2\text{Cl}_2(\text{CO})(\text{C}_2\text{S}_4)(\mu-\text{dppm})_2 \] is depicted below and shows that the \( \text{C}_2\text{S}_4 \) fragment forms a five membered metallocycle, \[ \text{Rh}-\text{S}-\text{C}(\text{S})-\text{S}-\text{C}(\text{S}) \] with one rhodium atom, while simultaneously bonding through an exocyclic sulphur atom to the second rhodium atom forming a four membered metallocycle \( \text{Rh} = \text{S} - \text{Rh} \).

The slow stepwise addition of carbon disulphide to \( \text{Rh}_2(\mu-\text{CO})\text{Cl}_2(\mu-\text{dppm})_2 \) (47) has demonstrated the initial, simultaneous formation of two symmetric species for which the structures \( [\text{Rh}_2(\mu-\text{Cl})(\mu-\text{CS}_2)(\text{CO})(\mu-\text{dppm})_2] \text{Cl} \) (58) and \( \text{Rh}_2(\mu-\text{CS}_2)\text{Cl}_2(\mu-\text{dppm})_2 \) (59) have been proposed (scheme 5). It is thought that these may then rearrange with the transfer of carbon monoxide from one species to another to give an intermediate \( [\text{Rh}_2(\mu-\text{CS}_2)\text{Cl}(\text{CO})(\mu-\text{dppm})_2] \text{Cl} \) (60) which may further react with carbon disulphide and chloride to give the asymmetric species \( \text{Rh}_2\text{Cl}_2(\text{CO})(\text{C}_2\text{S}_4)(\mu-\text{dppm})_2 \) (57). No evidence, however, is available to support the formation of the intermediate (60).
Schéma 5
The coordination chemistry of carbon disulphide has been reviewed by several authors.\textsuperscript{142,143} \(\text{Rh}_2\text{Cl}_2\text{(CO)}(\text{C}_2\text{S}_4)\)\(-\text{(μ-dppm)}_2\) represents the only structurally characterized example of a binuclear complex in which two carbon disulphide molecules are condensed to form two metallocycles. The condensation of two carbon disulphide molecules to form a \(\text{C}_2\text{S}_4\) fragment has, however, been observed previously for the mononuclear system \(\text{Rh}(\eta^5\text{-C}_5\text{H}_5)(\text{C}_2\text{S}_4)(\text{PMe}_3)\) \(\text{(61)}.\)\textsuperscript{144} The other structurally characterized bridging modes of \(\text{CS}_2\) are shown in (62) and (63). These bridging modes of carbon disulphide are observed in \(\text{Pt}_2(\mu-\text{CS}_2)\text{Cl}_2(\mu\text{-dppm})\)\(\text{2},\)\textsuperscript{89} and
respectively. Some coordination modes analogous to those observed for carbon disulphide when bound to a single metal centre have also been observed for carbon dioxide. As an example, the Ir(C$_2$O$_4$) heterometallocycle fragment has been observed in the iridium complex, IrCl-(C$_2$O$_4$)(PMe$_3$)$_3$ obtained by the reaction of IrCl(C$_8$H$_{14}$)(PMe$_3$)$_3$ with carbon dioxide. The growing interest in the activation of carbon disulphide with transition metal complexes is largely due to the ability of carbon disulphide to act as a probe in understanding the binding of carbon dioxide to transition metal complexes, since in the years to come carbon dioxide will likely be an important chemical feedstock in the synthesis of organic compounds if suitable transition metal catalysts for its modification become available.

1.2.3. Carboxylate-Bridged Complexes

Another class of rhodium-dppm complexes that demonstrates unique reactivity are those with carboxylate bridges. These complexes somewhat resemble the face to face dimers described previously and their unique reactivity can be largely attributed to the ability of the carboxylate group to ligate in a variety of ways. In this laboratory, the synthesis and reactivity of certain carboxylate bridged complexes has been investigated in some depth. Therefore the chemistry of carboxylate bridged complexes has been treated separately in this survey.
The syntheses of a variety of carboxylate bridged rhodium-dppm complexes have been reported independently by Eisenberg\textsuperscript{46} and Mague.\textsuperscript{77} Mague's work describes the synthesis of \([\text{Rh}_2(\mu-O_2\text{CCH}_3)(\text{CO})_2(\mu-\text{dppm})_2]^n \text{PF}_6 \) \((64)\) from the reaction of \([\text{Rh}_2(\mu-\text{Cl})(\text{CO})_2(\mu-\text{dppm})_2]^n \text{PF}_6 \) \((65)\) with silver acetate in tetrahydrofuran solution. \([\text{Rh}^+(\mu-O_2\text{CCH}_3)(\text{CO})_2(\mu-\text{dppm})_2]^n \text{PF}_6 \) \((65)\) so produced reacts with activated acetylenes \((\text{C}_2\text{R}_2: R = \text{CF}_3, \text{CO}_2\text{CH}_3)\) to yield \([\text{Rh}_2(\mu-\text{CO})(\mu-\text{C}_2\text{R}_2)(\text{CO})(\text{CO}_2\text{CCH}_3)(\mu-\text{dppm})_2]^n \text{PF}_6 \) \((66)\). Further reaction of these acetylene adducts with ligands \((L)\) such as tert-butyl isocyanide and trimethylphosphite displaces the terminal carbonyl group to give \([\text{Rh}_2(\mu-\text{CO})(\mu-\text{C}_2\text{R}_2)L(\text{O}_2\text{CCH}_3)(\mu-\text{dppm})_2]^n \text{PF}_6 \) \((67)\). All these transformations are shown in scheme 6. This work has also been extended to include the dpam analogues. The IR spectra of these acetylene adducts indicated the presence of a ketonic type bridging carbonyl group \((\nu(\text{CO}) = 1756-1712 \text{ cm}^{-1})\) and a presumably monodentate carboxylate function, since a pronounced shift in \(\nu_d(\text{CO})\) occurred to higher frequency. One member of this acetylene series, \([\text{Rh}_2(\mu-\text{CO})(\mu-\text{DMAD})(\text{P}(\text{OCH}_3)_3)(\text{O}_2\text{CCH}_3)(\mu-\text{dppm})_2]^n \text{PF}_6 \cdot (\text{CH}_3)_2\text{CO} \) has been structurally characterized by X-ray crystallography and, as anticipated, was shown to contain a ketonic type bridging carbonyl group \((<\text{Rh}-\text{C(0)}-\text{Rh} = 116.7(6)°)\) with the acetylene bound as a cis-dimetallated olefin. The carboxylate group, however, proved to be attached to one of the rhodium atoms in an unsymmetrical bidentate fashion, contrary
to the prediction based on the IR data. One unusual property of these acetylenic adducts is that they are all thirty-four electron species, yet the rhodium–rhodium separation of 3.386(1) Å in \([\text{Rh}_2(\mu-\text{CO})(\mu-\text{DMAD})(\text{P(OMe})_3)(\text{O}_2\text{CCH}_3)(\mu-\text{dppm})_2]\)PF_6 is indicative of the absence of a direct metal–metal bond. This can be rationalized by assigning a sixteen electron configuration to the five coordinate rhodium centre and an eighteen electron configuration to the six coordinate rhodium centre.

Eisenberg et al. have reported the syntheses of the carboxylate bridged dimers, \([\text{Rh}_2(\mu-\text{O}_2\text{CR})(\text{CO})_2(\mu-\text{dppm})_2]X\) (\(R = \text{H}, X = \text{PF}_6; R = \text{CH}_3, X = \text{BF}_4\)) by the reaction of trans-\(\text{Rh}_2\text{Cl}_2(\text{CO})_2(\mu-\text{dppm})_2\) with silver nitrate to give \([\text{Rh}_2(\mu-\text{Cl})(\text{CO})_2(\mu-\text{dppm})_2]^+\), followed by the addition of NaX (X = O_2CH, O_2CCH_3) and precipitation with either sodium hexafluorophosphate or sodium tetrafluoroborate respectively.

\([\text{Rh}_2(\mu-\text{O}_2\text{CH})(\text{CO})_2(\mu-\text{dppm})_2]\)PF_6 has also been prepared by the reaction of \([\text{Rh}_2(\mu-\text{H})(\text{CO})_2(\mu-\text{dppm})_2]\)PF_6 with CO_2. \([\text{Rh}_2(\mu-\text{O}_2\text{CH})(\text{CO})_2(\mu-\text{dppm})_2]\)PF_6 reacts with carbon monoxide with decomposition of the formate group to give \([\text{Rh}_2(\mu-\text{H})(\mu-\text{CO})(\text{CO})_2(\mu-\text{dppm})_2]\)PF_6. By way of contrast, \([\text{Rh}_2(\mu-\text{O}_2\text{CCH}_3)(\text{CO})_2(\mu-\text{dppm})_2]\)PF_6 did not react with carbon monoxide at room temperature. At -70 °C, however, the reaction occurs to form the bridging carbon monoxide adduct \([\text{Rh}_2(\mu-\text{CO})(\mu-\text{O}_2\text{CCH}_3)(\text{CO})_2(\mu-\text{dppm})_2]\)PF_6.

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1.3. Objective of This Thesis

The work described in this thesis originated with the desire to synthesize binuclear, bis(diphenylphosphino)methane complexes of rhodium possessing the A-frame structure. The principal emphasis was to be on the synthesis of binuclear complexes with bridgehead ligands such as those with light donor atoms, carboxylates, heterocumulenes and other unsaturated organic fragments. Having synthesized a range of such complexes the objective was then to study reactivity of the resultant A-frames with respect to a variety of small molecules. In particular, it was of interest to see whether variation of the bridging ligand in a systematic fashion had any discernible or predictable effects upon the ability of the A-frame to coordinate carbon monoxide and sulphur dioxide. Of even greater interest was the question of whether or not the introduction of a potentially reactive bridging group would alter the site of reactivity of the A-frame complexes to the bridging group itself.

Rhodium A-frame complexes are unusual by comparison to most other dimers and clusters in the sense that each metal centre is coordinatively unsaturated. Activation of the bridging group by coordination to two sixteen electron rhodium centres should in principle result in enhanced reactivity and possibly even totally new patterns of reactivity being observed.
Thus the main objective of this study was to vary the bridgehead ligand systematically and examine the effect that such a variation has on the chemistry of the complex as a whole and bridging ligand itself.
CHAPTER 2

SYNTHESIS OF DIMERIC BIS(DIPHENYLPHOSPHINO)METHANE COMPLEXES OF RHODIUM WITH VARIOUS BRIDGEHEAD LIGANDS

2.1. Introduction

A commonly observed phenomenon of low valent, platinum group metal hydroxide complexes is their ability to undergo acid cleavage reactions, enabling the hydroxide group to be replaced by a wide variety of other ligands. An extreme example of this behaviour is afforded by the monomeric complex, Pt(OH)(CH₃)(diphos) (68) (diphos = Ph₂P(CH₂)₂PPh₂). This complex reacts with a variety of weakly acidic reagents (HX), e.g. acetone, acetonitrile, nitromethane and acetylacetone, to give Pt(CH₃)X(diphos) (69) as shown in equation 12. Another system that exhibits

\[ \text{Pt(OH)(CH₃)(diphos)} \rightarrow \text{Pt(CH₃)X(diphos)} \]
This property is $\text{OsH(OH)(CO)(PPh}_3)_3$. This complex is known to react with acids ($\text{HX} : \text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}, \text{O}_2\text{CCH}_3$, $\text{O}_2\text{CCF}_3$, $\text{SC}_2\text{H}_7\text{OCIO}_3$) in ethanol suspension to give $\text{OsHX(CO)(PPh}_3)_3$.

The present chapter is devoted to a description of the synthesis of a series of dimeric, bis(diphenylphosphino)methane complexes of general formula $[\text{Rh}_2(\mu-\text{X})(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4$, where $\text{X}$ represents bridgehead ligands such as hydroxide, alkoxide, halides, carboxylate and the pseudohalides. With the exception of the carboxylates, all other complexes in this series represent examples of A-frame complexes. The synthesis of this series was made possible by the isolation of an hydroxide bridged A-frame complex which, as anticipated, was labile under acidic conditions. The similar behaviour of alkoxide groups was also noted in this study.

2.2. Results and Discussion

The IR and NMR ($^1\text{H}$ and $^{31}\text{P}[^1\text{H}]$) spectroscopic data for all new complexes described in this chapter are tabulated in table 1.1 and table 1.2 respectively, whereas all other relevant data are given in the experimental section immediately after each synthetic procedure.
2.2.1. A-frame Complexes with Bridging Hydroxide and Alkoxide Ligands

Maitlis and Kang\textsuperscript{149} have reported the synthesis of a triple hydroxide bridged complex $[\text{Rh}_2(\eta^5-\text{C}_5\text{Me}_5)(\mu-\text{OH})_3]\cdot\text{Cl}_4.4\text{H}_2\text{O}$ by the reaction of $\text{Rh}_2(\eta^5-\text{C}_5\text{Me}_5)_2\text{Cl}_4$ with aqueous base. Using $\text{trans-Rh}_2\text{Cl}_2(\text{CO})_2(\mu-\text{dppm})_2$ as the starting material a similar reaction was carried out in an attempt to synthesize a bridging hydroxide complex. This section deals with the success of this method and all transformations described in this section are summarized in scheme 7 (page 83).

$\text{trans-Rh}_2\text{Cl}_2(\text{CO})_2(\mu-\text{dppm})_2$ reacted with hydrated sodium carbonate in 95\% ethanol suspension producing a yellow-orange solution. The addition of diethyl ether to this solution precipitated a yellow crystalline material, analyzing approximately for $\text{Rh}_2(\text{OH})(\text{Cl})(\text{CO})_2(\mu-\text{dppm})_2\cdot\text{H}_2\text{O}$. The IR spectrum of this complex showed two terminal carbonyl stretching vibrations at 1976 (sh) and 1966 (vs) \text{cm}^{-1} (dichloromethane) and the band profile was very similar to that for an A-frame complex. The positions of these bands were significantly low by comparison to those of, for example, $[\text{Rh}_2(\mu-\text{Cl})(\text{CO})_2(\mu-\text{dppm})_2\cdot\text{BPh}_4]_2$ (2005 (s), 1989 (vs)) in dichloromethane\textsuperscript{41} suggesting the presence of an O-donor. The presence of a bridging hydroxide group is in fact indicated by comparison with the series $\text{IrX(CO)}(\text{PPh}_3)_2$ and
OsHX(CO)(PPh$_3$)$_2$, for which the lowest values of $v$(CO) occur when $X = OH$.\textsuperscript{148,150} Likewise, the $^{31}$P{$^1$H} NMR spectrum showed an equivalent environment for all four phosphorus atoms (20.79 ppm, $|1J_{Rh-P} + xJ_{Rh-P}| = 130.1$ Hz) and the pattern was very similar to those obtained for other symmetrical A-frames. No attempt was made to simulate this or any other spectrum, since only the chemical shift and the principal coupling constant ($|1J_{Rh-P} + xJ_{Rh-P}|$) were deemed necessary for the purpose of characterization.

An interesting observation with regard to this complex was the rather low equivalent conductance (4.9 cm$^2$ n$^{-1}$ mol$^{-1}$) in dichloromethane solution. This indicates that the chloride is either coordinated or otherwise attached to the complex. Since this observation seemed at odds with an A-frame formulation such as [Rh$_2$(μ-OH)(CO)$_2$(μ-dppm)$_2$]Cl, an X-ray structure determination of this yellow complex was performed by Prof. T.S. Cameron (see section 2.3.1) in order to resolve the resulting ambiguity. This established the structural formula of the yellow material as Rh$_2$(μ-OH.Cl)(CO)$_2$(μ-dppm)$_2$.H$_2$O (70) in which the chloride is hydrogen-bonded to the hydroxide group.

The inner coordination geometry of the complex, along with some relevant bond distances, is depicted in figure 2.1, with the phenyl rings and the water of solvation omitted. The structure of Rh$_2$(μ-OH.Cl)(CO)$_2$(μ-dppm)$_2$
Figure 2.1. Inner Coordination Geometry of
[Rh₂(μ-OH.Cl)(CO)₂(μ-dppm)₂]H₂O
(phenyl rings and water of solvation omitted)
H₂O has the expected A-frame geometry and consists of two essentially square planar rhodium centres bridged by two mutually trans dppm ligands (P(1)-Rh(1)-P(2) = 177.2(2)°, P(3)-Rh(2)-P(4) = 176.8(2)°) which are approximately trans to the oxygen of the OH·Cl bridge (O-Rh(1)-C(1) = 172(1)°, O-Rh(2)-C(2) = 177(1)°). The rhodium-rhodium separation was found to be 3.133(4) Å. This value is comparable to those found in [Rh₂(µ-Cl)(CO)₂(µ-dppm)₂]BF₄ (3.152(8) Å) and Rh₂(µ-S)(CO)₂(µ-dppm)₂ (3.154(2) Å) where no rhodium-rhodium single bond is present and significantly longer than those rhodium-rhodium distances found in systems such as [Rh₂(µ-Cl)(µ-CO)(CO)₂(µ-dppm)₂]BPh₄ (2.841(1) Å), Rh₂(µ-CO)Br₂(µ-dppm)₂ (2.7566(9) Å) and Rh₂(µ-SO₂)(Cl)₂(µ-dppm)₂ (2.7838(8) Å) in which rhodium-rhodium single bonds are found to occur. The absence of a rhodium-rhodium single bond in Rh₂(µ-OH·Cl)(CO)₂(µ-dppm)₂·H₂O could also be predicted by the conventional electron counting techniques which gives 16 electrons to each rhodium centre without imputing a rhodium-rhodium single bond.

The most remarkable feature of the structure of Rh₂(µ-OH·Cl)(CO)₂(µ-dppm)₂·H₂O is the appearance of the OH·Cl bridge. The bridge formed by this ligand is symmetrical within experimental error, with a Rh-O-Rh angle of 98.1(6)°; and the Rh-O bond lengths are within the range of 2.0 to 2.1 Å frequently encountered for Rh(1)-O.
distances. Although the hydrogen atom in the bridging position was not located, its position along the O-Cl vector can be inferred from the O-Cl distance of 3.12(2) Å, which is in good agreement with the distances commonly found for O-H---Cl bonds in crystalline hydrates. For example, barium chloride dihydrate has O---Cl distances in the range 3.13 - 3.22 Å. The Rh-P distances and Rh-C distances (figure 2.1) are comparable with the values normally observed for complexes of this type. Also, as found in all structurally characterized A-frame complexes, the methylene groups of the dpdm ligands are cis and bent towards the OH-Cl bridge. The iridium analogue of this complex, Ir₂(μ-OH.Cl)(CO)₂(μ-dppm)₂ has also been structurally characterized recently and is structurally remarkably similar to Rh₂(μ-OH.Cl)(CO)₂(μ-dppm)₂.H₂O. Knowledge of the solid state structure of Rh₂(μ-OH.Cl)(CO)₂(μ-dppm)₂.H₂O allowed for the ready interpretation of certain features of both the IR and ¹H NMR spectra of this complex. The IR spectrum of Rh₂(μ-OH.Cl)(CO)₂(μ-dppm)₂.H₂O, in addition to terminal carbonyl bands, exhibited broad, medium to weak intensity bands at ca. 3670, 3400, 3200 and 1620 cm⁻¹ which undoubtedly originated from the hydrogen bound hydroxide group and the solvated water molecule. When an hydroxide group is involved in hydrogen bonding, the position of ν(OH) is shifted to lower energy when compared to the stretching frequency of the free hydroxide.
group. Since $\nu$(OH) of the free hydroxide group appears at $3619 \text{ cm}^{-1}$ \textit{(vide infra)}, the band at $3400 \text{ cm}^{-1}$ could be assigned to the hydrogen bound hydroxide group. This leaves bands at $3670$, $3200$ and $1620 \text{ cm}^{-1}$ that should be attributed to the antisymmetric stretch, symmetric stretch and the HOH bend of the clathrate water molecule. The value of $3670 \text{ cm}^{-1}$, however, for the asymmetric stretch must be considered very high for a clathrate water molecule since the typical range for both antisymmetric and symmetric stretching frequencies is $3550 - 3200 \text{ cm}^{-1}$.155 As a result of this uncertainty these assignments must be considered tentative in nature. In dichloromethane-$d_2$, the $^1H$ NMR spectrum of $\text{Rh}_2(\mu$-OH.CI)(CO)$_2(\mu$-dppm)$_2H_2O$, in addition to phenyl proton resonances at $7.70$ ppm (40H), also exhibited four other absorptions centred at 5.29 (2H, m), 3.78 (1H, s, br), 3.06 (2H, m) and 1.71 (2H, s, br) ppm. The methylene protons of each dppm ligand in A-frame complexes are necessarily non-equivalent and as a result they should give rise to an AB quartet. Due to superimposed phosphorus and rhodium couplings, however, the methylene proton signals appear as two complex multiplets. Therefore, the multiplets at 5.29 and 3.06 ppm were readily assigned to the methylene protons of the dppm ligands because of their apparent complexity. Although this situation is characteristic of most rhodium A-frame complexes as mentioned earlier, the only difference here was the rather large
chemical shift of the low field multiplet (5.29 ppm). A more typical value would be ca. 4.0-4.2 ppm (table 2.2). The broad, featureless resonances at 3.78 and 1.71 ppm can probably be attributed to the OH.Cl proton and water respectively. This assignment was supported by the addition of D₂O, since both resonances disappeared. The most noteworthy observation here was the disappearance of the methylene resonances upon shaking with D₂O for ca. 1 hour. It seems likely that this exchange process occurs via tautomerism of the type depicted in equation 13, followed by both deuterium exchange at the bridging OH.Cl and OH₂.Cl groups and direct attack of D₂O on the bis(diphenyl-phosphino)methanide ligand in 71. The latter process has been observed directly in the reaction of Pt(n-C₄H₉)₃(P₂C₂H₅)₃(PPh₂CHPPh₂). The disappearance of the methylene protons of Rh₂(μ-OH.Cl)(CO)₂(μ-dppm)₂·H₂O suggests that there is significant interaction between the methylene protons (largely the equatorial protons) and the oxygen of
the OH·Cl bridge which might be caused by an enhancement of the basicity of the oxygen as a result of the OH···Cl hydrogen bonding. This interaction seems likely to be responsible for the downfield shift of one of the methylene multiplets and allows this multiplet to be assigned to the equatorial proton as a result of its close proximity to the OH·Cl bridge as shown below.

Attempts to deprotonate Rh₂(μ-OH·Cl)(CO)₂(μ-dppm)₂·H₂O to give Rh₂(μ-O)(CO)₂(μ-dppm)₂ were unsuccessful and it appears that the formation of a bis(diphenylphosphino)methanide complex may be responsible for the inability to isolate the bridging oxo complex. The reaction of Rh₂(μ-OH·Cl)(CO)₂(μ-dppm)₂·H₂O with bases such as n-butyllithium was immediate, generating red-orange solutions which rapidly faded to yellow in colour. To date, largely amorphous, poorly characterized substances only have been isolated from these solutions, even at -78 °C. It seems reasonable to assume that the initial red-orange
colouration generated in the reaction was due to the formation of $\text{Rh}_2(\mu-O)(\text{CO})_2(\mu\text{-dppm})_2$ (cf. $\text{Rh}_2(\mu-S)(\text{CO})_2(\mu\text{-dppm})_2$, which is deep red)\(^{29}\) which then undergoes an intramolecular proton transfer from the dppm methylene groups to the oxygen atom.

As anticipated, the bridging group in $\text{Rh}_2(\mu\text{-OH.CI})(\text{CO})_2(\mu\text{-dppm})_2\cdot\text{H}_2\text{O}$ was acid labile. The only product, however, was $[\text{Rh}_2(\mu\text{-Cl})(\text{CO})_2(\mu\text{-dppm})_2]^+$, regardless of the acid employed. This can be illustrated by the reaction of $\text{Rh}_2(\mu\text{-OH.CI})(\text{CO})_2(\mu\text{-dppm})_2\cdot\text{H}_2\text{O}$ with acetic acid to give $[\text{Rh}_2(\mu\text{-Cl})(\text{CO})_2(\mu\text{-dppm})_2]^+ (\nu(\text{CO}) = 2003(\text{s}), 1992(\text{vs})$ in dichloromethane) which could be isolated as the perchlorate salt upon the addition of sodium perchlorate. Hence, in order to be able to use $\text{Rh}_2(\mu\text{-OH.CI})(\text{CO})_2(\mu\text{-dppm})_2\cdot\text{H}_2\text{O}$ as a synthetic precursor, it proved necessary to replace the chloride with a non-coordinating anion such as perchlorate or hexafluorophosphate. Attempts to form $[\text{Rh}_2(\mu\text{-OH})(\text{CO})_2(\mu\text{-dppm})_2]\text{PF}_6$ met with failure since $\text{Rh}_2(\mu\text{-OH.CI})(\text{CO})_2(\mu\text{-dppm})_2\cdot\text{H}_2\text{O}$ with sodium hexafluorophosphate gave an orange complex, identified as $[\text{Rh}_2(\mu\text{-Cl})(\text{CO})_2(\mu\text{-dppm})_2]\text{PF}_6$ by comparison of the IR with that of an authentic sample. This was due to the demonstrated acidic nature of sodium hexafluorophosphate in aqueous and ethanolic solutions.

Attempts at exchanging the chloride in $\text{Rh}_2(\mu\text{-OH.CI})(\text{CO})_2(\mu\text{-dppm})_2\cdot\text{H}_2\text{O}$ using sodium perchlorate in alcoholic
solvents (ROH: R = CH₃, C₂H₅) yielded the bridging alkoxide complexes, [Rh₂(μ-OR)(CO)₂(μ-dppm)₂]ClO₄ (R = CH₃ (72), C₂H₅ (73)). Similar behaviour has been observed for the dimeric ruthenium hydroxide complex, [Ru₂(μ⁶-C₆H₆)₂(μ-OH)₃]⁻BPh₄. This complex reacts with alcohols (ROH: R = CH₃, C₂H₅) to give [Ru₂(μ⁶-C₆H₆)₂(μ-OR)₃]BPh₄ (R = CH₃, C₂H₅). A more direct synthesis of [Rh₂(μ-OR)(CO)₂(μ-dppm)₂]ClO₄ (R = CH₃, C₂H₅) was also accomplished by reacting a suspension of trans-Rh₂Cl₂(CO)₂(μ-dppm)₂ with freshly prepared sodium alkoxide in the appropriate alcohol, followed by the addition of sodium perchlorate. Although the exchange of chloride in Rh₂(μ-OH.Cl)(CO)₂(μ-dppm)₂·H₂O with perchlorate in alcoholic solvents gave alkoxide bridged complexes, it did prove possible to synthesize [Rh₂(μ-OH)(CO)₂(μ-dppm)₂]ClO₄ (74) by recrystallizing [Rh₂(μ-OC₂H₅)(CO)₂(μ-dppm)₂]ClO₄ from dichloromethane-diethyl ether in the presence of excess perchloric acid. This technique also allowed isolation of [Rh₂(μ-OD)(CO)₂(μ-dppm)₂]ClO₄ by employing deuter perchloric acid. Direct spectroscopic evidence for the hydroxide group in [Rh₂(μ-OH)(CO)₂(μ-dppm)₂]ClO₄ was seen both in the IR and ¹H NMR spectra. In the IR spectrum, ν(OH) appeared as a sharp, medium to weak intensity band at 3619 cm⁻¹, which shifted to 2672 cm⁻¹ upon deuteration. The ¹H NMR spectrum of [Rh₂(μ-OH)(CO)₂(μ-dppm)₂]ClO₄ in dichloromethane-d₂ showed a binomial quintet for the hydroxide proton at -0.13 ppm (J_H-P = 3.1 Hz). There
was no evidence for any rhodium-hydrogen coupling. Interestingly, \([\eta^5-C_5Me_5]_2\text{Rh}_2(\mu-\text{OH})_3\text{BPh}_4\) also failed to exhibit rhodium-hydrogen coupling and the \(^1H\) NMR signal of the hydroxyl proton remains as a singlet down to \(-60^\circ\text{C.}\)

As expected, the addition of deuterium oxide (D\(_2\)O) to a dichloromethane-\(d_2\) solution of \([\text{Rh}_2(\mu-\text{OH})(\text{CO})_2(\mu-\text{dppm})_2\text{ClO}_4\) resulted in exchange of the hydroxide proton, as evidenced by the disappearance of the multiplet at \(-0.13\) ppm.

Unlike \(\text{Rh}_2(\mu-\text{OH}Cl)(\text{CO})_2(\mu-\text{dppm})_2\text{H}_2\text{O}, [\text{Rh}_2(\mu-\text{OH})(\text{CO})_2(\mu-\text{dppm})_2\text{ClO}_4\) however, did not exchange dppm methylene protons even after 12 hours or on any other A-frame complexes discussed in this chapter indicating that the bridging OH.Cl group is necessary for such an exchange reaction.

The \(^1H\) NMR spectra of \([\text{Rh}_2(\mu-\text{OR})(\text{CO})_2(\mu-\text{dppm})_2\text{ClO}_4\) (R = CH\(_3\), C\(_2\)H\(_5\)) were complicated by the fact that hydrolysis took place to give a certain amount of \([\text{Rh}_2(\mu-\text{OH})(\text{CO})_2(\mu-\text{dppm})_2\text{ClO}_4\) and the free alcohol. Thus, the \(^1H\) NMR spectrum of \([\text{Rh}_2(\mu-\text{OC}_2\text{H}_5})(\text{CO})_2(\mu-\text{dppm})_2\text{ClO}_4\) displayed resonances at 0.65 ppm (t, \(2J_{\text{H-H}} = 7.0\) Hz) and 1.18 ppm (t, \(2J_{\text{H-H}} = 7.0\) Hz) that could be ascribed to the methyl group of both coordinated and free ethoxide groups respectively. Importantly, the sum of the integrated intensities of the coordinated and free methyl groups represented three protons supporting the contention that the
formation of free ethanol was by hydrolysis of 
$[\text{Rh}_2(\mu-\text{OC}_2\text{H}_5)(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4$. The corresponding methylene quartets of the free ethanol and the coordinated ethoxide group were found to overlap with the dppm methylene resonances and therefore it proved rather difficult to assign chemical shifts for these resonances. The presence of $[\text{Rh}_2(\mu-\text{OH})(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4$ was affirmed by the presence of a multiplet at -0.13 ppm ($\delta = 3.1$ Hz). The addition of deuterium oxide resulted in the loss of signals corresponding to the coordinated ethoxide and the hydroxide group of $[\text{Rh}_2(\mu-\text{OH})(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4$. The methyl and methylene signals due to free ethanol, however, suffered an increase in intensity. This indicated that on shaking with deuterium oxide, complete hydrolysis of $[\text{Rh}_2(\mu-\text{OC}_2\text{H}_5)(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4$ had taken place to form $[\text{Rh}_2(\mu-\text{OD})(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4$. Similar behaviour was exhibited by $[\text{Rh}_2(\mu-\text{OCH}_3)(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4\cdot 0.5\text{CH}_2\text{Cl}_2$ where singlets due to free methanol and coordinated methoxide were observed at 3.44 and 3.37 ppm respectively.

The IR spectra of the complexes $[\text{Rh}_2(\mu-\text{OR})(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4$ ($R = \text{H}, \text{CH}_3, \text{C}_2\text{H}_5$) each exhibited two absorptions in the terminal carbonyl region, both in the solid state and in solution (table 2.1). The band contours of these absorptions were very similar to those of other
A-frame complexes. In solution, the carbonyl absorption maxima were all very similar, although the same could not be said of the solid state values. The only direct IR evidence for coordinated alkoxide ligands occurred in the spectrum of $[\text{Rh}_2(\mu-\text{OCH}_3)(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4\cdot 0.5\text{CH}_2\text{Cl}_2$ wherein a weak band, assigned to the asymmetric C-H stretching mode of the methoxide group, was observed at 2802 cm$^{-1}$. Such a band is frequently considered diagnostic of methoxide complexes. For example, complexes with methoxide ligands such as $\text{ReCl}_2(\text{OCH}_3)(\text{NO})(\text{PPh}_3)_2$ and $\text{ReF}(\text{OCH}_3)(\text{CO})(\text{NO})(\text{PPh}_3)_2$ exhibit medium to weak intensity bands at ca. 2800 cm$^{-1}$.

The $^{31}\text{P}(^1\text{H})$ NMR spectra of $[\text{Rh}_2(\mu-\text{OR})(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4$ ($\text{R} = \text{H}; \text{CH}_3$ and $\text{C}_2\text{H}_5$) were virtually superimposable in both pattern and position. The spectra indicated an equivalent environment for all phosphorus atoms, as required by the structural assignments. The $^{31}\text{P}$ spectrum of $[\text{Rh}_2(\mu-\text{OC}_2\text{H}_5)(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4$ is shown in figure 2.2.

The conductivity measurements of the complexes, $[\text{Rh}_2(\mu-\text{OR})(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4$ ($\text{R} = \text{H}, \Lambda = 44.6$; $\text{R} = \text{CH}_3, \Lambda = 43.0$; $\text{R} = \text{C}_2\text{H}_5, \Lambda = 43.2$ cm$^2$ Ω$^{-1}$ mol$^{-1}$) showed that these complexes behaved as 1:1 electrolytes in dichloromethane. These values are comparable to those obtained for 1:1 electrolytes such as $[\text{Rh}_2(\mu-\text{Cl})(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4$ ($\Lambda' = 44.2$ cm$^2$ Ω$^{-1}$ mol$^{-1}$) and $[\text{Rh}_2(\mu-\text{Cl})(\mu-\text{CO})(\text{CO})_2(\mu-\text{dppm})_2]\text{BPh}_4$ ($\Lambda = 40.6$ cm$^2$ Ω$^{-1}$ mol$^{-1}$) in dichloromethane.
Scheme 7
Figure 2.2. $^{31}P(\text{H})$ Spectrum of $[\text{Rh}_2(\mu-\text{OC}_2\text{H}_6)(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4$ in Dichloromethane-\text{d}_2 (40.5 MHz)
2.2.2. Acid Cleavage Reactions of 

\[ \text{[Rh}_2(\mu-\text{OR})(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4 \quad (R = \text{H, CH}_3 \text{ and C}_2\text{H}_5) \]

As anticipated, the hydroxide and alkoxide functions of the complexes \([\text{Rh}_2(\mu-\text{OR})(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4 \) 

\((R = \text{H, CH}_3 \text{ and C}_2\text{H}_5)\) were found to be labile under acidic conditions. Thus, the innocence of the perchlorate ion in these complexes made these complexes of great synthetic utility by making it possible to displace the hydroxide and alkoxide groups by a wide variety of coordinating anions such as halides, carboxylates and pseudohalides. As a matter of convenience \([\text{Rh}_2(\mu-\text{OC}_2\text{H}_5)(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4 \) was used as the common precursor in these reactions. A speculative mechanism for the acid \((HX)\) cleavage reactions is shown in scheme 8.

2.2.2(i). Halide-Bridged Complexes

A useful method of adding stoichiometric amounts of the appropriate hydrohalic acids is to prepare their solid \(N,N\)-dimethylacetamide adducts, DMA.HX. Thus, the ethoxide complex \([\text{Rh}_2(\mu-\text{OC}_2\text{H}_5)(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4 \) when reacted with one equivalent of DMA.HX \((X = \text{Cl, Br and I})\) gave in good yields the halogen bridged \(A\)-frame complexes, \([\text{Rh}_2(\mu-X)(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4 \) as orange crystals. The well-known chloro bridged \(A\)-frame complex was characterized by comparison with authentic samples prepared as the
Scheme 8
perchlorate salt ($\nu$(CO) = 2003(s), 1992(vs) in dichloromethane). The solution IR spectra of $[\text{Rh}_2(\mu-X)(\text{CO})_2(\mu$-dpmm)$_2$]$\text{ClO}_4$ ($X = \text{Br}, I$) showed the presence of two terminal carbonyl absorptions whose frequencies were virtually identical to one another and very close to the value obtained for the chloro analogue. The $^{31}\text{P}^{1}\text{H}$ spectra of these two complexes confirmed that all four phosphorus atoms are in an equivalent environment. The conductivity data for $[\text{Rh}_2(\mu-X)(\text{CO})_2(\mu$-dpmm)$_2$]$\text{ClO}_4$ ($X = \text{Br}$, $\Lambda_M = 117$ cm$^{-2}$ Ω$^{-1}$ mol$^{-1}$, $X = I$, $\Lambda_M = 115$ cm$^{-2}$ Ω$^{-1}$ mol$^{-1}$) confirmed that these complexes behave as 1:1 electrolytes in acetone solution. While this work was in progress, the synthesis of $[\text{Rh}_2(\mu-$Br$)(\text{CO})_2(\mu$-dpmm)$_2$]$\text{BPh}_4$ by an independent method was reported in the literature. Although the synthesis of $[\text{Rh}_2(\mu-$I$)(\text{CO})_2(\mu$-dpmm)$_2$]$\text{ClO}_4$ has not been reported, this complex with different counter ions, has been prepared by other groups working in this field. Although $[\text{Rh}_2(\mu-X)-(\text{CO})_2(\mu$-dpmm)$_2$]$\text{ClO}_4$ ($X = \text{Cl}, \text{Br}$) were both very stable in dichloromethane solution, the same was not true for the iodo analogue. Thus, a freshly prepared orange solution of $[\text{Rh}_2(\mu-$I$)(\text{CO})_2(\mu$-dpmm)$_2$]$\text{ClO}_4$ became red-brown on standing in dichloromethane for 24 hours. Recording the IR spectrum of this solution showed the presence of a weak band at 1870 cm$^{-1}$ which can be attributed to a bridging carbonyl group. No significant change, however, was observed for the terminal carbonyl bands. The $^{31}\text{P}^{1}\text{H}$ spectrum, when
recorded after 24 hours, showed signals attributable to two symmetric species at 26.88 ppm ($|^{1}J_{Rh-P} + x^{1}J_{Rh-P}| = 93.6$ Hz) and 19.30 ppm ($|^{1}J_{Rh-P} + x^{1}J_{Rh-P}| = 114.0$ Hz), appearing at the expense of the signal due to $[\text{Rh}_2(\mu-I)\text{(CO)}_2(\mu-dppm)_2]\text{ClO}_4$. This transformation was only ca. 30% complete judging by the relative intensity of the peaks after 24 hours. The intensity of the high field signal was approximately half that of the low field signal. The low field symmetric signal agreed favourably with that reported for $[\text{Rh}_2(\mu-I)(\mu-CO)(\text{CO})_2(\mu-dppm)_2]\text{ClO}_4$ (26.93 ppm, $|^{1}J_{Rh-P} + x^{1}J_{Rh-P}| = 93.5$ Hz) (table 3.2). Although the coupling constant of the high field signal was in good agreement with that reported for the complex $[\text{Rh}_2(\mu-CO)I_2(\mu-dppm)_2]$ (16.30 ppm, $|^{1}J_{Rh-P} + x^{1}J_{Rh-P}| = 114.1$ Hz) the chemical shift differed by 3 ppm. Hence the nature of this species is somewhat uncertain. The peak at 1870 cm$^{-1}$ in the IR spectrum further substantiated the formation of $[\text{Rh}_2(\mu-I)(\mu-CO)(\text{CO})_2(\mu-dppm)_2]\text{ClO}_4$ ($\nu(\text{CO}) = 1870$ cm$^{-1}$, table 3.1). No $\nu(\text{CO})$ band at lower frequency was observed, however, that could be attributed to a species such as $\text{Rh}_2(\mu-CO)I_2(\mu-dppm)_2$. The absence of such a peak does not eliminate the formation of this complex, since it is formed only in small amounts. It would thus appear that $[\text{Rh}_2(\mu-I)(\text{CO})_2(\mu-dppm)_2]\text{ClO}_4$ breaks down in a rather complex manner with transfer of the carbonyl groups. Cowie et al. have reported the synthesis of an A-frame complex isomeric with
[\text{Rh}_2(\mu-\text{I})(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4$ in association with iodide as the counterion. The fact that no similar complex is observed with perchlorate as the counterion and that $[\text{Rh}_2(\mu-\text{CO})(\text{CO})\text{I}(\mu-\text{dppm})_2]\text{I}$ shows no tendency to isomerize to $[\text{Rh}_2(\mu-\text{I})(\text{CO})_2(\mu-\text{dppm})_2]\text{I}$ suggests that association (or lack of it) of the counterion is important in determining the relative stability of these isomeric A-frames.

The treatment of $[\text{Rh}_2(\mu-\text{OC}_2\text{H}_5)(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4$ in dichloromethane with a ten-fold excess of DMA.HBr gave an orange solution from which bright orange crystals, identified as $[\text{Rh}_2(\mu-\text{H})(\mu-\text{CO})\text{Br}_2(\mu-\text{dppm})_2]\text{Br}.\text{CH}_2\text{Cl}_2.0.05\text{C}_4\text{H}_{10}\text{O}$ (75) were isolated by the slow addition of diethyl ether. The IR spectrum of this complex indicated the absence of terminal carbonyl and ionic perchlorate groups. The presence of a single absorption at 1816(s) cm$^{-1}$ in the solid state confirmed the presence of a bridging carbonyl group. This band appeared at 1819(m) cm$^{-1}$ in dichloromethane solution. The $^1\text{H}$ NMR spectrum (360 MHz)
of this complex in dichloromethane-$d_2$ showed, in addition to the two complex multiplets arising from the dppm and p-tri-
le groups and signals attributable to both solvent mole-
cules, a septet at 1.2 ppm which was readily attributed to the bridging hydride resonance. The septet can be con-
sidered as arising from an overlapping triplet of quintets.

The $^{31}$P($^1$H) NMR spectrum exhibited a second order symmetri-
cal multiplet (18.26 ppm, $^{1}J_{Rh-P} + x^{1}J_{Rh-P} = 95.52$ Hz).

Microanalytical data confirmed the presence of three bromine
atoms per molecule. Acetone solutions of $[\text{Rh}_2(\mu-H)(\mu-CO)\text{Br}_3$$(\mu-dppm)_2]$ were non-conducting. The chloride analogue of 75
has been investigated by Cowie et al. and shown to exhibit
similar physical properties. Most significantly, $^{31}$P($^1$H) NMR of the chloride complex at room temperature was that
of a typical symmetrical A-frame, but at $-80^\circ$C the major
peaks coalesced into one broad one suggesting that the
third terminal chloride undergoes rapid site exchange.

Although no low temperature $^{31}$P NMR experiments were per-
formed, it is reasonable to assume that a similar situation
pertain in the case of 75. $[\text{Rh}_2(\mu-H)(\mu-CO)\text{Cl}_3(\mu-dppm)_2]$ results from the addition of HCl to $\text{Rh}_2(\mu-CO)\text{Cl}_2(\mu-dppm)_2$. 59

In order to confirm the identity of $\text{Rh}_2(\mu-H)(\mu-CO)\text{Br}_3$$(\mu-dppm)_2$ the neutral complex $\text{Rh}_2(\mu-CO)\text{Br}_2(\mu-dppm)_2$
was reacted with slight excess of DMA.HBr in
dichloromethane solution. The IR spectrum of the resulting
solution showed a medium intensity band at
1819 cm\(^{-1}\), confirming the formation of \([\text{Rh}_2(\mu-\text{H})(\mu-\text{CO})-\text{Br}_3(\mu-\text{dppm})]_2\).

When \([\text{Rh}_2(\mu-\text{OC}_2\text{H}_5)(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4\) was treated with a three fold excess of \text{DMA.HBr}, a mixture of products was obtained. This was evident from the \(^{31}\text{P}(^1\text{H})\) NMR spectrum of a dichloromethane solution containing \([\text{Rh}_2(\mu-\text{OC}_2\text{H}_5)(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4\) and a three fold excess of \text{DMA.HBr}. The spectrum showed two symmetrical second order patterns centred at 18.15 ppm (\(|J_{\text{Rh-P}} + XJ_{\text{Rh-P}}| = 95.6 \text{ Hz}\)) and 29.11 ppm (\(|J_{\text{Rh-P}} + XJ_{\text{Rh-P}}| = 94.9 \text{ Hz}\)). The low field signal agrees favourably with that of \([\text{Rh}_2(\mu-\text{Br})(\mu-\text{CO})(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4\) (29.15 ppm; \(|J_{\text{Rh-P}} + XJ_{\text{Rh-P}}| = 94.3 \text{ Hz}\)) (table 3.2, chapter 3) whereas the signal at higher field was identical to that of \([\text{Rh}_2(\mu-\text{H})(\mu-\text{CO})\text{Br}_3(\mu-\text{dppm})_2]\) (18.26 ppm, \(|J_{\text{Rh-P}} + XJ_{\text{Rh-P}}| = 95.5 \text{ Hz}\)). Further evidence for the formation of these products came from the IR spectrum of the solid isolated from the reaction mixture by the addition of diethyl ether, which showed bands at 2014 (m), 1974 (s), 1814 (m) and 1816 (m) cm\(^{-1}\). The first three bands were identical to those obtained for \([\text{Rh}_2(\mu-\text{Br})(\mu-\text{CO})(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4\) (table 3.1, chapter 3) whereas the band at 1816 cm\(^{-1}\) was the same as that observed for \([\text{Rh}_2(\mu-\text{H})(\mu-\text{CO})\text{Br}_2(\mu-\text{dppm})_2]\text{Br}\). Hence the reaction of \([\text{Rh}_2(\mu-\text{OC}_2\text{H}_5)(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4\) with a three fold excess of \text{DMA.HBr} proceeds with the
transfer of a carbonyl group. The possibility of DMA.HBr acting as the source of carbon monoxide was ruled out by observing identical behaviour when \([\text{Rh}_2(\mu-\text{OC}_2\text{H}_5)(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4\) was reacted with excess aqueous hydrogen bromide. A possible pathway for the formation of 
\([\text{Rh}_2(\mu-\text{Br})(\mu-\text{CO})(\text{CO})_2(\mu-\text{dppm})_2]^+\) (77) and 
\([\text{Rh}_2(\mu-\text{H})(\mu-\text{CO})-\text{Br}_3(\mu-\text{dppm})_2]\) (75) is shown in scheme 9.

The difference in behaviour observed between the reaction of \([\text{Rh}_2(\mu-\text{OC}_2\text{H}_5)(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4\) with either a three fold excess or a vast excess of DMA.HBr can be attributed to the increased bromide ion concentration. The initial product formed between the reaction of \([\text{Rh}_2(\mu-\text{OC}_2\text{H}_5)(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4\) (73) with excess DMA.HBr is the symmetric species \([\text{Rh}_2(\mu-\text{Br})(\mu-\text{CO})(\mu-\text{dppm})_2]ClO_4\) (76). This complex in the presence of excess bromide ions can be considered to be in equilibrium with the asymmetric species, 
\([\text{Rh}_2(\mu-\text{CO})(\text{CO})\text{Br}(\mu-\text{dppm})_2]\text{Br}\) (44). In the presence of vast excess of bromide ions the equilibrium will be strongly favoured to the right (scheme 9) and the product formed will be exclusively \([\text{Rh}_2(\mu-\text{CO})(\text{CO})\text{Br}(\mu-\text{dppm})_2]\text{Br}\). This then rapidly rearranges with the loss of carbon monoxide to give \([\text{Rh}_2(\mu-\text{CO})\text{Br}_2(\mu-\text{dppm})_2]\) (45) which further reacts with acid (HBr) to form \([\text{Rh}_2(\mu-\text{H})(\mu-\text{CO})\text{Br}_3(\mu-\text{dppm})_2]\) (75). In the presence of modest excess of DMA.HBr there will be a finite amount of \([\text{Rh}_2(\mu-\text{Br})(\text{CO})_2(\mu-\text{dppm})_2]^+\) in solution.
Scheme 9
to react with carbon monoxide liberated in the rearrangement of \([\text{Rh}_2(\mu-\text{CO})(\text{CO})\text{Br}(\mu-\text{dppm})_2]\text{Br}\) and hence \([\text{Rh}_2(\mu-\text{Br})(\mu-\text{CO})(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4\) (77) is also observed.

The \(31^\text{P}(^1\text{H})\) NMR spectrum of the solid obtained from the reaction of \([\text{Rh}_2(\mu-\text{OC}_2\text{H}_5)(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4\) with a three fold excess of DMA.HI in dichloromethane showed the presence of at least two symmetrical products at 26.85 ppm (\(|^1J_{\text{Rh-P}} + XJ_{\text{Rh-P}}| = 93.5 \text{ Hz}\)) and 17.20 ppm (\(|^1J_{\text{Rh-P}} + XJ_{\text{Rh-P}}| = 108.5 \text{ Hz}\)) with an intensity ratio of ca. 4:3 respectively. These values compare very well with those obtained for \([\text{Rh}_2(\mu-\text{I})(\mu-\text{CO})(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4\) (26.93 ppm, \(|^1J_{\text{Rh-P}} + XJ_{\text{Rh-P}}| = 93.5 \text{ Hz}\) (table 3.2, chapter 3) and \([\text{Rh}_2(\mu-\text{I})(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4\) (17.31 ppm, \(|^1J_{\text{Rh-P}} + XJ_{\text{Rh-P}}| = 108.6 \text{ Hz}\) (table 2.2). The formation of the \([\text{Rh}_2(\mu-\text{I})(\mu-\text{CO})(\text{CO})_2(\mu-\text{dppm})_2]^+\) cation was further substantiated by recording the solution IR spectrum. This showed a medium to weak intensity band at 1870 cm\(^{-1}\), identical to that obtained for this complex (table 3.1). Recording of the IR spectrum of a dichloromethane solution of \([\text{Rh}_2(\mu-\text{OC}_2\text{H}_5)(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4\) containing a twelve fold excess of DMA.HI showed terminal carbonyl band at 1995 cm\(^{-1}\) and bridging carbonyl bands at 1870 and 1816 cm\(^{-1}\). The bands at 1995 and 1870 cm\(^{-1}\) were identical with those of \([\text{Rh}_2(\mu-\text{I})(\mu-\text{CO})(\text{CO})(\mu-\text{dppm})_2]^+\). This was confirmed by both IR and \(^1\text{H}\) NMR spectroscopy as follows: The addition of
three fold excess of DMA.HI to a dichloromethane solution of \( \text{Rh}_2(\mu-\text{CO})I_2(\mu-\text{dppm})_2 \) showed a band at 1816 cm\(^{-1} \) in the infrared spectrum whereas the \( ^1\text{H NMR spectrum (80 MHz)} \) of \( \text{[Rh}_2(\mu-\text{OC}_2\text{H}_5)(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4 \) in dichloromethane-\( d_2 \) containing a twelve fold excess of DMA.HI showed a multiplet at -19.15 ppm that could be attributed to the bridging hydride by comparison with that obtained for \( \text{[Rh}_2(\mu-\text{H})(\mu-\text{CO})\text{Br}_2(\mu-\text{dppm})_2]\text{Br} \). By way of contrast, the formation of \( \text{[Rh}_2(\mu-\text{H})(\mu-\text{CO})\text{Cl}_2(\mu-\text{dppm})_2]\text{Cl} \) was not evident either by both \( ^1\text{H NMR (360 MHz) or IR spectroscopy, when} \)

\[ \text{[Rh}_2(\mu-\text{OC}_2\text{H}_5)(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4 \]

was treated with up to a twelve fold excess of DMA.HCl. The only product that was formed appears to be \( \text{[Rh}_2(\mu-\text{Cl})(\text{CO})_2(\mu-\text{dppm})_2]^+ \) \( (\nu(\text{CO}) 2003(\text{s}), 1992(\text{vs})) \). As a result of time limitations, the \( ^3\text{P}[^1\text{H}] \) spectra of \( \text{[Rh}_2(\mu-\text{OC}_2\text{H}_5)(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4 \) containing excess DMA.HI or DMA.HCl have not been recorded.

The behaviour exhibited by the reaction of

\[ \text{[Rh}_2(\mu-\text{OC}_2\text{H}_5)(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4 \]

with a vast excess of DMA.HX \( (X = \text{Cl, Br, I}) \) can be rationalized to some extent by comparison of results with those observed by Cowie and Dwight.\(^{22} \) In the reaction of \( \text{[Rh}_2(\mu-\text{OC}_2\text{H}_5)(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4 \) with a vast excess of DMA.HBr as mentioned earlier, \( \text{[Rh}_2(\mu-\text{CO})(\text{CO})\text{Br}_2(\mu-\text{dppm})_2]\text{Br} \) appears to be formed exclusively before rearranging rapidly to form \( \text{[Rh}_2(\mu-\text{CO})\text{Br}_2(\mu-\text{dppm})_2} \). This then adds hydrogen bromide to give
[Rh₂(μ-H)(μ-CO)Br₃(μ-dppm)₂]. With excess DMA·HI, however, [Rh₂(μ-H)(μ-I)I₃(μ-dppm)₂] is not formed exclusively and appears to be only a minor product in the reaction. This demonstrates the reluctance of cationic [Rh₂(μ-I)(μ-CO)(CO)₂(μ-dppm)₂]⁺ or any other iodo species formed, to coordinate the second iodide to give Rh₂(μ-CO)I₂(μ-dppm)₂, to which the addition of hydrogen iodide would give [Rh₂(μ-H)(μ-CO)I₃(μ-dppm)₂]. Unlike with bromide and iodide examples, both carbonyls and chlorides can be accommodated without any considerable steric interactions. As a result, Rh₂(μ-CO)Cl₂(μ-dppm)₂ is not formed and hence [Rh₂(μ-H)(μ-CO)Cl₃(μ-dppm)₂] is not observed.

2.2.2(ii). Carboxylate-Bridged Dimers

Unlike the reactions with hydrohalic acids, the reactions of [Rh₂(μ-OC₂H₅)(CO)₂(μ-dppm)₂]ClO₄ with carboxylic acids (RCOOH, R=H, CH₃, CH₂Cl, CHCl₂, CCl₃ and CF₃) did not require stoichiometric amounts of acid, except in the case of R = CCl₃. The addition of excess CCl₃COOH resulted in the formation of [Rh₂(μ-Cl)(CO)₂(μ-dppm)₂]ClO₄ which was characterized by comparison of its IR spectrum with that of an authentic sample. The addition of the appropriate carboxylic acid to a dichloromethane solution of [Rh₂(μ-OC₂H₅)(CO)₂(μ-dppm)₂]ClO₄ (73) gave a dark red solution from which were isolated red crystals of
[Rh$_2$(μ-Ο₂CR)(CO)$_2$(μ-dppm)$_2$]ClO$_4$ (78) (R = H, CH$_3$, CH$_2$Cl, CHCl$_2$, CCl$_3$ and CF$_3$) in excellent yields (equation 14). While this work was in progress, reports detailing the independent synthesis of [Rh$_2$(μ-Ο₂CH)(CO)$_2$(μ-dppm)$_2$]PF$_6$ and [Rh$_2$(μ-Ο₂CCH$_3$)(CO)$_2$(μ-dppm)$_2$]X (X = BF$_4$, PF$_6$) appeared in the literature. The methods employed in synthesizing these complexes were discussed in section 1.2.3.

Carboxylate ligands can bridge between two metal centres either in the monodentate (79) or bidentate (80).
bridging mode and, in both instances, donate three electrons to the dimer. Of these two bridging modes, the bidentate case is the more common.\textsuperscript{155, 160} The $^{31}$P\textsubscript{1H} NMR spectra of the carboxylate complexes $[\text{Rh}_2(\mu-O\text{CR})_2\text{(CO)}_2(\mu$-dppm)$_2\text{]}\text{ClO}_4$ ($R = H, \text{CH}_3, \text{CH}_2\text{Cl}, \text{CHCl}_2, \text{CCl}_3$ and \text{CF}_3), cannot distinguish between these two bridging modes since both would give rise to symmetrical patterns.

Similarly, IR spectroscopy is also of little value in differentiating the possible structures because of the already low symmetry (C\textsubscript{2v}) of the free ion. Electronic spectra, however, were useful in determining the bridging mode of the carboxylate ligands. All the complexes $[\text{Rh}_2(\mu-O\text{CR})_2\text{(CO)}_2(\mu$-dppm)$_2\text{]}\text{ClO}_4$ ($R = H, \text{CH}_3, \text{CH}_2\text{Cl}, \text{CHCl}_2, \text{CCl}_3$ and \text{CF}_3) showed bands around 490 nm, which can be attributed to proximity shifted charge transfer absorptions,\textsuperscript{14} in contrast to $[\text{Rh}_2(\mu-O\text{C}_2\text{H}_5)(\text{CO})_2(\mu$-dppm)$_2\text{]}\text{ClO}_4$ in which the band appeared at a more normal value of 422 nm. Such a large shift to lower energy for the carboxylate bridged dimers can only be possible if there is a close, face to face approach of the two rhodium coordination planes which, in turn is possible only when the carboxylate ligand binds as a bidentate bridging ligand between the metal centres. The bridging bidentate mode has been confirmed by structural characterization of one member, $[\text{Rh}_2(\mu-O\text{CCF}_3)(\text{CO})_2(\mu$-dppm)$_2\text{]}\text{ClO}_4$, of the carboxylate series (chapter 5).
The $^{31}$P($^1$H) NMR spectra of all the carboxylate complexes prepared showed a symmetric, second order pattern establishing that all four phosphorus atoms are equivalent. As required, the IR spectra of these carboxylate bridged complexes showed the presence of two terminal carbonyl groups and the carboxylate group (table 2.1). All complexes exhibited the antisymmetric stretch of the carboxylate group in the region 1640 to 1560 cm$^{-1}$, which was in good agreement with those reported for other bridged bidentate carboxylate complexes. Furthermore, for the complexes, $[\text{Rh}_2(u-O_2CR)(CO)_2(u-dppm)]ClO_4$ ($R = H, CH_3, CF_3$) the symmetric stretch to lower energy was obscured by other ligand absorptions and therefore not visible in the IR spectrum. This low energy band, however, became visible in these complexes with $R = CH_2Cl$, $\nu$(CO$_2$) = 1418(m); CHCl$_2$, $\nu$(CO$_2$) = 1402(m) and CCl$_3$, $\nu$(CO$_2$) = 1376(s) cm$^{-1}$. As expected, the $^1$H NMR spectra of all the carboxylate complexes showed two complex multiplets for the methylene protons of the dppm ligands. Although the proton of the formate group was not visible in the $^1$H NMR spectrum, the IR spectrum exhibited a band at 1352 cm$^{-1}$ which was attributed to the C-H bend of the formate group. The $^1$H resonances of acetate, monochloroacetate and dichloroacetate groups were seen at 0.73, 2.58 and 4.82 ppm respectively. There were no apparent rhodium and/or phosphorus couplings associated with these signals.
[Rh$_2$(μ-O$_2$CCF$_3$)(μ-Cl)$_2$(μ-dppm)$_2$]ClO$_4$ was found to be extremely reactive in contrast with its congeners. This extreme reactivity was evidenced by the fact that the trifluoroacetate ligand readily underwent hydrolysis and alcoholysis to yield the hydroxide and alkoxide A-frames. Furthermore, the trifluoroacetate group of [Rh$_2$(μ-O$_2$CCF$_3$)(μ-dppm)$_2$]ClO$_4$ could be readily substituted with other anions (vide infra). Even dichloromethane solutions of [Rh$_2$(μ-O$_2$CCF$_3$)(μ-dppm)$_2$]ClO$_4$ underwent exchange when in contact with sodium chloride cell windows, to eventually yield [Rh$_2$(μ-Cl)(μ-dppm)$_2$]ClO$_4$, identified by the appearance of ν(CO) bands at 2003(s) and 1992(vs).

2.2.2(iii). Pseudohalide-Bridged Complexes

In 1981, Sanger reported the synthesis of dimeric, rhodium dppm and dpam complexes with terminal pseudohalide ligands with the general formulae Rh$_2$(CO)$_2$X$_2$(μ-L)$_2$ (X = NCO, L = dppm (81), dpam) and Rh$_2$(CO)$_4$X$_2$(μ-L)$_2$ (82) (X = NCS, CN; L = dppm (82), dpam). Since the procedures involved the use of a large excess of the pseudohalide salt, no A-frame complexes with pseudohalide bridges were isolated. Hence an attempt was made to prepare complexes with pseudohalide bridges by reacting [Rh$_2$(μ-OC$_2$H$_5$)(μ-dppm)$_2$]ClO$_4$ with pseudohalide salts under acidic conditions. As a result of the unusual lability of the
trifluoroacetate group of \( [\text{Rh}_2(\mu-O_2CCF_3)(\text{CO})_2(\mu\text{-dppm})_2]^- ClO_4^- \), the synthesis of bridged pseudohalide complexes via simple substitution reactions was also explored. Both these methods indeed proved to be very successful.

No attempt will be made to give a detailed description of the coordination geometry of pseudohalides prior to the discussion of the reactivity of \( \text{Rh}_2(\mu-O\text{C}_2\text{H}_5)(\text{CO})_2(\mu\text{-dppm})_2 ClO_4^- \) and \( [\text{Rh}_2(\mu-O_2CCF_3)(\text{CO})_2(\mu\text{-dppm})_2] ClO_4^- \) with pseudohalides. The reader is referred to several extensive review articles dealing with the coordination geometries and IR spectra of pseudohalide complexes.\(^{161,162}\)

A brief summary of the various coordination geometries, however, will be given by way of introduction. Three fundamentally different bonding modes are known for pseudohalides anions (e.g. thiocyanate, cyanate and azides) denoted by XYZ. These include (i) terminal binding via X or Z (ii) bridging through both X and Z (iii) bridging
through X or Z. These bonding modes are shown in figure 2.3.

\[ \text{M} \rightarrow \text{XYZ} \quad \text{M} \rightarrow \text{ZYX} \]

Figure 2.3. Bonding Modes of Pseudohalide Anions

The thiocyanate anion is known to bind through N or S to a single metal centre depending primarily upon the nature of the metal, electronic and steric effects of the ligands surrounding the metal and the solvent in which the reaction is performed.\textsuperscript{163} Furthermore, the thiocyanate group is also capable of bridging two metals either via nitrogen or sulphur or by both. Several empirical criteria based upon IR spectroscopy have been established in order to distinguish between the various bonding modes of the thiocyanate ligand.\textsuperscript{160} These must all be applied with great caution but of them all, the most
reliable criterion is the position of $\nu_s$(NCS) (vide infra).

The cyanate anion is also known to bind to a metal centre via either nitrogen or oxygen. The coordination through oxygen is much less common than bonding through nitrogen. Additionally, two bridging modes are also known for the cyanate anion. These include bridging through nitrogen or both nitrogen and oxygen with the former being the most frequently observed bridging mode. Due to the small number of structurally characterized cyanate complexes, no generalizations have been made to distinguish between the various bridging modes. The coordination modes of the azide ligand also include (i) complexes containing the azide ligand attached to one metal centre (ii) bridging of two metal centres via one nitrogen atom and (iii) bridging of two metals by the two nitrogen atoms.

The addition of stoichiometric amounts of potassium cyanate along with excess perchloric acid simultaneously to an acetone-dichloromethane solution (4:1) of $[\text{Rh}_2(\mu-\text{OC}_2\text{H}_5)\{\text{CO}\}_2(\mu-\text{dppm})_2]\text{ClO}_4$ resulted in the formation of the A-frame complex, $[\text{Rh}_2(\mu-\text{NCO})(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4$, in which the cyanate ligand appears to be $\text{N}$-bound to the rhodium centres. The presence of the cyanate group was affirmed by the appearance of a very strong absorption band at 2196 cm$^{-1}$ in the IR spectrum, attributable to $\nu_{as}$(NCO). The corresponding $\nu_s$(NCO) band, expected at around
1300-1350 cm\(^{-1}\), proved too weak to identify unambiguously. The band at 2196 cm\(^{-1}\) compares quite favourably with those seen in other complexes containing bridged N-bound cyanate groups, as exemplified by MnL\(_2\)(NCO)\(_2\) (\(\nu_{as}(\text{NCO}) = 2185\text{(s)}\)), FeL\(_2\)(NCO)\(_2\) (\(\nu_{as}(\text{NCO}) = 2180\text{(s)}\)) and NiL\(_2\)(NCO)\(_2\) (\(\nu_{as}(\text{NCO}) = 2180\text{(s)}\)) \(L = 3\text{-cyanopyridine}\). Although the frequency of the bridging cyanate group is less than that for terminal cyanates, it should be noted that in general the position of \(\nu_{as}(\text{NCO})\) is sufficiently diagnostic to distinguish between bridging and terminal modes as a result of the overlapping or ranges. However, by comparison of the position of \(\nu_{as}(\text{NCO})\) of Rh\(_2\)(NCO)\(_2\)(CO)\(_2\)(\(\mu\text{-dppm}\))\(_2\) (\(\nu_{as}(\text{NCO}) = 2236\text{ cm\(^{-1}\)}\)) which has terminal cyanate ligands \((\text{vide infra})\), the band 2196 cm\(^{-1}\) seems quite reasonable for a bridging cyanate ligand. The band envelope and position of the terminal carbonyl stretching absorptions of [Rh\(_2\)(\(\mu\text{-NCO}\))(CO)\(_2\)(\(\mu\text{-dppm}\))\(_2\)]ClO\(_4\), which occurred at 2003(sh) and 1995(vs) cm\(^{-1}\) (dichloromethane) were typical of those normally seen for A-frame complexes bridged by halide ligands (table 2.1). The \(^{31}\text{P}\{\text{H}\} NMR spectrum of [Rh\(_2\)(\(\mu\text{-NCO}\))(CO)\(_2\)(\(\mu\text{-dppm}\))\(_2\)]ClO\(_4\) both at room temperature and at \(-70\text{ °C}\) showed an equivalent environment for all phosphorus atoms, consistent with the A-frame structure proposed. This observation, however, does not necessarily eliminate a rapid bridging-terminal exchange process resulting in an equivalent environment for the phosphorus atoms (equation 15). In view of the existence
of a number of stable N-bound bridging cyanate complexes, however, invoking such a process would seem to lack merit. 

$^1$H NMR spectra of $[\text{Rh}_2(\mu-\text{NCO})(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4$ and indeed those of all other pseudohalide bridged complexes reported herein, were unusual in that the signals due to the non-equivalent dppm methylene protons could not be resolved at 80 MHz. At 360 MHz, however, the two characteristic complex multiplets could be identified around 3.6 and 3.8 ppm. This difference in the chemical shifts of these methylene protons is significantly less than that reported for other A-frames (table 2.2). This may be due to some effect caused by ring currents associated with the $\pi$-electrons in the pseudohalide ligands. $[\text{Rh}_2(\mu-\text{NCO})(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4$ could also be prepared in comparable yield, by the treatment of an acetone solution of $[\text{Rh}_2(\mu-\text{O}_2\text{CCF}_3)(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4$ with one mole of potassium.
cyanate. The physical properties of the complex obtained by the latter method were identical to that obtained by the reaction of \([\text{Rh}_2(\mu-\text{OC}_2\text{H}_5)(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4\) with potassium cyanate and perchloric acid.

The addition of excess potassium cyanate, however, to an acetone solution of \([\text{Rh}_2(\mu-\text{O}_2\text{CCF}_3)(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4\) immediately precipitated a red-orange solid. This solid was identified as \(\text{Rh}_2(\text{CO})_2(\text{NCO})_2(\mu-\text{dppm})_2\) by comparison of its physical properties with a sample prepared according to the method of Sanger, which involved the reaction of \(\text{Rh}_2\text{Cl}_2(\text{CO})_2(\mu-\text{dppm})_2\) with excess potassium cyanate, dppm and carbon monoxide in acetone-methanol solution. The IR spectrum of \(\text{Rh}_2(\text{CO})_2(\text{NCO})_2(\mu-\text{dppm})_2\) showed, in addition to a single terminal carbonyl absorption at 1969 cm\(^{-1}\), two bands at 2239(vs) and 1336(m) cm\(^{-1}\) which could be attributed to \(\nu_{as}(\text{NCO})\) and \(\nu_{s}(\text{NCO})\) of the cyanate group respectively. The IR spectrum also indicated the absence of the perchlorate ion. The bands assigned to \(\nu_{as}(\text{NCO})\) and \(\nu_{s}(\text{NCO})\) were comparable to other \(\nu_{as}(\text{NCO})\) and \(\nu_{s}(\text{NCO})\) values reported for terminal N-bound cyanate groups (typically 2240 - 2100 cm\(^{-1}\)). \(\text{Rh}_2(\text{NCO})_2(\text{CO})_2(\mu-\text{dppm})_2\) was either only sparingly soluble or insoluble in most common organic solvents.

In similar fashion, the treatment of \(\text{Rh}_2(\mu-\text{O}_2\text{CCF}_3)(\text{CO})_2(\mu-\text{dppm})_2\text{ClO}_4\) with \(\text{Rh}_2(\mu-\text{OC}_2\text{H}_5)(\text{CO})_2(\mu-\text{dppm})_2\text{ClO}_4\)
with excess ammonium thiocyanate immediately produced a very insoluble golden yellow material almost quantitatively. This product was identified as the face to face dimer, on the basis of IR and microanalytical data. The IR spectrum showed bands at 2077(s), 1994(vs) and 831(w) cm\(^{-1}\) which could be ascribed to \(\nu_{as}(NCS)\), \(\nu(CO)\) and \(\nu_{s}(NCS)\) respectively. Furthermore, the absence of the perchlorate band was also evident from the IR spectrum. Although a number of empirical criteria can be used to distinguish N-bonded from S-bonded thiocyanates, the most reliable criterion is the position of the \(\nu_{s}(NCS)\) frequency. N-bonded thiocyanates have a weak band in the region 800 - 830 cm\(^{-1}\) whereas bands around the 700 cm\(^{-1}\) region are characteristic of S-bonding. To date, no examples are known that tend to violate this criterion. Hence the band at 831(w) cm\(^{-1}\) implied that the thiocyanate group was N-bound. Another criterion that has been used to distinguish N-bonding from S-bonding is the position of the \(\nu_{as}(NCS)\) frequency. In general, N-bound thiocyanates lead to a shifting of \(\nu_{as}(NCS)\) below the free ion (2053 cm\(^{-1}\) for potassium thiocyanate) and bonding through sulphur leads to frequencies \(\nu_{as}(NCS)\) well above that of the free ion. However, there are numerous exceptions to this criterion and \(\text{Rh}_2(NCS)_2(CO)_2(\mu-dppm)_2\) appears to be one such exception. This complex exhibited almost the same IR spectrum as the previously reported complex.
Rh$_2$(NCS)$_2$(CO)$_4$(μ-dppm)$_2$ (ν$_{as}$(NCS) = 2073, ν(CO) = 1992 and ν$_s$(NCS) = 830 cm$^{-1}$) suggesting that the complexes may in fact be identical. Accordingly, a sample of Rh$_2$(NCS)$_2$(CO)$_4$(μ-dppm)$_2$ was prepared according to the literature method (analogous to that for Rh$_2$(NCO)$_2$(CO)$_2$(μ-dppm)$_2$) and on the instrumentation available proved to have exactly the same ν$_{as}$(NCS), ν(CO) and ν$_s$(NCS) values exhibited by Rh$_2$(NCS)$_2$(CO)$_2$(μ-dppm)$_2$. Since the complex Rh$_2$(NCS)$_2$(CO)$_2$(μ-dppm)$_2$ was prepared in 96% yield from a dicarbonyl reactant in the absence of carbon monoxide, it seems apparent that Rh$_2$(NCS)$_2$(CO)$_4$(μ-dppm)$_2$ should be reformulated.

IR spectroscopy cannot distinguish between the carbonyl arrangement of Rh$_2$(NCO)$_2$(CO)$_2$(μ-dppm)$_2$ and Rh$_2$(NCS)$_2$(CO)$_2$(μ-dppm)$_2$ unequivocally since both cis and trans orientations would give rise to one single absorption. However, a comparison of their solubility with that of structurally characterized trans-Rh$_2$Cl$_2$(CO)$_2$(μ-dppm)$_2$ suggests a trans arrangement for the terminal carbonyl groups in these face to face dimers.

The reaction of [Rh$_2$(μ-OC$_2$H$_5$)(CO)$_2$(μ-dppm)$_2$]ClO$_4$ with one mole of ammonium thiocyanate in the presence of perchloric acid gave a bright yellow crystalline complex in excellent yield. This complex has been characterized as [Rh$_2$(μ-NCS)(CO)$_2$(μ-dppm)$_2$]ClO$_4$ in which the thiocyanate
ligand bridges the two rhodium centres through nitrogen.

The IR spectrum in the solid state was in support of the bridging thiocyanate being N-bound. In the carbonyl stretching region, three bands at 1997(s), 1984(vs) and 1957(s) cm\(^{-1}\) were observed, although in dichloromethane solution, the highest frequency band was less clearly defined and maxima at 2005(sh), 1996(vs) and 1952(s) cm\(^{-1}\) could be identified. The band envelope of the 2005 and 1996 cm\(^{-1}\) pair was closely comparable to other N-bound pseudohalide complexes such as [Rh\(_2\)(\(\mu\)-X)(CO)\(_2\)(\(\mu\)-dppm)\(_2\)]ClO\(_4\) (X = N\(_3\), NCO) (table 2.1), implying that the band at 1952 cm\(^{-1}\) was due to \(\nu_{as}\) (NCS), despite its rather low value. In order to confirm this assignment [Rh\(_2\)(\(\mu\)-NCS)(\(^{13}\)CO)\(_2\)(\(\mu\)-dppm)\(_2\)]ClO\(_4\) was prepared from [Rh\(_2\)(\(\mu\)-OC\(_2\)H\(_5\))(\(^{13}\)CO)\(_2\)(\(\mu\)-dppm)\(_2\)]ClO\(_4\). The latter was prepared by dissolving 0.05 g of the unlabelled material in 5 mL of dichloromethane and stirring under 13-carbon monoxide (90%) at a partial pressure of 250 mm Hg for 15 min. The solution IR spectrum of [Rh\(_2\)(\(\mu\)-NCS)(\(^{13}\)CO)\(_2\)(\(\mu\)-dppm)\(_2\)]ClO\(_4\) exhibited no bands other than one intense band at 1952(vs, br) cm\(^{-1}\) due to \(\nu_{as}\) (CO) which overlaps with the \(\nu_{as}\) (NCS) at 1952 cm\(^{-1}\).

In the chemical literature there is only one other example of a bridging N-bound thiocyanate. This complex, \((^3\text{Bu}_4\text{N})_3\text{Re}_2(\text{NCS})_10\) which has been structurally characterized, contains two thiocyanate ligands bridging two rhenium atoms.
in a symmetric fashion. Both bridging ligands in this complex are linear and, despite the centrosymmetric structure of the anion, two strong absorptions at 1920 and 1885 cm$^{-1}$ are attributed to $\nu_{as}$(NCS) of these ligands. In the light of this example, and the lower $\nu_{as}$(NCO) range exhibited by N-bridging cyanate ligands, the $\nu_{as}$(NCS) value of 1952 cm$^{-1}$ in $[\text{Rh}_2(\mu\text{-NCS})(\text{CO})_2(\mu\text{-dppm})_2]\text{ClO}_4$ seems perfectly reasonable. The presence of an N-bound thiocyanate group in $[\text{Rh}_2(\mu\text{-NCS})(\text{CO})_2(\mu\text{-dppm})_2]\text{ClO}_4$ was also evident from an examination of the IR spectrum in the low frequency region (800 - 900 cm$^{-1}$). The presence of an N-bound thiocyanate group was also indicated by the appearance of two sharp but weak bands at 872 and 842 cm$^{-1}$, both of which lie in the region normally associated with $\nu_{as}$(NCS) of N-bound thiocyanate groups. Both of these bands were unique to this complex since neither occurred in the spectra of other A-frame complexes investigated in this study. The splitting of the $\nu_{as}$(NCS) band, although not very common, is not without precedent. Alternatively, one of these bands could be assigned to $\nu_{as}$(NCS) and other to the first overtone of the bending vibration of the thiocyanate ligand which also can appear in this region. The $^{31}$P{$^1$H} NMR spectrum of $[\text{Rh}_2(\mu\text{-NCS})(\text{CO})_2(\mu\text{-dppm})_2]\text{ClO}_4$ both at room temperature and -70$^\circ$ showed a second order symmetric pattern indicating that all four phosphorus atoms are in an equivalent environment. The presence of a single thiocyanate ligand was not only
supported by elemental analysis but also by the reaction of
\[ \text{[Rh}_2(\mu-\text{NCS})(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4 \] with one equivalent of
ammonium thiocyanate to give \( \text{Rh}_2(\text{NCS})_2(\text{CO})_2(\mu-\text{dppm})_2 \) in 86% yield.

The addition of one mole of ammonium thiocyanate to
an acetone solution of \[ \text{[Rh}_2(\mu-\text{O}_2\text{CCF}_3)(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4 \]
resulted in a relatively slow reaction from which could be
isolated a small quantity of \( \text{Rh}_2(\text{NCS})_2(\text{CO})_2(\mu-\text{dppm})_2 \) and
\( \text{Rh}_2(\mu-\text{NCS})(\text{CO})_2(\mu-\text{dppm})_2 \text{ClO}_4 \), characterized by comparison
of their IR spectra with authentic samples.

When, however, the reaction of \[ \text{[Rh}_2(\mu-\text{OC}_2\text{H}_5)(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4 \]
with one mole of ammonium thiocyanate was
performed in dichloromethane-acetone solution, in the absence
of excess perchloric acid, an immediate color change from
red to orange resulted with the precipitation of 15–20% of
\( \text{Rh}_2(\text{NCS})_2(\text{CO})_2(\mu-\text{dppm})_2 \). The addition of diethyl ether to
the filtrate precipitated an orange solid analyzing for
\[ \text{[Rh}_2(\text{SCN})(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4 \] whose structure is as not
known yet. The presence of a thiocyanate group in the
molecule was confirmed not only by microanalytical data but
also by reacting \[ \text{[Rh}_2(\text{SCN})(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4 \] with one mole
of ammonium thiocyanate to give \( \text{Rh}_2(\text{NCS})_2(\text{CO})_2(\mu-\text{dppm})_2 \) in
83% yield. Both IR and \(^{31}\text{P}(^1\text{H})\) NMR spectra of this orange
solid established that this complex differs from its isomer,
[Rh$_2$(μ-NCS)(CO)$_2$(μ-dppm)$_2$]ClO$_4$. In the solid state, the IR spectrum of the orange solid showed bands at 2073(m), 1987(vs) and 1970(sh) cm$^{-1}$. The band at 2073 cm$^{-1}$ probably indicates that the thiocyanate is S-bound since it appears higher than that for the free thiocyanate ion. Several exceptions, however, are known to violate this criterion. The absence of a band in the 800-900 cm$^{-1}$ region also supports this as a S-bound complex. The $^{31}$P($^1$H) NMR spectrum in dichloromethane at room temperature showed two broad poorly resolved centred approximately at 23 ppm and four other poorly resolved minor peaks in the region 16-19 ppm. On cooling down to $-40^\circ$C, the resonances centred at ca. 23 ppm sharpened to give what appears to be an AA'BB'XY multiplet. Of the four minor peaks, the two to lower field appeared to belong to a typical A-frame complex at 18.37 ppm with separation between the major lines equal to 113.9 Hz. Very little can be said about the other two minor peaks because of their low intensity as well as the less resolved nature of the peaks, except to note that they were separated by 124.3 Hz. A number of possibilities can be considered to account for the unusual spectroscopic behaviour of this complex. (a) The orange solid is known to break down in solution quite rapidly (vide supra). Assuming the minor peaks are due to rearranged or decomposed product(s), these observations could be rationalized by assuming a σ-π bridging mode for the thiocyanate ligand and invoking a
"wind shield wiper" type motion for this ligand (equation 16) as observed for $[\text{Rh}_2(\mu-\text{CN})(\mu-\text{CO})(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4\cdot\text{CH}_2\text{Cl}_2$ (Chapter 3) and $[\text{Rh}_2(\mu-\text{C}_2^t\text{Bu})(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4$ (Chapter 6).

If the coalescence temperature for this motion is approximately at room temperature, then a broad, poorly resolved spectrum would result. Cooling to $-40 \, ^\circ\text{C}$, however, this motion would be frozen and hence an AA'BB'XY spin system would result. This explanation is weakened by the observation that in both $[\text{Rh}_2(\mu-\text{CN})(\mu-\text{CO})(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4$ and $[\text{Rh}_2(\mu-\text{C}_2^t\text{Bu})(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4$, this motion is rapid, even at $-70 \, ^\circ\text{C}$. (b) If one assumes the two upfield minor peaks result from decomposition products, these observations can also be explained by a bridge-terminal exchange of the S-bound thiocyanate (equation 17). Once again in order to explain the room temperature spectrum, it is necessary to assume that the coalescence temperature for this process is only slightly above room temperature. It is also conceivable
that only the dominant absorptions in the spectrum belong to \([\text{Rh}_2(\text{SCN})(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4\) and that the fluxional process occurring involves a terminal exchange mechanism possibly proceeding via the S-bridged intermediate. Although an asymmetric type structure (83) has not been encountered in rhodium-dppm chemistry, an analogous palladium complex, \([\text{Pd}_2(\text{CH}_3)I_2(\mu-\text{dppm})_2]\text{BF}_4\) is known.\(^{84,138}\)

Both \([\text{Rh}_2(\mu-\text{NCS})(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4\) and \([\text{Rh}_2(\text{SCN})(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4\) were found to be unstable when kept in dichloromethane solution for long periods of time. \([\text{Rh}_2(\text{SCN})(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4\) when dissolved in dichloromethane changed colour from orange to red-brown within a period of four hours and after twenty-four hours a green solid had separated. The IR spectrum of the green solid showed both terminal and bridging carbonyl groups (1997(s), 1970(m) and 1807(m)) and what was assumed to be a cyanide (2114(w)). Qualitative tests also showed the presence of sulphur in the molecule. Hence it would appear that
[Rh₂(SCN)(CO)₂(μ-dppm)₂]ClO₄ breaks down in a complex manner with redistribution of carbonyl groups and S-C bond scission. The decomposition of the N-bound occurred at a somewhat slower rate since, after four hours, no noticeable change of the colour was observed. The yellow solution eventually turned red enabling a red-brown solid to be isolated by slow evaporation of the solid. To date, the products resulting from the break down of these thiocyanate complexes have defied analysis.

Unlike the reactions with potassium cyanate and ammonium thiocyanate, the reaction of [Rh₂(μ-OC₂H₅)(CO)₂(μ-dppm)₂]ClO₄ or [Rh₂(μ-OC₂H₅)(CO)₂(μ-dppm)₂]ClO₄ (the latter carried out in the presence of excess HClO₄) with sodium azide gave [Rh₂(μ-N₃)(CO)₂(μ-dppm)₂]ClO₄ in excellent yields. The IR spectrum of [Rh₂(μ-N₃)(CO)₂(μ-dppm)₂]ClO₄ showed the two expected terminal carbonyl bands at 1996 (s) and 1983 (vs) and νₐs(N₃) at 2077 (s) cm⁻¹. The band profile and position of the terminal carbonyl groups compare well with those obtained for the other N-bound pseudohalide complexes (table 2.1). The $^{31}$P{¹H} NMR spectrum showed the equivalence of all four phosphorus atoms and the chemical shift and coupling constants compare favourably with the other N-bound pseudohalide complexes. The foregoing data therefore, indicate that the azide bridges the rhodium atoms through one nitrogen atom. As required by the
structural assignments, all the pseudohalide bridged complexes, \([\text{Rh}_2(\mu-X)(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4 ~ (X = \text{NCS}, \text{N}_3, \text{NCO}, \text{SCN})\) behaved as 1:1 electrolytes in acetone solution.

The reaction of the \([\text{Rh}_2(\mu-\text{CF}_3)(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4\) with diethylamine (98%) has also been examined in the hope of isolating an amide complex such as, \([\text{Rh}_2(\mu-\text{NC}_2\text{H}_5)(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4\). The physical data associated with orange microcrystalline complex isolated in this reaction, however, has led to a tentative formulation of the complex as \([\text{Rh}_2(\mu-\text{OH}.\text{NH}(\text{C}_2\text{H}_5)_2)(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4\), in which diethylamine is hydrogen bound to a bridging hydroxide group. The IR spectrum of this complex in the solid state showed two terminal carbonyl absorptions at 1978(s) and 1961(vs). These carbonyl absorptions in dichloromethane solution appeared at 1983(vs) and 1975(sh) which were very close to that observed for \([\text{Rh}_2(\mu-\text{OH})(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4\) (\(v(\text{CO}): \text{1984} \text{(vs)}, \text{1978} \text{(sh)}\)). Furthermore, absence of the trifluoroacetate group was also evident from the IR spectrum. The \(^{31}\text{P}\{^1\text{H}\} \text{NMR spectrum of}\) \([\text{Rh}_2(\mu-\text{OH}.\text{NH}(\text{C}_2\text{H}_5)_2)(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4\) showed that all four phosphorus atoms are in an equivalent environment (20.14 ppm, \(1_J^{\text{Rh-P}} + X_J^{\text{Rh-P}} = 128.2 \text{ Hz}\)) in favour of the proposed A-frame geometry. The chemical shift and coupling constant are also very close to that observed for \([\text{Rh}_2(\mu-\text{OH})(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4\) (20.65 ppm, 128.1 Hz). The \(^1\text{H}\) NMR in dichloromethane-d\(_2\), in addition to phenyl
(7.53 ppm) and dppm-methylene multiplets (4.02, 3.29, 4H), exhibited four other resonances at 0.07 ppm (distorted quintet, 1H), 1.19 (t, 6H), 2.80 (q, 4H) and 5.57 (br, s, 1H) ppm. The resonance at 0.07 and 5.57 ppm could be attributed to the hydroxy proton and amino proton respectively. This assignment was supported by the addition of deuterium oxide since both these resonances disappeared. The most interesting observation was the slow disappearance of the dppm methylene after prolonged contact with deuterium oxide. This supports the formulation as

\[ \text{[Rh}_2(\mu-\text{OH}.\text{NH}(C_2H_5)_2)(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4 \]

since similar behaviour was observed for \( \text{Rh}_2(\mu-\text{OH}.\text{Cl})(\text{CO})_2(\mu-\text{dppm})_2\text{H}_2\text{O} \). Unlike in \( \text{Rh}_2(\mu-\text{OH}.\text{Cl})(\text{CO})_2(\mu-\text{dppm})_2\text{H}_2\text{O} \), however, the chemical shift of the low field methylene dppm resonances (4.02 ppm) was not unusual and compares well with other A-frame complexes. The presence of a hydroxide group in this orange material can also be supported by IR spectrum (3500(br,w) cm\(^{-1}\)). The same material could also be obtained from the reaction of \( \text{[Rh}_2(\mu-\text{OH}).(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4 \) with diethylamine lending further support for the proposed formulation. The formation of a bridging hydroxide group in this reaction is not altogether surprising since, in independent experiments, \( \text{[Rh}_2(\mu-\text{O}_2\text{CF}_3).(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4 \) was observed to undergo alcoholysis in alcohols and hydrolysis to \( \text{[Rh}_2(\mu-\text{OH})(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4 \) in wet dichloromethane.
2.3. General Experimental

The contents of this section apply to the experimental sections of all chapters. All preparative procedures were carried out routinely under an atmosphere of prepurified dinitrogen (H$_2$O $<$ 5 ppm; O$_2$ $<$ 3 ppm) although most complexes prepared proved stable to air and moisture. All complexes prepared were subjected to vacuum drying prior to the recording of physical data, unless otherwise stated. Labelling of complexes with labelled carbon monoxide ($^{13}$CO, 90% enriched) was achieved by subjecting dichloromethane solutions of the complexes to labelled carbon monoxide at a partial pressure of ca. 250 mm Hg on a standard Toepler line.

2.3.1. Physical Measurements

All new complexes were characterized by means of elemental analysis, conductivity measurements, UV and IR spectroscopy, $^1$H, $^{31}$P($^1$H) and $^{13}$C($^1$H) NMR spectroscopy or by a combination of these methods. X-ray crystal structure determination of a number of compounds described in this thesis were performed by Prof. T.S. Cameron of this department, ably assisted by W. Tacreiter, and Prof. M. Cowie of the Department of Chemistry, University of Alberta. Since these structural studies were performed independently, the results are reported in Appendices I to V. The discussion of the structures in the main body of the text has been
restricted only to a brief discussion of the inner coordination geometries and other relevant aspects of the complexes with the aid of structural diagrams.

IR spectra were recorded on a Perkin-Elmer 180 or 283B grating spectrophotometer and calibrated with polystyrene film. The samples were recorded as Nujol mulls on potassium bromide plates and/or dichloromethane solutions in sodium chloride cells. $^1$H NMR spectra were recorded either on Varian CFT-20 or FT-80 (Atlantic Research Laboratory) (80 MHz) spectrometers, and the Nicolet-360 MHz spectrometer of the Atlantic Region Magnetic Resonance Centre. The chemical shifts are quoted in ppm relative to tetramethylsilane at 0.005 as an internal standard. $^{31}$P($^1$H) NMR were obtained on a Varian XL-100 (40 MHz, Atlantic Regional Laboratory) or Nicolet-360 MHz (157 MHz). Samples were run either in dichloromethane-$d_2$ in 5 mm tubes, dichloromethane in 12 mm concentr tubes with dichloromethane-$d_2$ lock or in dichloromethane-$d_2$ - dichloromethane (1:4 v/v) solution in 10 mm tubes. In all cases, chemical shifts are given in ppm (positive downfield) relative to 85% phosphoric acid, used as an external standard. $^{13}$C($^1$H) were recorded on a Nicolet-360 MHz (90 MHz) spectrometer in dichloromethane-$d_2$ - dichloromethane solutions (1:4 v/v) using dichloromethane as an internal calibrant. However, all chemical shifts are given in ppm (positive downfield) with respect to tetra-
methylsilane. UV spectra were recorded on Pye-Unicam SP-800A spectrometer using 1 mm quartz wells with dichloromethane as solvent. Conductivity measurements were obtained with an Industrial Instruments conductivity bridge using ca. 1 x 10^{-3} M solutions in dichloromethane or acetone. The cell was calibrated with a 0.0100 M potassium chloride solution. Elemental analyses were performed by Guelph Chemical Laboratories Ltd., Guelph, Ontario and the Canadian Microanalytical Service Ltd., British Columbia.

2.3.2. Materials

Hydrated rhodium trichloride was obtained from Strem Chemicals Inc. in addition to a generous loan from Johnson Mathey and Co., which is gratefully acknowledged. The ligand bis(diphenylphosphino)methane (Strem) and gases, purified carbon monoxide (Union Carbide), labelled carbon monoxide (^{13}CO, 90%; Stohler Isotopes), sulphur dioxide (Union Carbide), hydrogen (Union Carbide), 1:1 mixture of carbon monoxide and hydrogen (Union Carbide), acetylene (Matheson), chlorine (Matheson) were used as received. All solvents employed were either commercial or reagent grade and were appropriately dried, distilled and stored over type 4A molecular sieves. Hydrogen halide adducts of N,N-dimethylacetamide (DMA.HX: X = Cl, Br, I) were prepared by bubbling the appropriate hydrogen halide gas into a benzene solution of N,N-dimethylacetamide until precipitation of DMA.HX was
complete. The moisture and air sensitive \((X = I)\) crystals were collected under nitrogen, washed with benzene to remove traces of \(N,N\)-dimethylacetamide and stored under nitrogen after drying in vacuo. \text{Trans-Rh}_2\text{Cl}_2\text{(CO)}_2(\mu\text{-dppm})_2\) was prepared using a previously published procedure\(^{29}\) which involved the reaction of \(\text{Rh}_2\text{Cl}_2(\text{COD})_2\) with carbon monoxide followed by the addition of bis(diphenylphosphino)methane.

2.4. Experimental

2.4.1. List of Complexes Synthesized

<table>
<thead>
<tr>
<th>Complex</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Rh}_2(\mu\text{-OH}\text{.Cl})\text{(CO)}_2(\mu\text{-dppm})_2\text{.H}_2\text{O})</td>
<td>123</td>
</tr>
<tr>
<td>([\text{Rh}_2(\mu\text{-OCH}_3)\text{(CO)}_2(\mu\text{-dppm})_2]\text{ClO}_4\text{.0.5CH}_2\text{Cl}_2)</td>
<td>123</td>
</tr>
<tr>
<td>([\text{Rh}_2(\mu\text{-OC}_2\text{H}_5)\text{(CO)}_2(\mu\text{-dppm})_2]\text{ClO}_4)</td>
<td>124</td>
</tr>
<tr>
<td>([\text{Rh}_2(\mu\text{-OH})\text{(CO)}_2(\mu\text{-dppm})_2]\text{ClO}_4)</td>
<td>125</td>
</tr>
<tr>
<td>([\text{Rh}_2(\mu\text{-OD})\text{(CO)}_2(\mu\text{-dppm})_2]\text{ClO}_4)</td>
<td>125</td>
</tr>
<tr>
<td>([\text{Rh}_2(\mu\text{-Cl})\text{(CO)}_2(\mu\text{-dppm})_2]\text{PF}_6)</td>
<td>125</td>
</tr>
<tr>
<td>([\text{Rh}_2(\mu\text{-Cl})\text{(CO)}_2(\mu\text{-dppm})_2]\text{ClO}_4)</td>
<td>126, 127</td>
</tr>
<tr>
<td>([\text{Rh}_2(\mu\text{-Br})\text{(CO)}_2(\mu\text{-dppm})_2]\text{ClO}_4)</td>
<td>127</td>
</tr>
<tr>
<td>([\text{Rh}_2(\mu\text{-I})\text{(CO)}_2(\mu\text{-dppm})_2]\text{ClO}_4)</td>
<td>127</td>
</tr>
<tr>
<td>([\text{Rh}_2(\mu\text{-H})\text{(μ-CO)Br}_3(\mu\text{-dppm})_2]\text{0.5CH}_2\text{Cl}_2\text{.0.5C}_4\text{H}_10\text{O})</td>
<td>127</td>
</tr>
<tr>
<td>([\text{Rh}_2(\mu\text{-O}_2\text{CH})\text{(CO)}_2(\mu\text{-dppm})_2]\text{ClO}_4)</td>
<td>128</td>
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<tr>
<td>([\text{Rh}_2(\mu\text{-O}_2\text{CCH}_3)\text{(CO)}_2(\mu\text{-dppm})_2]\text{ClO}_4)</td>
<td>128</td>
</tr>
<tr>
<td>([\text{Rh}_2(\mu\text{-O}_2\text{CCH}_2\text{Cl})\text{(CO)}_2(\mu\text{-dppm})_2]\text{ClO}_4)</td>
<td>128</td>
</tr>
</tbody>
</table>
Complex | Page
--- | ---
$[\text{Rh}_2(\mu-O_2\text{CCl}_2)(\text{CO})_2(\mu\text{-dppm})_2]\text{ClO}_4$ | 128
$[\text{Rh}_2(\mu-O_2\text{CCl}_3)(\text{CO})_2(\mu\text{-dppm})_2]\text{ClO}_4$ | 128
$[\text{Rh}_2(\mu-O_2\text{CCF}_3)(\text{CO})_2(\mu\text{-dppm})_2]\text{ClO}_4$ | 128
$\text{Rh}_2(\text{NCO})_2(\text{CO})_2(\mu\text{-dppm})_2$ | 129
$[\text{Rh}_2(\mu\text{-NCO})(\text{CO})_2(\mu\text{-dppm})_2]\text{ClO}_4$ | 130
$\text{Rh}_2(\text{NCS})_2(\text{CO})_2(\mu\text{-dppm})_2$ | 131
$[\text{Rh}_2(\mu\text{-NCS})(\text{CO})_2(\mu\text{-dppm})_2]\text{ClO}_4$ | 132
$[\text{Rh}_2(\mu\text{-N}_3)(\text{CO})_2(\mu\text{-dppm})_2]\text{ClO}_4$ | 133
Reaction of $[\text{Rh}_2(\mu\text{-OC}_2\text{H}_5)(\text{CO})_2(\mu\text{-dppm})_2]\text{ClO}_4$ with ammonium thiocyanate | 134
Reaction of the product obtained in the preceding reaction with ammonium thiocyanate | 135
Reaction of $[\text{Rh}_2(\mu\text{-NCS})(\text{CO})_2(\mu\text{-dppm})_2]\text{ClO}_4$ with ammonium thiocyanate | 135
Reaction of $[\text{Rh}_2(\mu\text{-O}_2\text{CCF}_3)(\text{CO})_2(\mu\text{-dppm})_2]\text{ClO}_4$ with diethylamine | 135
Reaction of $[\text{Rh}_2(\mu\text{-OH})(\text{CO})_2(\mu\text{-dppm})_2]\text{ClO}_4$ with diethylammine | 136
2.4.2. Synthetic Procedures

Preparation of $\text{Rh}_2(\mu-\text{OH.CI})(\text{CO})_2(\mu-\text{dppm})_2 \cdot \text{H}_2\text{O}$

A mixture of trans-$\text{Rh}_2\text{Cl}_2(\text{CO})_2(\mu-\text{dppm})_2$ (0.50 g, 0.45 mmol) and sodium carbonate decahydrate (0.50 g, 1.7 mmol) in 50 mL of 95% aqueous ethanol was stirred for 12 h. The yellow-orange suspension so formed was allowed to settle for 30 min and filtered through a pad of Celite, which was then washed with dichloromethane. The resultant filtrate was reduced to ca. 10 mL under reduced pressure and the product precipitated by the addition of excess diethyl ether. The precipitate was removed by filtration, washed with water and diethyl ether, and recrystallized from dichloromethane-diethyl ether to give the product as bright yellow crystals (0.38-0.43 g, 75-85%).

Anal. Calcd for $\text{C}_{52}\text{H}_{47}\text{P}_4\text{ClO}_4\text{Rh}_2$: C, 56.72; H, 4.31; P, 11.25; Cl, 3.22%. Found: C, 55.80; H, 4.22; P, 11.41; Cl, 3.06%. $\Lambda_M = 4.83 \text{ cm}^2 \Omega^{-1} \text{ mol}^{-1}$ (dichloromethane)

Preparation of $[\text{Rh}_2(\mu-\text{OCH}_3)(\text{CO})_2(\mu-\text{dppm})_2\text{ClO}_4 \cdot 0.5 \text{ CH}_2\text{Cl}_2$

Method A: To a solution of $\text{Rh}_2(\mu-\text{OH.CI})(\text{CO})_2(\mu-\text{dppm})_2 \cdot \text{H}_2\text{O}$ (0.25 g, 0.23 mmol) in 20 mL of dichloromethane was added sodium perchlorate monohydrate (0.060 g, 0.43 mmol) in 20 mL of absolute methanol. The resultant solution was stirred for ca. 30 min and filtered through Celite to remove sodium chloride. Evaporation under reduced pressure precipitated
the product which was recrystallized from dichloromethane-methanol as bright yellow crystals (0.20 g, 73%).

Method B: A suspension of trans-Rh$_2$Cl$_2$(CO)$_2$(μ-dppm)$_2$ (0.25 g, 0.23 mmol) in absolute methanol was treated with freshly prepared sodium methoxide solution (0.070 g of sodium in 10 mL of methanol, 3.0 mmol). The turbid, yellow-orange solution which resulted after 15 min of stirring was filtered through Celite and excess sodium perchlorate monohydrate added (0.060 g, 0.43 mmol). The product separated on stirring and, when precipitation was judged complete, was removed by filtration, washed with methanol and hexane; and recrystallized from dichloromethane-methanol (0.21 g, 77%).

Anal. Calcd for C$_{53}$H$_{53}$P$_4$Cl$_2$Rh$_2$: C, 53.39; H, 3.94; P, 10.29%. Found: C, 53.45; H, 3.98; P, 10.75%.

$\Lambda_M = 43.6$ cm$^2$ g$^{-1}$ mol$^{-1}$ (dichloromethane).

Preparation of [Rh$_2$(μ-OC$_2$H$_5$)(CO)$_2$(μ-dppm)$_2$]ClO$_4$

This complex was prepared using both the procedures described above for its methoxide analogue, with ethanol being used instead of methanol at all points. The complex was recrystallized from dichloromethane-methanol as bright yellow crystals (method A: 0.23 g, 85%; method B: 0.23 g, 87%).

Anal. Calcd for C$_{54}$H$_{49}$P$_4$Cl$_2$Rh$_2$: C, 55.19; H, 4.20; P, 10.54%. Found: C, 54.91; H, 4.28; P, 10.92%.
$\lambda_M = 43.2 \, \text{cm}^2 \, \text{mol}^{-1} \, \Omega^{-1}$ (dichloromethane). UV: $\lambda_{\text{max}} = 423 \, \text{nm}$ (dichloromethane).

Preparation of $\text{Rh}_2(\mu-\text{OH})(\text{CO})_2(\mu-\text{dppm})_2\text{ClO}_4$

To a solution of $\text{Rh}_2(\mu-\text{OC}_2\text{H}_5)(\text{CO})_2(\mu-\text{dppm})_2\text{ClO}_4$ (0.20 g, 0.17 mmol) in 5 mL of dichloromethane was added 2 mL of absolute ethanol containing perchloric acid (70%, 0.13 mL (8 drops)). The solution was allowed to stir for 5 min and the product made to crystallize by the addition of diethyl ether. Recrystallization from dichloromethane-diethyl ether in the presence of perchloric acid gave the complex in the form of yellow microcrystals (0.17, 85%).

Anal. Calcd for $C_{52}H_{45}P_4\text{ClO}_7\text{Rh}_2$: C, 54.45; H, 3.96; P, 10.80; Cl, 3.09%. Found: C, 54.20; H, 3.98; P, 9.77; Cl, 3.18%. $\lambda_M = 44.6 \, \text{cm}^2 \, \text{mol}^{-1} \, \Omega^{-1}$ (dichloromethane).

Preparation of $[\text{Rh}_2(\mu-\text{OD})(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4$

This was prepared by a method analogous to $[\text{Rh}_2(\mu-\text{OH})(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4$, using deuterio perchloric acid (30%, 0.2 mL) and 1 mL of deuterio ethanol-$d_1$ to give yellow microcrystals (0.16 g, 80%).

Attempted Exchange of Chloride in $\text{Rh}_2(\mu-\text{OH.Cl})(\text{CO})_2(\mu-\text{dppm})_2\text{H}_2\text{O}$ with hexafluorophosphate - Preparation of $[\text{Rh}_2(\mu-\text{Cl})(\text{CO})_2(\mu-\text{dppm})_2]\text{PF}_6$

To a solution of $\text{Rh}_2(\mu-\text{OH.Cl})(\text{CO})_2(\mu-\text{dppm})_2\text{H}_2\text{O}$ (0.10 g, 0.091 mmol) in 10 mL of dichloromethane was added
a filtered solution of sodium hexafluorophosphate (0.076 g, 0.45 mmol) dissolved in 15 mL of ethanol. The solution was stirred for ca. 10 min and then concentrated under reduced pressure to precipitate the product as an orange crystalline solid. The product was filtered, washed with hexane and recrystallized from dichloromethane-ethanol (0.085 g, 77%).

Anal. Calcd for $C_{52}H_{44}P_5O_2F_6ClRh_2$: C, 51.55; H, 3.62; P, 12.78%. Found: C, 50.93; H, 3.62; P, 13.37%.

Reaction of $\text{Rh}_2(\mu-OH-\text{Cl})(\text{CO})_2(\mu-\text{dppm})_2\cdot\text{H}_2\text{O}$ with acetic acid:

Preparation of $[\text{Rh}_2(\mu-\text{Cl})(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4$

$\text{Rh}_2(\mu-OH-\text{Cl})(\text{CO})_2(\mu-\text{dppm})_2\cdot\text{H}_2\text{O}$ (0.10 g, 0.091 mmol) was partially dissolved in 10 mL of absolute ethanol and acetic acid (0.03 mL, 0.53 mmol) was added to the solution with stirring. The color of the solution immediately turned red with complete dissolution of the yellow starting material. The addition of sodium perchlorate monohydrate (0.05 g, 0.36 mmol) in 10 mL of absolute ethanol to the red solution precipitated a yellow-orange solid. The product was filtered, washed with ethanol followed by hexane and recrystallized from dichloromethane-diethyl ether (0.082, 77%). $\Lambda_M = 44.2 \text{ cm}^2 \text{ mol}^{-1} \text{ cm}^{-1}$ (dichloromethane), 123 cm$^2$ mol$^{-1}$ (acetone).
Preparation of \([\text{Rh}_2(\mu-\text{X})(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4\) \((X = \text{Cl}, \text{Br}, \text{I})\)

To a solution of \([\text{Rh}_2(\mu-\text{OC}_2\text{H}_5)(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4\) \((0.20 \text{ g}, 0.17 \text{ mmol})\) in 10 \text{ mL} of dichloromethane was added 1.0 \text{ moI} of solid DMA.HX with stirring. A red-orange solution (red or sometimes red-brown for \(X = \text{I}\)) immediately resulted, the addition of diethyl ether to which resulted in the deposition of orange crystalline solids. Recrystallization was from dichloromethane-diethyl ether \((X = \text{Cl}: 0.17 \text{ g, 87\%; X = Br: 0.19 g, 90\%; X = I: 0.16-0.19 g, 75-90\%})\). In the case of \(X = \text{Cl}\), characterization was by comparison of the physical and chemical properties of the product with those of an authentic sample prepared as the perchlorate salt.

\(X = \text{Br}\): Anal. Calcd for \(\text{C}_{52}\text{H}_{44}\text{P}_4\text{O}_6\text{ClBrRh}_2\): C, 51.6\%; H, 3.67; P, 10.23\%. Found: C, 51.34; H, 3.59; P, 11.14\%. \(\Lambda_M = 117 \text{ cm}^2 \text{ mol}^{-1} \text{ mol}^{-1}\) (acetone). \(X = \text{I}\): Anal. Calcd for \(\text{C}_{52}\text{H}_{44}\text{P}_4\text{O}_6\text{ClIRh}_2\): C, 49.68; H, 3.53; P, 9.86\%. Found: C, 49.89; H, 3.47; P, 10.45\%. \(\Lambda_M = 115 \text{ cm}^2 \text{ mol}^{-1} \text{ mol}^{-1}\) (acetone).

Preparation of \([\text{Rh}_2(\mu-H)(\mu-\text{CO})\text{Br}_2(\mu-\text{dppm})_2]\). 0.5 \text{ CH}_2\text{Cl}_2-0.5 \text{ C}_4\text{H}_10\text{O}

\([\text{Rh}_2(\mu-\text{OC}_2\text{H}_5)(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4\) \((0.20 \text{ g}, 0.17 \text{ mmol})\) was dissolved in 10 \text{ mL} of dichloromethane and to it added a ten fold excess of solid DMA.HBr \((0.28 \text{ g}, 1.7 \text{ mmol})\). The yellow solution immediately turned red-orange which was then
stirred for 10 min. The addition of diethyl ether precipitated the excess DMA.HBr. Filtration, followed by addition of diethyl ether to the filtrate slowly precipitated bright orange crystals. These crystals were filtered off, washed with diethyl ether and recrystallized from dichloromethane-diethyl ether (0.14-0.18 g, 62-80%). Anal. Calcd for C\textsubscript{53.5}H\textsubscript{51}P\textsubscript{4}Br\textsubscript{3}O\textsubscript{1.5}ClRh\textsubscript{2}: C, 48.56; H, 3.85; P, 9.37; Br, 18.15%. Found: C, 48.12; H, 3.57; P, 10.69; Br, 17.53%. \( \lambda_M = 0.00° \) (acetone).

Preparation of \( [\text{Rh}_2(\mu-O_2\text{CR})(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4 \) (\( R = \text{H, CH}_3, \text{CF}_3, \text{CH}_2\text{Cl}, \text{CHCl}_2, \text{CCl}_3 \))

A solution of \( [\text{Rh}_2(\mu-O_2\text{C}_2\text{H}_5)(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4 \) (0.20 g, 0.17 mmol) in 5 mL of dichloromethane was treated with appropriate carboxylic acid (RCOOH: \( R = \text{H, CH}_3, \text{CF}_3, \text{CH}_2\text{Cl}, \text{CHCl}_2, \text{CCl}_3 \)) in excess (0.05 mL, \( R = \text{H, CH}_3, \text{CF}_3; R = \text{CH}_2\text{Cl}, \text{CHCl}_2 \)) except in the case of \( R = \text{CCl}_3 \) where one mole of acid was added. This resulted in an immediate colour change from yellow to deep red. Careful addition of diethyl ether resulted in the deposition of red crystals of the various products in good yields. Recrystallization of the complexes was from dichloromethane-diethyl ether (\( R = \text{H}: 0.18 \text{ g}, 90%; R = \text{CH}_3: 0.19 \text{ g}, 95%; R = \text{CF}_3: 0.20 \text{ g}, 95%; R = \text{CH}_2\text{Cl}: 0.19 \text{ g}, 89%; R = \text{CHCl}_2: 0.17 \text{ g}, 79%; R = \text{CCl}_3: 0.16 \text{ g}, 71\% \text{(av.)}) \). In the case \( R = \text{CF}_3 \), the recrystallization was carried out in the
presence of excess trifluoroacetic acid (3-4 drops).

X = H: Anal. Calcd for C_{53}H_{45}P_{4}O_{8}ClRh_{2}: C, 54.17; H, 3.86; P, 10.54%. Found: C, 54.42; H, 3.60; P, 10.68%.

\[ \Lambda_{M} = 126 \text{ cm}^2 \Omega^{-1} \text{ mol}^{-1} \text{ (acetone).} \quad \text{UV: } \lambda_{\text{max}} = 490 \text{ nm.} \]

X = CH_{3}: Anal. Calcd for C_{54}H_{47}P_{4}O_{8}ClRh_{2}: C, 54.55; H, 3.98; P, 10.42%. Found: C, 54.64; H, 3.96; P, 10.91%.

\[ \Lambda_{M} = 121 \text{ cm}^2 \Omega^{-1} \text{ mol}^{-1} \text{ (acetone).} \quad \text{UV: } \lambda_{\text{max}} = 492 \text{ nm.} \]

X = CF_{3}: Anal. Calcd for C_{54}H_{44}P_{4}O_{8}ClRh_{2}: C, 52.18; H, 3.57; P, 9.97; F, 4.58%. Found: C, 52.11; H, 3.49; P, 10.24; F, 5.09%. \[ \Lambda_{M} = 115 \text{ cm}^2 \Omega^{-1} \text{ mol}^{-1} \text{ (acetone).} \quad \text{UV: } \lambda_{\text{max}} = 494 \text{ nm.} \]

Analytical data of \([\text{Rh}_2(\mu-O_2CR)(CO)_2(\mu-dppm)_2]ClO_4\) (R = CH_{2}Cl, CHCl_{2}, CCl_{3}) have not been obtained and characterization of these complexes was by spectroscopic means only. X = CH_{2}Cl: \[ \Lambda_{M} = 123 \text{ cm}^2 \Omega^{-1} \text{ mol}^{-1} \text{ (acetone).} \quad \text{UV: } \lambda_{\text{max}} = 493 \text{ nm.} \]

X = CHCl_{2}: \[ \Lambda_{M} = 126 \text{ cm}^2 \Omega^{-1} \text{ mol}^{-1} \text{ (acetone).} \quad \text{UV: } \lambda_{\text{max}} = 494 \text{ nm.} \]

X = CF_{3}: \[ \Lambda_{M} = 117 \text{ cm}^2 \Omega^{-1} \text{ mol}^{-1} \text{ (acetone).} \quad \text{UV: } \lambda_{\text{max}} = 494 \text{ nm.} \]

Preparation of \([\text{Rh}_2(NCO)_2(CO)_2(\mu-dppm)_2]ClO_4\)

To a solution of \([\text{Rh}_2(\mu-O_2CCF_3)(CO)_2(\mu-dppm)_2]ClO_4\) (0.20 g, 0.16 mmol) in 10 mL of acetone was added four fold excess of potassium cyanate (0.052 g, 0.64 mmol) dissolved in a minimum quantity of water. The solution immediately turned red-orange and deposited a red-orange solid. The
product was removed by filtration and washed with water followed by ethanol. Recrystallization of small portions of the sparingly soluble red-orange product could be achieved from dichloromethane-diethyl ether (0.13 g, 70% crude). Characterization of Rh$_2$(NCO)$_2$(CO)$_2$(μ-dppm)$_2$ was by comparison with an authentic sample.

Preparation of [Rh$_2$(μ-NCO)(CO)$_2$(μ-dppm)$_2$]ClO$_4$ -

Method A: To a solution of [Rh$_2$(μ-O$_2$CCF$_3$)(CO)$_2$(μ-dppm)$_2$]ClO$_4$ (0.15 g, 0.12 mmol) in 5 mL of acetone was added one mole of potassium cyanate (0.0098 g, 0.12 mmol) dissolved in a minimum quantity of water. The addition of diethyl ether to the resultant yellow-orange solution precipitated the product which was removed by filtration and washed with diethyl ether. Recrystallization from dichloromethane-diethyl ether gave bright yellow crystals of the complex (0.10 g, 70%).

Method B: To a solution of [Rh$_2$(μ-OC$_2$H$_5$)(CO)$_2$(μ-dppm)$_2$]ClO$_4$ (0.10 g, 0.085 mmol) dissolved in 5 mL of dichloromethane/acetone mixture (1:4 v/v) was added perchloric acid (70%, 0.07 mL (4 drops)) simultaneously with potassium cyanate (0.0069 g, 0.085 mmol) dissolved in a minimum quantity of water. After stirring for ca. 5 min, the product was crystallized by the addition of diethyl ether. Recrystallization of the product from dichloromethane-diethyl ether
yielded bright yellow crystals (0.070 g, 72%). Anal. Calcd for C_{53}H_{44}NO_{7}P_{4}ClRh_{2}: C, 54.31; H, 3.78; N, 1.19%.
Found: C, 54.29; H, 4.11; N, 1.21%.
\[ \lambda_M = 119 \text{ cm}^{-1} \text{ mol}^{-1} \text{ (acetone)} \]

Preparation of Rh\(_2\)(NCS)\(_2\)(CO)\(_2\)(\(\mu\)-dppm)\(_2\)

Method A: To a solution of [Rh\(_2\)(\(\mu\)-O\(_2\)CCF\(_3\))(CO)\(_2\)(\(\mu\)-dppm)\(_2\)]ClO\(_4\) (0.20 g, 0.16 mmol) in 10 mL of acetone was added four fold excess of NH\(_4\)NCS (0.049 g, 0.64 mmol) dissolved in 2 mL of acetone. On stirring the solution became red-orange and precipitated a golden-yellow solid almost quantitatively. The product was removed by filtration and washed with water followed by ethanol (0.18 g, 96%).

Method B: [Rh\(_2\)(\(\mu\)-OC\(_2\)H\(_5\))(CO)\(_2\)(\(\mu\)-dppm)\(_2\)]ClO\(_4\) (0.10 g, 0.085 mmol) was dissolved in 5 mL of dichloromethane and to it added excess ammonium thiocyanate (0.029 g, 0.34 mmol) dissolved in 10 mL of acetone with stirring. The solution immediately turned from yellow to dark red and precipitated a golden-yellow solid almost quantitatively. The product was filtered off, and washed with water followed by ethanol (0.095 g, 97%). Anal. Calcd for C\(_{54}\)H\(_{44}\)N\(_2\)S\(_2\)P\(_4\)O\(_2\)Rh\(_2\): C, 56.56; H, 3.87; N, 2.44; S, 5.59%. Found: C, 56.48; H, 3.71; N, 2.47; S, 6.05%.
Preparation of $[\text{Rh}_2(\mu\text{-NCS})(\text{CO})_2(\mu\text{-dppm})_2]\text{ClO}_4$

Method A: To a solution of $[\text{Rh}_2(\mu\text{-O}_2\text{CCF}_3)(\text{CO})_2(\mu\text{-dppm})_2]\text{ClO}_4$ (0.25 g, 0.20 mmol) in 10 mL of acetone added one mole of ammonium thiocyanate (0.0153 g, 0.20 mmol). The solution was stirred for 30 min during which time a golden-yellow product began to separate which was identified as $\text{Rh}_2(\mu\text{-NCS})(\text{CO})(\mu\text{-dppm})_2$ (0.013-0.019 g). Filtration, followed by addition of diethyl ether to the filtrate precipitated a yellow-orange material which was found to be contaminated with some of the neutral complex (0.13-0.16 g). The yellow-orange crude material was purified by successive fractional dissolution-filtration-recrystallization cycle (usually 2-3 cycles) from dichloromethane-diethyl ether until a pure yellow colour complex was obtained (0.042-0.071 g, 18-30%). The overall yield of the reaction depends upon the scale used. For example, yellow product can be obtained in 55% yield by starting with 0.40 g of $[\text{Rh}_2(\mu\text{-OC}_2\text{H}_5)(\text{CO})_2(\mu\text{-dppm})_2]\text{ClO}_4$.

Method B: To a solution of $[\text{Rh}_2(\mu\text{-OC}_2\text{H}_5)(\text{CO})_2(\mu\text{-dppm})_2]\text{ClO}_4$ (0.10 g, 0.085 mmol) in 5 mL of dichloromethane/acetone (1:4 v/v) was added ammonium thiocyanate (0.085 mmol) dissolved in 2 mL of acetone containing perchloric acid (70%, 0.07 mL (4 drops)). The solution immediately turned orange and on stirring precipitated a bright yellow crystalline material. The precipitation was
completed by the addition of diethyl ether and the product filtered and recrystallized from dichloromethane-diethyl ether as bright yellow crystals (0.090 g, 80%).

Anal. Calcd for C_{53}H_{44}N_{6}O_{6}P_{4}ClRh_{2}: C, 53.57; H, 3.73; N, 1.19; S, 2.70%. Found: C, 53.39; H, 3.66; N, 1.21; S, 2.56%. \( \lambda = 117 \text{ cm}^2 \text{ mol}^{-1} \text{ mol}^{-1} \) (acetone).

Preparation of \([\text{Rh}_2(\mu-N_3)(\text{CO})_2(\mu-dppm)]\text{ClO}_4\)

Method A: To a solution of \([\text{Rh}_2(\mu-O_2CCF_3)(\text{CO})_2(\mu-dppm)]\text{ClO}_4\) (0.15 g, 0.12 mmol) in 10 mL of acetone was added a solution of sodium azide (0.032 g, 0.49 mmol) in a minimum of water. Addition of diethyl ether to the resultant yellow-orange solution yielded a crude yellow-orange product, which was removed by filtration and washed with water and diethyl ether. Recrystallization from dichloromethane-diethyl ether gave the product in the form of bright yellow crystals (0.12 g, 78%).

Method B: To a solution of \([\text{Rh}_2(\mu-OC_2H_5)(\text{CO})_2(\mu-dppm)]\text{ClO}_4\) (0.10 g, 0.085 mmol) dissolved in 5 mL of dichloromethane/acetone (1:4 v/v) was added sodium azide (0.0213 g, 0.328 mmol) dissolved in a minimum quantity of water to which was added perchloric acid (70%, 0.07 mL (4 drops)). The solution was stirred for 5 min and the product isolated by the addition of diethyl ether. Recrystallization from dichloromethane-diethyl ether gave bright yellow...
crystals (0.094 g, 94%). Anal. Calcd for C_{52}H_{44}P_{4}N_{3}O_{6}ClRh_{2}: C, 53.29; H, 3.78; P, 10.57; N, 3.59%. Found: C, 53.18; H, 3.63; P, 10.78; N, 3.50%. \( \Lambda_M = 117 \text{ cm}^2 \text{ mol}^{-1} \) (acetone).

Reaction of \([\text{Rh}_2(\mu-\text{OC}_2\text{H}_5)(\text{CO})_2(\mu-\text{dppm})_2]\)ClO_4 with Ammonium Thiocyanate

To a solution of \([\text{Rh}_2(\mu-\text{OC}_2\text{H}_5)(\text{CO})_2(\mu-\text{dppm})_2]\)ClO_4 (0.20 g, 0.17 mmol) in 5 mL of dichloromethane was added ammonium thiocyanate (0.0129 g, 0.170 mmol) dissolved in 10 mL of acetone. The solution immediately turned dark red in colour and on stirring deposited a golden-yellow solid, identified as \(\text{Rh}_2(\text{NCS})_2(\text{CO})_2(\mu-\text{dppm})_2\) (0.029-0.039 g, 15-20\% 15-20\%). After filtering, the filtrate was reduced in volume to ca. 7-8 mL and upon addition of diethyl ether an orange precipitate was obtained. Recrystallization from dichloromethane-diethyl ether yielded the product as an orange microcrystalline solid (0.13-0.14 g, 65-70\%). This product has been tentatively identified as \([\text{Rh}_2(\text{SCN})(\text{CO})_2(\mu-\text{dppm})_2]\)ClO_4. Anal. Calcd for C_{53}H_{44}NSO_{6}P_{4}ClRh_{2}: C, 53.57; H, 3.73; N, 1.19; S, 2.70%. Found: C, 53.38; H, 3.83; N, 1.52; S, 2.90%. \( \Lambda_M = 117 \text{ cm}^2 \text{ mol}^{-1} \) (acetone).
Reaction of the Product Obtained in the Preceding Reaction with Ammonium Thiocyanate

To a solution of $[\text{Rh}_2(\text{SCN})(\text{CO})_2(\mu\text{-dppm})_2]\text{ClO}_4$ (0.100 g, 0.084 mmol) in 5 mL of dichloromethane was added ammonium thiocyanate (0.0064 g, 0.084 mmol) in 10 mL of acetone. The solution immediately turned red and deposited a golden-yellow solid of $[\text{Rh}_2\text{(NCS)}_2(\text{CO})_2(\mu\text{-dppm})_2]$, which was worked up in the above fashion (0.080 g, 83%).

Reaction of $[\text{Rh}_2(\mu\text{-NCS})(\text{CO})_2(\mu\text{-dppm})_2]\text{ClO}_4$ with Ammonium Thiocyanate

To a solution of $[\text{Rh}_2(\mu\text{-NCS})(\text{CO})_2(\mu\text{-dppm})_2]\text{ClO}_4$ (0.050 g, 0.042 mmol) in 5 mL of dichloromethane was added ammonium thiocyanate (0.0032 g, 0.042 mmol) in 10 mL of acetone. The solution immediately turned red and a golden-yellow product deposited on stirring. The product, identified as $\text{Rh}_2\text{(NCS)}_2(\text{CO})_2(\mu\text{-dppm})_2$, was separated by filtration, washed with water, ethanol (0.041 g, 86%).

Reaction of $[\text{Rh}_2(\mu\text{-O}_2\text{CCF}_3)(\text{CO})_2(\mu\text{-dppm})_2]\text{ClO}_4$ with Diethylamine

To a solution of $[\text{Rh}_2(\mu\text{-O}_2\text{CCF}_3)(\text{CO})_2(\mu\text{-dppm})_2]\text{ClO}_4$ (0.20 g, 0.16 mmol) in 10 mL of dichloromethane was added excess diethylamine (0.5 mL, 4.8 mmol). The colour of the solution immediately turned from red to orange. The
solution was stirred for 30 min and diethyl ether was added to precipitate the product as bright orange microcrystals. Recrystallization was achieved from dichloromethane-diethyl ether in the presence of diethylamine and the product was thoroughly washed to remove all traces of excess amine (0.15 g, 76%). This product has been tentatively identified as \([\text{Rh}_2(\mu-\text{OH}.\text{NH(C}_2\text{H}_5)\text{)}_2(\text{CO})_2(\mu-\text{dpmm})_2]\text{ClO}_4\). Anal. Calcd for \(\text{C}_{56}\text{H}_{56}\text{P}_4\text{N}_7\text{ClRh}_2\): C, 55.08; H, 4.59; P, 10.16; N, 1.15%. Found: C, 54.36, 54.23, 54.32; H, 3.70, 3.64, 4.27; P, 10.91; N, 1.20%. 

\(\lambda_M = 120 \text{ cm}^{-1} \text{ mol}^{-1} \text{ (acetone)}\).

Reaction of \([\text{Rh}_2(\mu-\text{OH})(\text{CO})_2(\mu-\text{dpmm})_2]\text{ClO}_4\) with Diethylamine

To a solution of \([\text{Rh}_2(\mu-\text{OH})(\text{CO})_2(\mu-\text{dpmm})_2]\text{ClO}_4\) (0.10 g, 0.087 mmol) in 10 mL of dichloromethane was added excess diethylamine (0.5 mL, 4.8 mmol). The colour of the solution immediately turned from yellow to orange. The solution was stirred for 15 min and precipitated the product by the addition of diethyl ether. Filtration followed by recrystallizing with dichloromethane-diethyl ether in the presence of 4-5 drops of diethylamine gave bright orange microcrystals (0.08 g, 75%). The physical and chemical properties of this product were found to be identical in all respect to those obtained in the preceding reaction.
### Table 2.1. IR Data of Dimeric Bis(diphenylphosphino)methane Complexes of Rhodium with Different Bridgehead Ligands

<table>
<thead>
<tr>
<th>Compound</th>
<th>(v(\text{CO})) (a), cm(^{-1})</th>
<th>(v(\text{CO})) (b), cm(^{-1})</th>
<th>Others (b), cm(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Rh}_2(\mu-\text{OH},\text{Cl})(\text{CO})_2(\mu-\text{dppm})_2\cdot\text{H}_2\text{O})</td>
<td>(1976\text{(sh)}, 1966\text{(vs)})</td>
<td>(1937\text{(s)}, 1962\text{(vs)})</td>
<td>(\tilde{\nu}(\text{OH,H}_2\text{O}), 3670, 3400\text{br})</td>
</tr>
<tr>
<td>(\text{[Rh}_2(\mu-\text{OCH}_3)(\text{CO})_2(\mu-\text{dppm})_2\cdot\text{ClO}_4\cdot0.5\text{CH}_2\text{Cl}_2)</td>
<td>(1993\text{(sh)}, 1982\text{(vs)})</td>
<td>(1976\text{(s)}, 1961\text{(vs)})</td>
<td>(\tilde{\nu}(\text{CH}), 2862\text{(w)})</td>
</tr>
<tr>
<td>(\text{[Rh}_2(\mu-\text{OC}_2\text{H}_5)(\text{CO})_2(\mu-\text{dppm})_2\cdot\text{ClO}_4)</td>
<td>(1992\text{(sh)}, 1981\text{(vs)})</td>
<td>(1976\text{(s)}, 1967\text{(vs)})</td>
<td>--</td>
</tr>
<tr>
<td>(\text{[Rh}_2(\mu-\text{OH})(\text{CO})_2(\mu-\text{dppm})_2\cdot\text{ClO}_4)</td>
<td>(1984\text{(vs)}, 1978\text{(sh)})</td>
<td>(1905\text{(s)}, 1968\text{(vs)})</td>
<td>(\tilde{\nu}(\text{OH}), 3619\text{(w)})</td>
</tr>
<tr>
<td>(\text{[Rh}_2(\mu-\text{OD})(\text{CO})_2(\mu-\text{dppm})_2\cdot\text{ClO}_4)</td>
<td>(1984\text{(vs)}, 1978\text{(sh)})</td>
<td>(1985\text{(s)}, 1968\text{(vs)})</td>
<td>(\tilde{\nu}(\text{OD}), 2672\text{(m)})</td>
</tr>
<tr>
<td>(\text{[Rh}_2(\mu-\text{Cl})(\text{CO})_2(\mu-\text{dppm})_2\cdot\text{PF}_6)</td>
<td>(2003\text{(s)}, 1992\text{(vs)})</td>
<td>(1992\text{(s)}, 1975\text{(vs)})</td>
<td>--</td>
</tr>
<tr>
<td>(\text{[Rh}_2(\mu-\text{Cl})(\text{CO})_2(\mu-\text{dppm})_2\cdot\text{ClO}_4)</td>
<td>(2003\text{(s)}, 1992\text{(vs)})</td>
<td>(1992\text{(s)}, 1975\text{(vs)})</td>
<td>--</td>
</tr>
<tr>
<td>(\text{[Rh}_2(\mu-\text{Br})(\text{CO})_2(\mu-\text{dppm})_2\cdot\text{ClO}_4)</td>
<td>(2003\text{(s)}, 1992\text{(vs)})</td>
<td>(1995\text{(s)}, 1983\text{(vs)})</td>
<td>--</td>
</tr>
<tr>
<td>(\text{[Rh}_2(\mu-\text{I})(\text{CO})_2(\mu-\text{dppm})_2\cdot\text{ClO}_4)</td>
<td>(2003\text{(s)}, 1991\text{(vs)})</td>
<td>(1994\text{(sh)}, 1996\text{(vs)})</td>
<td>--</td>
</tr>
<tr>
<td>(\text{[Rh}_2(\mu-\text{H})(\mu-\text{CO})\text{Br}_2(\mu-\text{dppm})_2\cdot\text{Br}\cdot\text{Cl}_2\cdot0.5\text{CH}_2\text{Cl}_2\cdot0.5\text{C}_4\text{H}_10)</td>
<td>(1819\text{(m)})</td>
<td>(1816\text{(s)})</td>
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</tr>
<tr>
<td>(\text{[Rh}_2(\mu-\text{O}_2\text{CH})(\text{CO})_2(\mu-\text{dppm})_2\cdot\text{ClO}_4)</td>
<td>(2001\text{(vs)}, 1991\text{(s)})</td>
<td>(1989\text{(vs)}, 1965\text{(s)})</td>
<td>(\tilde{\nu}(\text{CO}), 1568\text{(s)}; \tilde{\nu}(\text{CH}), 1352\text{(m)})</td>
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<td>(\text{[Rh}_2(\mu-\text{O}_2\text{CCCH}_3)(\text{CO})_2(\mu-\text{dppm})_2\cdot\text{ClO}_4)</td>
<td>(2001\text{(vs)}, 1985\text{(s)})</td>
<td>(1980\text{(vs)}, 1968\text{(vs)})</td>
<td>(\tilde{\nu}(\text{CO}), 1545\text{(m)})</td>
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<td>(\text{[Rh}_2(\mu-\text{O}_2\text{CCF}_3)(\text{CO})_2(\mu-\text{dppm})_2\cdot\text{ClO}_4)</td>
<td>(2009\text{(vs)}, 1996\text{(s)})</td>
<td>(1996\text{(vs)}, 1970\text{(vs)})</td>
<td>(\tilde{\nu}(\text{CO}), 1634\text{(s)})</td>
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<tr>
<td>(\text{[Rh}_2(\mu-\text{O}_2\text{CCCH}_2\text{Cl})(\text{CO})_2(\mu-\text{dppm})_2\cdot\text{ClO}_4)</td>
<td>(2002\text{(vs)}, 1992\text{(s)})</td>
<td>(1996\text{(vs)}, 1982\text{(s)})</td>
<td>(\tilde{\nu}(\text{CO}), 1567\text{(s)}; \tilde{\nu}(\text{CO}), 1418\text{(m)})</td>
</tr>
</tbody>
</table>

(continued)
Table 2.1. (continued)

<table>
<thead>
<tr>
<th>Compound</th>
<th>(v(CO)^a), cm(^{-1})</th>
<th>(v(CO)^b), cm(^{-1})</th>
<th>Others(^b), cm(^{-1})</th>
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</thead>
<tbody>
<tr>
<td>([\text{Rh}_2(\mu-O_2\text{CCHCl}_2)(\text{CO})_2(\mu-dppm)_2]\text{ClO}_4)</td>
<td>2004(vs), 1993(sh)</td>
<td>1996(vs), 1981(sh)</td>
<td>(v_{as}(\text{CO}_2)), 1602(s); (v_s(\text{CO}_2)), 1402(m)</td>
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<tr>
<td>([\text{Rh}_2(\mu-O_2\text{CCCI}_3)(\text{CO})_2(\mu-dppm)_2]\text{ClO}_4)</td>
<td>2005(vs), 1995(sh)</td>
<td>2007(vs), 1999(vs), 1979(s)</td>
<td>(v_{as}(\text{CO}_2)), 1625(s); (v_s(\text{CO}_2)), 1376(s)</td>
</tr>
<tr>
<td>([\text{Rh}_2(\text{NCO})_2(\text{CO})_2(\mu-dppm)_2]</td>
<td>--</td>
<td>1969(vs)</td>
<td>(v_{as}(\text{NCO})), 2239(s); (v_s(\text{NCO})), 1336(m)</td>
</tr>
<tr>
<td>([\text{Rh}_2(\text{NCS})_2(\text{CO})_2(\mu-dppm)_2]</td>
<td>--</td>
<td>1994(vs)</td>
<td>(v_{as}(\text{NCS})), 2077(s); (v_s(\text{NCS})), 831(w)</td>
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<td>([\text{Rh}_2(\mu-NCO)(\text{CO})_2(\mu-dppm)_2]</td>
<td>2003(sh), 1996(vs)</td>
<td>1996(s), 1981(vs)</td>
<td>(v_{as}(\text{NCO})), 2196(vs);</td>
</tr>
<tr>
<td>([\text{Rh}_2(\mu-NCS)(\text{CO})_2(\mu-dppm)_2]</td>
<td>2005(sh), 1996(vs)</td>
<td>1997(s), 1884(vs)</td>
<td>(v_{as}(\text{NCS})), 1952(s); (v_s(\text{NCS})), 872(w), 842(w)</td>
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<tr>
<td>([\text{Rh}_2(\mu-N_3)(\text{CO})_2(\mu-dppm)_2]</td>
<td>2002(sh), 1995(vs)</td>
<td>1996(s), 1983(vs)</td>
<td>(v(N_3)), 2077(s)</td>
</tr>
<tr>
<td>([\text{Rh}_2(\text{SCN})(\text{CO})_2(\mu-dppm)_2]</td>
<td>1996(vs), 1952(w), 1987(s)</td>
<td>1970(sh)</td>
<td>(v_{as}(\text{SCN})), 2073(m)</td>
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<td>([\text{Rh}_2(\mu-OH, NH(C_2H_5)_2)(\mu-dppm)_2]</td>
<td>1977(s), 1961(vs)</td>
<td>1983(vs), 1975(sh)</td>
<td>(v(OH)), 3500(w,br)</td>
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</table>

(a) Recorded in dichloromethane solution.

(b) Recorded as nujol mulls on potassium bromide plates.
Table 2.2. NMR Data \((^1H\ and\ ^31P[^1H])\) of Dimeric Bis(diphenylphosphino)methane Complexes of Rhodium with Different Bridgehead Ligands

<table>
<thead>
<tr>
<th>Compound</th>
<th>(\delta^{31}P\left[3J_{\text{Rh-P}} - XJ_{\text{Rh-P}}\right])</th>
<th>(\delta_{1H}\ b,c,d)</th>
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<tbody>
<tr>
<td>(\text{Rh}_2(\mu-\text{OH})\text{Cl}_2\text{(CO)}_2(\mu\text{-dppm})_2\text{H}_2\text{O})</td>
<td>20.79 (130.1)</td>
<td>5.29, 3.06 (m, CH(_2)-dppm); 3.75 (s, br, 1H, OH); 1.71 (s, br, 2H, H(_2)O)</td>
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<tr>
<td>(\text{Rh}_2(\mu-\text{OCH}_3)\text{(CO)}_2(\mu\text{-dppm})_2\text{ClO}_4\cdot 0.5\text{CH}_2\text{Cl}_2)</td>
<td>20.64 (128.1)</td>
<td>4.05, 3.22 (m, CH(_2)-dppm); 3.37 (s, OCH(_3)); 5.32 (s, CH(_2))</td>
</tr>
<tr>
<td>(\text{Rh}_2(\mu-\text{OC}_2\text{H}_5)\text{(CO)}_2(\mu\text{-dppm})_2\text{ClO}_4)</td>
<td>20.67 (128.2)</td>
<td>4.15, 3.34 (m, CH(<em>2)-dppm); 0.65 (t, (3J</em>{\text{H-H}} = 7.0) Hz, OCH(_3))</td>
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<tr>
<td>(\text{Rh}_2(\mu-\text{OH})\text{(CO)}_2(\mu\text{-dppm})_2\text{ClO}_4)</td>
<td>20.65 (128.1)</td>
<td>4.06, 3.24 (m, CH(<em>2)-dppm); -0.13 (qt, (3J</em>{\text{H-H}} = 3.1) Hz, OH)</td>
</tr>
<tr>
<td>(\text{Rh}_2(\mu-\text{Cl})\text{(CO)}_2(\mu\text{-dppm})_2\text{ClO}_4)</td>
<td>--</td>
<td>4.10, 3.49 (m, CH(_2)-dppm)</td>
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<tr>
<td>(\text{Rh}_2(\mu-\text{Br})\text{(CO)}_2(\mu\text{-dppm})_2\text{ClO}_4)</td>
<td>18.48 (111.3)</td>
<td>4.40, 3.88 (m, CH(_2)-dppm)</td>
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<tr>
<td>(\text{Rh}_2(\mu-\text{I})\text{(CO)}_2(\mu\text{-dppm})_2\text{ClO}_4)</td>
<td>17.31 (108.6)</td>
<td>4.60, 3.30 (m, CH(_2)-dppm)</td>
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<tr>
<td>(\text{Rh}_2(\mu-\text{H})\text{(CO)Br}_2(\mu\text{-dppm})_2\text{Br}^{-}\cdot 0.5\text{CH}_2\text{Cl}_2\cdot 0.5\text{C}_10\text{H}_10)</td>
<td>18.26 (95.52)</td>
<td>3.92, 3.57 (m, CH(<em>2)-dppm); -17.12 (qt, 1H, (2J</em>{\text{Rh-H}} = 20.0) Hz, (3J_{\text{H-H}} = 10.0) Hz); 5.32 (s, CH(<em>2)); 3.34 (t, 2H, (3J</em>{\text{H-H}} = 7.0) Hz); 1.15 (t, 3H, (3J_{\text{H-H}} = 7.0) Hz)</td>
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<tr>
<td>(\text{Rh}_2(\mu-\text{OCH}_2\text{CH}_3)\text{(CO)}_2(\mu\text{-dppm})_2\text{ClO}_4)</td>
<td>23.83 (125.4)</td>
<td>4.05, 3.23 (m, CH(_2)-dppm)</td>
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<tr>
<td>(\text{Rh}_2(\mu-\text{OCCF}_3)\text{(CO)}_2(\mu\text{-dppm})_2\text{ClO}_4)</td>
<td>23.00 (126.3)</td>
<td>3.95, 3.43 (m, CH(_2)-dppm); 0.73 (s, 1H, CH(_3))</td>
</tr>
<tr>
<td>(\text{Rh}_2(\mu-\text{OCCCH}_3)\text{(CO)}_2(\mu\text{-dppm})_2\text{ClO}_4)</td>
<td>23.04 (126.3)</td>
<td>3.95, 3.43 (m, CH(_2)-dppm); 0.73 (s, 1H, CH(_3))</td>
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<tr>
<td>(\text{Rh}_2(\mu-\text{OCCH}_2\text{Cl})\text{(CO)}_2(\mu\text{-dppm})_2\text{ClO}_4)</td>
<td>23.39 (125.1)</td>
<td>3.80, 3.39 (m, CH(_2)-dppm); 2.58 (s, 2H, CH(_2)Cl)</td>
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<tr>
<td>(\text{Rh}_2(\mu-\text{OC(CHCl)_2})\text{(CO)}_2(\mu\text{-dppm})_2\text{ClO}_4)</td>
<td>23.04 (126.3)</td>
<td>3.95, 3.43 (m, CH(_2)-dppm); 0.73 (s, 1H, CH(_3))</td>
</tr>
<tr>
<td>(\text{Rh}_2(\mu-\text{OCICCl})\text{(CO)}_2(\mu\text{-dppm})_2\text{ClO}_4)</td>
<td>23.77 (123.3)</td>
<td>4.02, 2.97 (m, CH(_2)-dppm)</td>
</tr>
<tr>
<td>(\text{Rh}_2(\mu-\text{NCO})\text{(CO)}_2(\mu\text{-dppm})_2\text{ClO}_4)</td>
<td>19.95 (117.0)</td>
<td>3.69 (m, CH(_2)-dppm); 3.88, 3.66 (m, CH(_2)-dppm)</td>
</tr>
<tr>
<td>(\text{Rh}_2(\mu-\text{NCS})\text{(CO)}_2(\mu\text{-dppm})_2\text{ClO}_4)</td>
<td>21.18 (115.8)</td>
<td>3.66 (m, CH(_2)-dppm); 3.73, 3.51 (m, CH(_2)-dppm)</td>
</tr>
</tbody>
</table>

(continued)
Table 2.2. (continued)

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \delta ^{31}P(1 J_{\text{Rh-P}} + X_{\text{Rh-P}}) )</th>
<th>( \delta ^1H ) b, c, d</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Rh}_2(\text{SCN})(\text{CO})_2(\mu-\text{dppm})_2])\text{ClO}_4)</td>
<td>e</td>
<td>3.77 (m, 4H, CH(_2)-dppm)(^f), 3.89, 3.62 (m, 4H, CH(_2)-dppm)(^g)</td>
</tr>
<tr>
<td>([\text{Rh}_2(\mu-\text{N}_3)(\text{CO})_2(\mu-\text{dppm})_2])\text{ClO}_4)</td>
<td>20.20 (119.7)</td>
<td>3.70 (m, 4H, CH(_2)-dppm)(^f), 3.81, 3.58 (m, 4H, CH(_2)-dppm)(^g)</td>
</tr>
<tr>
<td>([\text{Rh}_2(\mu-\text{OH.NH(C}_2\text{H}_5)_2)(\text{CO})_2(\mu-\text{dppm})_2])\text{ClO}_4)</td>
<td>20.14 (12842)</td>
<td>5.57 (s, br, 1H, NH), 4.02, 3.29 (m, 4H, CH(<em>2)-dppm); 2.81 (q, 4H, (3J</em>{\text{H-H}} = 7) Hz, CH(<em>2); 1.19 (t, 6H, (3J</em>{\text{H-H}} = 7) Hz, CH(_3)); 0.07 (distorted q, 1H, OH)</td>
</tr>
</tbody>
</table>

(a) \( ^{31}P \) chemical shifts (in ppm) relative to external 85% H\(_3\)PO\(_4\), positive downfield separation between the two major lines (\(1 J_{\text{Rh-P}} + X_{\text{Rh-P}}\)) in Hz.
(b) Chemical shifts (in ppm) relative to tetramethylsilane (TMS).
(c) Dichloromethane-\(d_2\)
(d) Resonance due to phenyl protons (7.7 - 7.0 ppm) have not been included.
(e) See text.
(f) 80 MHz.
(g) 360 MHz.
(h) The degree of dichloromethane solvation was determined by recording the \( ^1H \) NMR spectrum in acetone-\(d_6\) (5.60, s, 1H).
CHAPTER 3

REACTIVITY OF A-FRAME COMPLEXES WITH CARBON MONOXIDE AND SULPHUR DIOXIDE

3.1. Introduction

It will be recalled from Chapter 1 that some binuclear complexes with the A-frame geometry are capable of binding small molecules such as carbon monoxide and sulphur dioxide in the endo pocket. This chapter deals with the reactivity of the A-frame complexes, \( \text{Rh}_2(\mu-\text{OH}, \text{Cl})(\text{CO})_2(\mu-\text{dppm})_2 \cdot \text{H}_2\text{O} \) and \( \text{[Rh}_2(\mu-\text{X})(\text{CO})_2(\mu-\text{dppm})_2 \text{ClO}_4 \) \( (X = \text{OH}, \text{OCH}_3, \text{OC}_2\text{H}_5, \text{Br}, \text{I}, \text{NCS}, \text{N}_3, \text{NCO}) \) described in Chapter 2 with carbon monoxide and sulphur dioxide. Also, the reaction of the face to face dimer, \( \text{Rh}_2(\text{NCS})_2(\text{CO})_2(\mu-\text{dppm})_2 \) with carbon monoxide will be discussed. The most notable feature of many of these A-frame complexes is that, unlike their halide and sulphur bridged analogues, the bridging ligand was involved where reaction occurred.

3.2. Results and Discussion

3.2.1. Reactions with Carbon Monoxide

Carbon monoxide had no effect upon the A-frame complexes \( \text{Rh}_2(\mu-\text{OH}, \text{Cl})(\text{CO})_2(\mu-\text{dppm})_2 \cdot \text{H}_2\text{O} \) and \( \text{[Rh}_2(\mu-\text{OR})(\text{CO})_2(\mu-\text{dppm})_2 \text{ClO}_4 \) \( (R = \text{H}, \text{CH}_3, \text{C}_2\text{H}_5) \) at one atmosphere
pressure. The situation was somewhat different, however, when these complexes were subjected to carbon monoxide under pressure. \( \text{Rh}_2(\mu-\text{OH.Cl})(\text{CO})_2(\mu-\text{dppm})_2\cdot \text{H}_2\text{O} \) when subjected to carbon monoxide under pressure (30 psi) for 2 h in dichloromethane, gave a red-brown solution, the addition of diethyl ether to which slowly precipitated an orange solid. The orange solid was identified as trans-\( \text{Rh}_2\text{Cl}_2(\text{CO})_2(\mu-\text{dppm})_2 \) \((\nu(\text{CO}) = 1974(\text{vs}), 1937(\text{sh})) \) by comparison of its IR spectrum with that of an authentic sample. This behaviour indicated that the initial product of this reaction was not trans-\( \text{Rh}_2\text{Cl}_2(\text{CO})_2(\mu-\text{dppm})_2 \), since this complex is known to be very insoluble in most commonly used organic solvents including dichloromethane. A plausible formulation for one of the initial products in this reaction is \( [\text{Rh}_2(\mu-\text{Cl})-(\mu-\text{CO})(\text{CO})_2(\mu-\text{dppm})_2] \cdot \text{Cl} \), since this compound is known to lose carbon monoxide in solution under a dinitrogen purge as well as in the solid state to give trans-\( \text{Rh}_2\text{Cl}_2(\text{CO})_2(\mu-\text{dppm})_2 \). The solution IR spectrum of the red-brown solution obtained in the reaction of \( \text{Rh}_2(\mu-\text{OH.Cl})(\text{CO})_2(\mu-\text{dppm})_2\cdot \text{H}_2\text{O} \) with carbon monoxide under pressure was recorded after a period of 2 h. The presence of IR bands at 1992(\text{vs}) and 1873(\text{m}) cm\(^{-1}\) supported the formation of \( [\text{Rh}_2(\mu-\text{Cl})(\mu-\text{CO})(\text{CO})_2(\mu-\text{dppm})_2] \cdot \text{Cl} \). Attempts to isolate and identify other product(s) of this reaction were totally unsuccessful. The analogous iridium dimer, \( \text{Ir}_2(\mu-\text{OH.Cl})-(\text{CO})_2(\mu-\text{dppm})_2 \), reacts with carbon monoxide at one
atmosphere, with the oxidation of carbon monoxide to carbon dioxide. This oxidation process probably arises from an intra-molecular group transfer of hydroxide ion to carbon monoxide to generate a metallocarboxylate \((\text{HOCO}^-)\) species which then eliminates carbon dioxide to generate a hydride complex similar to that observed for \([\text{PtCl}(\text{CO})_2]^+\) (84) \((L = \text{PET}_3)\) as shown in equation 18. A similar process could be envisaged to take place with the rhodium analogue with a stoichiometry tentatively given by the equation 23, although it must be emphasized that no effort was made to detect any gaseous by-products. The possible steps involved in this reaction are summarized in equations 19 to 22.

\[
\begin{align*}
2 \text{Rh}_2(\mu-\text{OH.CI})(\text{CO})_2(\mu-\text{dppm})_2 + 2 \text{CO} & \rightarrow 2 \text{Rh}_2(\text{CO})_2(\mu-\text{dppm})_2 + 2 \text{CO}_2 + 2 \text{HCl} \quad (19) \\
2 \text{Rh}_2(\text{CO})_2(\mu-\text{dppm})_2 + 2 \text{CO} & \rightarrow 2 \text{Rh}_2(\mu-\text{CO})(\text{CO})_2(\mu-\text{dppm})_2 \quad (20) \\
\text{Rh}_2(\mu-\text{CO})(\text{CO})_2(\mu-\text{dppm})_2 + \text{HCl} & \rightarrow [\text{Rh}_2(\mu-\text{H})(\mu-\text{CO})(\text{CO})_2(\mu-\text{dppm})_2]\text{Cl} \quad (21)
\end{align*}
\]
The first step of the proposed scheme (equation 19) involves oxidation of carbon monoxide to carbon dioxide with the formation of the Rh(0) dimer, \( \text{Rh}_2(\text{CO})_2(\text{µ-dppm})_2 \). This complex would then add carbon monoxide across the metal-metal bond to give \( \text{Rh}_2(\text{µ-CO})(\text{CO})_2(\text{µ-dppm})_2 \) and also subsequently react with one mole of hydrochloric acid to give \([\text{Rh}_2(\mu-\text{H})(\mu-\text{Cl})(\text{µ-CO})(\text{CO})_2(\text{µ-dppm})_2]\text{Cl}\). This intermediate would then react with a further mole of hydrochloric acid to give \([\text{Rh}_2(\mu-\text{Cl})(\mu-\text{CO})(\text{CO})_2(\text{µ-dppm})_2]\text{Cl} + 2 \text{CO}_2 + \text{H}_2 \) (equation 23).

The reaction of the complexes, \([\text{Rh}_2(\mu-\text{OR})(\text{CO})_2(\text{µ-dppm})_2]\text{ClO}_4 \) \((\text{R} = \text{H}, \text{CH}_3 \text{ and } \text{C}_2\text{H}_5)\) with carbon monoxide pressure also involved the bridgehead ligands, but instead gave an unsaturated trinuclear rhodium cluster, \([\text{Rh}_3(\mu-\text{CO})(\text{CO})_3(\mu-\text{dppm})_2]\text{ClO}_4 \cdot \text{CH}_2\text{Cl}_2 \) whose synthesis, structure and reactivity will be discussed in Chapter 4.

The reaction of \([\text{Rh}_2(\mu-X)(\text{CO})_2(\text{µ-dppm})_2]\text{ClO}_4 \) \((X = \text{Br, I})\) with carbon monoxide gave, as expected, \([\text{Rh}_2(\mu-X)(\mu-\text{CO})(\text{CO})_2(\text{µ-dppm})_2]\text{ClO}_4 \) \((X = \text{Br, I})\), this behaviour being similar
to that of the chloro analogue. These products were identified by both IR and $^{31}$P{H} NMR spectroscopy (table 3.1 and 3.2). The IR spectrum of Rh$_2$(μ-Br)(μ-CO)(CO)$_2$(μ-dppm)$_2$ClO$_4$ both in the solid state and in solution showed the presence of two terminal carbonyl groups and one bridging carbonyl group, and the $^{31}$P{H} spectrum established an equivalent environment for all four phosphorus atoms. Similar spectroscopic data were observed for [Rh$_2$(μ-I)(μ-CO)(CO)$_2$-(μ-dppm)$_2$]ClO$_4$ except that two bridging carbonyl bands were observed in the solid state IR spectrum. This ostensibly arises from some solid state effect since only one band was observed in solution. These complexes lost carbon monoxide neither in the solid state nor in solution even after a period of one week. While this work was in progress, the preparation of [Rh$_2$(μ-Br)(CO)$_2$(μ-dppm)$_2$]$^{+}$ as their tetraphenylborate salts was reported by Sanger by an independent method. He observed, however, that the bridging carbonyl ligand of Rh$_2$(μ-Br)(μ-CO)(CO)$_2$(μ-dppm)$_2$BPh$_4$ could be removed by bubbling nitrogen through a dichloromethane solution of the complex over a period of several days.

With the exception of [Rh$_2$(μ-NCO)(CO)$_2$(μ-dppm)$_2$]ClO$_4$ the pseudohalide bridged A-frame complexes [Rh$_2$(μ-X)(CO)$_2$-(μ-dppm)$_2$]ClO$_4$ (X = NCS, N$_3$) reacted with carbon monoxide. These reactions, however, did not lead to simple bridging carbonyl adducts. [Rh$_2$(μ-N$_3$)(CO)$_2$(μ-dppm)$_2$]ClO$_4$, in a slow
reaction with carbon monoxide over a period of 72 h at one atmosphere or 24 h at 40 psi gave \([\text{Rh}_2(\mu-\text{NCO})(\text{CO})_2]^{-(\mu-\text{dppm})}_2\text{ClO}_4\) identified by comparison of its spectrum with that of an authentic sample. This reaction could be easily monitored by solution IR spectroscopy by the disappearance of \(v_{\text{as}}(\text{N}_3)\) at 2086 cm\(^{-1}\) and concomitant growth of \(v_{\text{as}}(\text{NCO})\) at 2198 cm\(^{-1}\) in dichloromethane solution. The conversion of terminal azides to a cyanate ligand with carbon monoxide is not uncommon but would appear to be less so when the azide group acts as a bridging ligand.\(^{35,168}\) Conversion of terminal azides to cyanate ligands is exemplified by the reactions given in equations 24 to 26. Transformation of a bridging azide to a bridging cyanate group has been observed in \([\text{Pd}(\text{N}_3)_2\text{L}]_2\) (\(\text{L} = \text{PPh}_3, \text{AsPh}_3\)) (equation 27).

\[
\text{M}(\text{N}_3)_2(\text{PPh}_3)_2 + \text{CO} \rightarrow \text{M}(\text{NCO})_2(\text{PPh}_3)_2
\]  
\(\text{M} = \text{Pd}, \text{Pt}\)  
\(\text{RhN}_3(\text{PPh}_3)_2 + \text{CO} \rightarrow \text{Rh}(\text{NCO})(\text{PPh}_3)_2\)  
\(\text{IrN}_3(\text{CO})(\text{PPh}_3)_2 + \text{CO} \rightarrow \text{Ir}(\text{NCO})(\text{CO})(\text{PPh}_3)_2\)  

\[
\text{L}\underset{\text{Pd}}{\text{N}_3}\text{Pd}\underset{\text{L}}{\text{N}_3} + \text{CO} \rightarrow \text{L}\underset{\text{Pd}}{\text{Pd}}\underset{\text{NCO}}{\text{N}_3}\text{N}_3\text{L} + \text{L}\underset{\text{Pd}}{\text{N}_3}\text{Pd}\underset{\text{L}}{\text{NCO}}\text{N}_3\text{L}  
\]  

\(\text{L} = \text{PPh}_3, \text{AsPh}_3\)
Prior to this work, the only other rhodium-dppm azide complex to be reported was prepared by Sanger from the reaction of Rh$_2$Cl$_2$(COD)$_2$, excess sodium azide and dppm in the presence of one atmosphere of carbon monoxide. The product obtained from the reaction was tentatively identified as Rh$_2$(μ-N$_3$)Cl(CO)$_2$(μ-dppm)$_2$ (85) (ν$_{as}$(N$_3$) = 2236; ν(CO) = 2080, 1968 cm$^{-1}$). The results obtained in this laboratory suggested that this product can probably best be regarded as a mixture of products containing bridging azide and cyanate ligands. Since this reaction was carried out in an atmosphere of carbon monoxide, the IR bands reported at 2236 and 2080 cm$^{-1}$ are probably better attributed to ν$_{as}$(NCO) and ν$_{as}$(N$_3$) rather than ν$_{as}$(N$_3$) and ν(CO) as proposed.

The reaction of [Rh$_2$(SCN)(CO)$_2$(μ-dppm)$_2$]ClO$_4$ with carbon monoxide was found to be very complex. Thus, when carbon monoxide was bubbled through a dichloromethane solution of [Rh$_2$(SCN)(CO)$_2$(μ-dppm)$_2$]ClO$_4$, a rapid colour.
change from orange to brown was observed. A greenish-brown product was isolated by the slow diffusion of diethyl ether into this brown solution. An IR spectrum of this greenish-brown product in the solid state showed bands at 2118(w), 1996(s), 1881(mw), 1815(m) (2121(w), 2024(s), 1997(vs), 1892(mw), 1818(m) in dichloromethane). The $^{31}$P{H} spectrum of this green product showed a complex second order multiplet centred at 21.35 ppm indicating that this product is in fact asymmetric. To date, however, the characterization has been unsuccessful.

In contrast, however, the reaction of the N-bound isomer $[\text{Rh}_2(\mu-\text{NCS})(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4$ with carbon monoxide proceeded smoothly to give a well-characterized product. When carbon monoxide was slowly bubbled through a dichloromethane solution of $[\text{Rh}_2(\mu-\text{NCS})(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4$, the colour progressively changed from yellow to red-brown and finally to red-orange over a period of 10 min. The addition of diethyl ether resulted in the deposition of an orange crystalline solid, whose structural formula has been established as $[\text{Rh}_2(\mu-\text{CN})(\mu-\text{CO})(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4\cdot\text{CH}_2\text{Cl}_2$ (86) from elemental analysis, IR, $^1$H, $^{13}$C{H}, $^{31}$P{H} NMR spectroscopy and X-ray crystallography. 169

An X-ray structure determination of this complex was performed by Prof. T.S. Cameron. The equatorial plane of the cation is depicted in figure 3.1 with some relevant bond
distances. Differentiation between the bridging cyano group and the bridging carbonyl group shown in figure 3.1 has been made by consideration of the spectroscopic data (vide infra) since it proved impossible to distinguish between nitrogen and oxygen on the basis of the crystallographic evidence. The most conspicuous feature of this complex is the unusual, asymmetric or σ-π bridging mode of the cyanide ligand. This is the second example to be structurally characterized in which a cyanide ligand bridges two metals in this fashion. The only other structurally characterized example of an asymmetrically bridging σ-π cyano group was observed by Curtis et al. in (NET₄)[Cp₂Mo₂(u-CN)(CO)₄].¹⁷⁰ Prior to this observation Curtis et al. developed a criterion based on the asymmetry parameter (α), defined as α = (d₂-d₁)/d₁ (d₁ and d₂ are the short and long M-C distances respectively (87)) to distinguish between two electron acceptor semi-bridging carbonyl groups (88) and four electron (σ-π)
It has been shown by these authors, that a plot of the asymmetry parameter \( (\alpha) \) versus the MCO angle \( (\theta) \) for various complexes with semi-bridging carbonyl groups gives rise to two distinct types of behaviour. For two electron acceptor semi-bridging carbonyl groups, the asymmetry parameter was found to decrease with a decrease in \( \theta \), whereas for the \( \sigma-\pi \) bridging mode, \( \theta \) was found to be almost invariant with the asymmetry parameter. At the time Curtis reported the structure of \( \text{NET}_4[\text{Cp}_2\text{Mo}_2(\mu-\text{CN})(\text{CO})_4] \), he applied this criterion successfully to determine the bridging mode of the cyanide group. Applying this criterion to the present complex,

\[
[\text{Rh}_2(\mu-\text{CN})(\mu-\text{CO})(\text{CO})_2(\mu-dppm)_2]\text{ClO}_4\cdot\text{CH}_2\text{Cl}_2,
\]
Rh(2)-C(6)-N bond angle of 177(1)° and the asymmetry parameter of 0.12 clearly places the bridging cyanide in the domain established for the σ-π bridging mode. In contrast, the bond angle, Rh(1)-C(5)-O(3) = 142(1)° and α = 0.05 for the bridging carbonyl group, places it on the published curve for simple two electron donor bridging carbonyl ligands.

The rhodium-rhodium distance of 2.816(2) Å in this complex indicates the presence of a rhodium-rhodium single bond and falls in the range (2.8415(7)-2.7838(8)) Å found in other complexes with rhodium-rhodium single bonds. The presence of a metal-metal bond is also in agreement with conventional electron counting techniques when considering the cyanide as a three electron donor. Excluding the metal-metal bond, the geometry around the Rh(1) centre can be best described as a distorted trigonal bipyramid whereas the Rh(2) centre can probably be described as a distorted square pyramid (Appendix II, Table II.3). The approximate square basal plane consist of the two trans dppm phosphorus atoms, a terminal carbonyl group and the cyanide group. The bridging carbonyl group is the apical ligand. The coordination geometries of the metal centres in this complex is in contrast to the coordination geometry of the well-characterized doubly bridged A-frame complex [Rh₂(μ-Cl)₂(μ-CO)(CO)₂(μ-dppm)₂]ClO₄ in which both metals are described
Figure 3.1. The Equatorial Plane of the Cation

$[\text{Rh}_2(\mu-\text{CN})(\mu-\text{CO})_2(\mu-\text{dppm})_2]^+$

Esd's of bond lengths are indicated by subscripts.
as having distorted trigonal bipyramidal geometry. Also, structurally characterized A-frame complexes with carbon monoxide in the endo pocket are known where both metal centres exhibit square pyramidal geometry. These include \([\text{Rh}_2(\mu-\text{H})(\mu-\text{CO})(\mu-\text{dppm})_2\text{CH}_3\text{SO}_3]^{46}\) and \([\text{Ir}_2(\mu-\text{S})(\mu-\text{CO})-(\mu-\text{dppm})_2]\).^31 Hence, this appears to be the first example of a rhodium-dppm complex to possess two different geometries at the metal centres.

The Rh-C distances (1.86(1), 1.88(2) Å) of the terminal carbonyl groups are not unusual and compare favourably with those observed for similar complexes. \(^30,133\) The terminal carbonyl group attached to the Rh(1) centre is almost colinear (\(<\text{Rh}(2)-\text{Rh}(1)-\text{C} = 175.9(5)^\circ>\) with the rhodium-rhodium single bond and only slightly bent towards the bridging carbonyl group whereas the terminal carbonyl group associated with the Rh(2) centre is significantly bent towards the bridging carbonyl group (\(\text{Rh}(1)-\text{Rh}(2)-\text{C}(4) = 147.8(5)^\circ\)). The Rh-C distances (2.16(2) and 2.06(1) Å) of the bridging carbonyl group are comparable to the values of 2.15(2) and 2.13(2) Å and 2.104(7) and 2.034(7) Å observed in \([\text{Rh}_2(\mu-\text{Cl})(\mu-\text{CO})(\mu-\text{dppm})_2\text{BPh}_4]\) and \([\text{Rh}_2(\mu-\text{H})(\mu-\text{CO})-(\mu-\text{dppm})_2]\text{CH}_3\text{SO}_3\) respectively. The bridging carbonyl group is bonded to the rhodium centres in an asymmetric fashion and forms Rh-C-O angles 133.8(1)^\circ and 142(1)^\circ. This observation is in agreement with other bridging.
carbonyls wherein the shorter M-C bond (M = metal) forms a more linear MCO angle than the other. As observed in other A-frames and doubly bridged A-frame complexes, the methylenes of the dppm ligands are cis and bent towards the bridging cyanide group (See figure II.1 in Appendix II).

The IR spectrum of [Rh₂(μ-CN)(μ-CO)(CO)_2(μ-dppm)_2] ClO₄.CH₂Cl₂ established the presence of the two terminal carbonyl groups and the bridging carbonyl group. In the solid state, terminal carbonyl absorptions appeared at 2012(m) and 1984(vs) and the bridging carbonyls at 1884(m). In dichloromethane these appeared at 2019(sh), 2000(vs) and 1893(m). No band, however, could be located in the IR spectrum that could be attributed to a bridging cyanide. Hence, the complex was labelled with 13-carbon monoxide (¹³CO, 90%) in order to verify whether or not the cyanide band was hidden under the terminal carbonyl band envelope. Labelling experiments were carried out by dissolving 20 mg of the complex in 5 mL of dichloromethane and stirring under 250 mm Hg of labelled carbon monoxide for 10 min. IR spectroscopy revealed that both terminal and bridging carbonyl groups were completely exchanged with the appearance of carbonyl absorptions at 1978(sh) and 1851(m) in dichloromethane. The most interesting feature of the spectrum was the appearance of a weak band at 2044 cm⁻¹, that could be ascribed to ν(CN). This value is low by comparison with the
range (2250–2092 cm\(^{-1}\)) normally associated with bridging cyanide groups, presumably as a consequence of its unusual bridging mode. A similarly low value (\(\nu(CO) = 1645\) cm\(^{-1}\)) has also been observed for the \(\sigma-\pi\) bridging carbonyl group in Mn\(_2\)(μ-CO)(CO)\(_4\)(μ-dppm)\(_2\).

Monitoring the reaction of [Rh\(_2\)(μ-NCS)(CO)\(_2\)(μ-dppm)\(_2\)]ClO\(_4\) with the slow addition of carbon monoxide using solution IR spectroscopy revealed the transitory existence of an intermediate (or intermediates) by the appearance of new bands at 2120 (w), 2030 (m) and 1835 (w) cm\(^{-1}\), which disappeared upon completion of the reaction. The formation of an intermediate(s) was also evident from the colour change from yellow to red-brown before the final colour of red-orange was visible. The weak band at 2120 (w) may possibly be attributed to a terminal cyanide ligand by comparison with those observed for Rh\(_2\)(CO)\(_4\)(CN)\(_2\)(μ-dppm)\(_2\). The bands at 2030 (m) and 1835 (w) may be attributed to terminal carbonyl and bridging carbonyl groups. A tentative structure for the intermediate could be [Rh\(_2\)(μ-CO)(CO)(CN)(μ-dppm)\(_2\)]ClO\(_4\) (90) which may then further react with carbon monoxide to give [Rh\(_2\)(μ-CN)(μ-CO)(CO)\(_2\)(μ-dppm)(μ-CN)ClO\(_4\) .CH\(_2\)Cl\(_2\). Recording the \(^{31}\)P\(^{1}\)H NMR spectrum of [Rh\(_2\)(μ-NCS)(CO)\(_2\)(μ-dppm)\(_2\)]ClO\(_4\) during the slow addition of carbon monoxide would be informative with regard to the nature of the intermediate formed during the course of this reaction. Such
studies, however, have yet to be performed and would be a suitable subject for future work. Attempts to prepare the complex, \([\text{Rh}_2(\mu\text{-CO})(\text{CO})(\text{CN})(\mu\text{-dppm})_2]\text{ClO}_4\) have not been successful.

Variable temperature NMR (\[^1\text{H}, ^{13}\text{C}\{^1\text{H}\} \text{ and } ^{31}\text{P}\{^1\text{H}\}\)} spectroscopy established that \([\text{Rh}_2(\mu\text{-CN})(\mu\text{-CO})(\text{CO})_2(\mu\text{-dppm})_2]\text{ClO}_4\cdot\text{CH}_2\text{Cl}_2\) is a fluxional molecule with at least two different fluxional processes taking place. Recording of the \(^{13}\text{C}\{^1\text{H}\}\)} NMR spectrum of a 13-carbon monoxide enriched sample (ca. 40%) at 22 °C showed two broad unresolved peaks in the approximate ratio of 1:2 at 203.4 ppm and 189.2 ppm respectively. On cooling down to -35 °C, however, these peaks sharpened to give a doublet of multiplets for the terminal carbonyls (188.6 ppm, \(^1J_{\text{Rh-C}_t} = 72.8\) Hz) and for the bridging carbonyl a triplet of quintets (203.4 ppm, \(^1J_{\text{Rh-C}_b} = 36.2\) Hz, \(^2J_{\text{C}_t-p} = 4.7\) Hz). As a result of incomplete exchange with 13-labelled carbon
monoxide in this sample, no coupling due to $^{13}C_t - ^{13}C_b$ was observed. When an 80% enriched sample was used, however, this coupling was observed and the bridging carbonyl resonance appeared as an overlapping triplet of triplet of quintets with $^{2}J_{C_b-C_t} = 9.5$ Hz (av.) and $^{2}J_{P-C_b} = 5.2$ Hz (av.). Figure 3.2 shows the $^{13}C(^{1}H)$ NMR spectrum of $[\text{Rh}_2(\mu-CN)(\mu-^{13}CO)(^{13}CO)(\mu-dppm)_2]^2\text{ClO}_4\cdot\text{CH}_2\text{Cl}_2$ (80% enriched) at 22 °C and -35 °C. The $^{13}C$ chemical shifts and coupling constants obtained for this complex agree reasonably well with those obtained for $[\text{Rh}_2(\mu-\text{Cl})(\mu-\text{CO})(\text{CO})_2(\mu-dppm)_2]^2\text{BPh}_4$. This molecule also exhibited a triplet of triplet of quintets from the bridging carbonyl (203.9 ppm, $^{1}J_{\text{Rh-C_b}} = 41.0$ Hz, $^{2}J_{P-C_b} = 6.8$ Hz, $^{2}J_{C_t-C_b} = 13.7$ Hz) and a doublet of multiplets for the terminal carbonyls (188.6 ppm, $^{1}J_{\text{Rh-C_t}} = 85.0$ Hz) at -35 °C, all of which collapsed to a singlet at 29.5 °C (coalescence temperature, +5 °C). This behaviour has been attributed to the rapid intermolecular exchange of both terminal and bridging carbonyl groups.

At 22 °C, the $^{1}H$ NMR spectrum (360 MHz) of $[\text{Rh}_2(\mu-CN)(\mu-\text{CO})(\text{CO})_2(\mu-dppm)_2]^2\text{ClO}_4\cdot\text{CH}_2\text{Cl}_2$ showed only a broad, featureless and barely resolved doublet centred at
Figure 3.2. $^{13}\text{C}^{1}\text{H}$ NMR Spectrum of $[\text{Rh}_2(\mu-\text{CN})(\mu-^{13}\text{CO})-(^{13}\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4\cdot\text{CH}_2\text{Cl}_2$ (ca. 80% enriched). (a) at 22 °C (b) at -35 °C (c) peaks expanded at -35 °C
Figure 3.3. The Methylene Region of NMR Spectrum (360 MHz) of $[\text{Rh}_2(\mu-\text{CN})(\mu-\text{CO})(\text{CO})_2(\mu-\text{dppm})_2]^{-}\text{ClO}_4\cdot\text{CH}_2\text{Cl}_2$  
(a) at 22°C  (b) at -35°C  
$X = \text{Impurity (diethyl ether)}$
3.72 ppm for the dppm methylene protons which on cooling to -35 °C, yielded two well-separated multiplets at 3.77 ppm and 3.56 ppm (figure 3.3). As observed for the pseudohalide bridged complexes, the separation between the two multiplet was relatively small by comparison to other A-frames (table 2.2).

The coalescence temperatures for both the H and $^{13}$C NMR spectra of $[\text{Rh}_2(\mu-CN)(\mu-CO)(\text{CO})_2(\mu-dppm)_2\text{ClO}_4\cdot\text{CH}_2\text{Cl}_2]$ have not been obtained. Assuming, however, these temperatures to be the same which appears reasonable on the basis of the observed peaks, both $^1$H and $^{13}$C($^1$H) NMR spectra can be explained by invoking the same fluxional process. This may involve the "walking" of the carbonyl and cyanide groups around the equatorial plane of the molecule via a series of terminal to bridging rearrangements (figure 3.4), similar to that observed for many polynuclear carbonyl complexes such as $M_3(\text{CO})_{12}$ ($M = \text{Ru, Os}$). The motion of the carbonyl groups and the cyanide in the equatorial plane at room temperature will force the dppm methylene groups to achieve chemical equivalence as the cyanide and bridging carbonyl groups interchange bridging positions. The broad, featureless resonance for the methylene groups arises as a result of the process being close to coalescence. On cooling down, however, the "walking" motion is inhibited and hence the methylene protons appear as a normal
Figure 3.4. "Walking" of Cyanide and Carbonyl-Ligands in the Equatorial Plane of the Cation $\left[\text{Rh}_2(\mu-CN)(\mu-CO)(CO)_2(\mu-dppm)_2\right]^+$. 
AB quartet with superimposed rhodium and phosphorus coupling.

The $^{31}$P{\textsuperscript{1}H} spectrum of $[\text{Rh}_2(\mu\text{-CN})(\mu\text{-CO})(\text{CO})_2(\mu\text{-dppm})_2]\text{ClO}_4\cdot\text{CH}_2\text{Cl}_2$ also reflected the fluxional behaviour. At room temperature (figure 3.5(a)), the spectrum consisted of a broad, unresolved second order multiplet which at $-35$ °C (figure 3.5(b)) showed a symmetrical well resolved AA'A"A" XX' pattern, characteristic of a typical A-frame complex with a metal-metal bond. The chemical shift (30.36 ppm) and the coupling constant ($|^{1}J_{\text{Rh-P}} + ^{X}J_{\text{Rh-P}}| = 97.1$ Hz) obtained were also in good agreement with other doubly bridging A-frames with metal-metal bonds. For example, $[\text{Rh}_2(\mu\text{-Cl})(\mu\text{-CO})(\text{CO})_2(\mu\text{-dppm})_2]\text{BPh}_4$ showed a $^{31}$P chemical shift of 26.0 ppm and $|^{1}J_{\text{Rh}} + ^{X}J_{\text{Rh-P}}| = 94.2$ Hz. 75 These data indicate that the solid state structure persists in solution. Observation of a symmetrical $^{31}$P pattern, however, must mean that the cyanide flips from one metal to another in a "wind shield wiper" type motion (figure 3.6) similar to that seen in $\text{NET}_4[\text{Mo}_2(\mu\text{-CN})(\text{CO})_4]$. Although it was possible to freeze this motion of the cyanide in $\text{NET}_4[\text{Mo}_2(\mu\text{-CN})(\text{CO})_4]$ at $-60$ °C, the same was not observed for $[\text{Rh}_2(\mu\text{-CN})(\mu\text{-CO})(\text{CO})_2(\mu\text{-dppm})_2]\text{ClO}_4\cdot\text{CH}_2\text{Cl}_2$ even at $-80$ °C. A similar "wind shield wiper motion" was observed in the $\sigma$-acylidylic complex $[\text{Rh}_2(\mu\text{-C}_2\text{Bu})(\text{CO})_2(\mu\text{-dppm})_2]^{-}\text{ClO}_4$ which also remained fast at $-80$ °C (Chapter 6).
Figure 3.5. $^{31}P^{1}H$ Spectrum of $[\text{Rh}_2(\mu-\text{CN})(\mu-\text{CO})(\text{CO})_2]^{2-}$

(a) at 22°C (b) at -35°C
Figure 3.6. "Wind Shield Wiper" Motion of the Cyanide Ligand

The reaction of \( [\text{Rh}_2(\mu-\text{NCS})(\text{CO})_2(\mu-\text{dppm})]^{2+} \) with carbon monoxide takes place with loss of sulphur. There was no evidence, however, for the deposition of elemental sulphur during its formation. Hence, it is tempting to assume that sulphur has been removed as carbonyl sulphide (COS). An example of the reverse of such a reaction is given by the decomposition of carbonyl sulphide in the presence of \( \text{Pt}(\text{PPh}_3)_3 \) to give a product containing both carbonyl and sulphide ligands (equation 28). 174

\[
2 \text{Pt}(\text{PPh}_3)_3 + \text{COS} \rightarrow \text{OC} \quad \text{Pt} \quad \text{Pt} \quad \text{PPh}_3
\]

Hence, it does not seem unreasonable to assume that the reverse can occur.
Carbon monoxide had no effect on Rh\(_2\)(NCS)\(_2\)(CO)\(_2\)\(_{\mu\text{-dppm}}\) either in dichloromethane or in methanol suspension when at one atmosphere pressure. When subjected to carbon monoxide, however, under pressure (25 psi) for 15 h in dichloromethane, the suspension gradually dissolved to give a bright red solution from which red crystals were obtained upon the addition of diethyl ether. Both qualitative and quantitative analyses indicated the presence of sulphur and nitrogen, and the complex analyzed approximately for Rh\(_2\)(S)(CO)\(_2\)(CN)\(_2\)\(_{\mu\text{-dppm}}\)\(_2\)\(_{1.5\text{CH}_2\text{Cl}_2}\). The IR spectrum of this red complex in the solid state showed a single band at 1996 (vs) cm\(^{-1}\) (2001 (vs) cm\(^{-1}\) in dichloromethane) in the terminal carbonyl region as well as a bridging carbonyl absorption at 1826 (vs) cm\(^{-1}\) (1840 (s) cm\(^{-1}\) in dichloromethane). Furthermore, two well-separated bands were observed at 2141 (w) and 2125 (mw) cm\(^{-1}\) (2236 (w) and 2224 (mw) cm\(^{-1}\) in dichloromethane) which could be attributed to two terminal cyanide ligands present in the molecule. These positions compare favourably with terminal cyanide groups associated with other rhodium-dppm complexes such as Rh\(_2\)(CN)\(_2\)(CO)\(_2\)\(_{\mu\text{-dppm}}\)\(_2\) and Rh\(_2\)(CN)\(_2\)(CO)\(_4\)\(_{\mu\text{-dppm}}\)\(_2\) \(\text{(vide supra)}\). The \(^{1}\text{H}\) NMR spectrum of the red complex in dichloromethane showed a complex multiplet having a mirror symmetry at 20.07 ppm which appears to be consistent with an AA'BB'XY spin system. This indicated that the two rhodium centres are non-equivalent. The \(^{1}\text{H}\) NMR spectrum
(dichloromethane-d₂) in addition to phenyl peaks at 7.71 ppm, showed the methylene resonances at 5.10 and 2.70 ppm and the solvated dichloromethane at 5.32 ppm. The degree of dichloromethane solvation could not be determined as a result of the poor solubility of this complex in other solvents. As a result, the amount of dichloromethane present has been postulated solely on the analytical data obtained. Conductivity measurements in acetone indicated that this complex behaved as a non-electrolyte. Based on the foregoing data, a structure for this red complex, \( \text{Rh}_2(\mu-S)(\mu-CO)(CO)(CN)_2(\mu-dppm)_2 \cdot 1.5 \text{CH}_2\text{Cl}_2 \) (91), has been assigned tentatively. This is a 34 electron complex with five and six coordinate rhodium centres excluding the rhodium-rhodium single bond. An attempt was made to verify

\[
\text{OC} \quad \text{S} \quad \text{Rh} \quad \text{CN} \quad \text{Rh} \quad \text{CO}
\]

the ratio of bridging to terminal carbonyl groups by recording the \( ^{13}\text{C}^{1}\text{H} \) NMR spectrum. This was unsuccessful, however, since only the terminal carbonyl group could be exchanged with labelled carbon monoxide. The IR spectrum.
(dichloromethane) of a 13-carbon monoxide enriched sample showed the new terminal carbonyl band at 1962 cm\(^{-1}\) whereas the bridging position remained unchanged even after stirring \(^{13}\text{CO}, 90\%, 250 \text{ mm Hg}\) for 3 h. The \(^{13}\text{C}{{^1}\text{H}}\) NMR spectrum of this enriched sample showed a doublet of triplets at 189.34 ppm with \(1J_{\text{Rh-C}_1} = 69.01\) Hz and \(2J_{P-C}_1 = 13.8\) Hz. The chemical shift and coupling constants are in good agreement with those obtained for other rhodium-dppm complexes. Final confirmation of the structure of the red complex awaits an X-ray structure determination for which suitable crystals appear to have been obtained.

3.2.2. Reaction with Sulphur Dioxide

Unlike with carbon monoxide, the hydroxide and alkoxide complexes all reacted with sulphur dioxide at one atmosphere pressure. When sulphur dioxide was bubbled through a dichloromethane solution of \(\text{Rh}_2(\mu-\text{OH,Cl})(CO)_2(\mu-\text{dppm})_2\cdot\text{H}_2\text{O}\), for example, a dramatic colour change from yellow to magenta resulted. The slow diffusion of diethyl ether into such solutions precipitated a red-brown solid. The solution spectrum of the magenta solution showed terminal carbonyl absorptions at 2016(vs) and 1991(s) cm\(^{-1}\) and in addition to these, the solid-state spectrum showed a number of bands in the 1300-800 cm\(^{-1}\) region at 1231(m), 1189(m), 1064(s) and 855(m) cm\(^{-1}\). These data suggested
that this crude material may contain the cation \([\text{Rh}_2(\mu-\text{Cl})(\mu-\text{SO}_2)(\mu-\text{dppm})_2]^+\) (cf. \([\text{Rh}_2(\mu-\text{Cl})(\mu-\text{SO}_2)(\text{CO})_2(\mu-\text{dppm})_2]B\text{Ph}_4\). \(\nu(\text{CO}) = 2015(\text{s})\), 1985(\text{s, sh}); \(\nu(\text{SO}_2) = 1229(\text{m}), 1070(\text{m})\). The presence of a chloro bridged species was established by recrystallizing the red-brown material from dichloromethane and diethyl ether after purging the solution with dinitrogen. The yellow-orange product obtained showed terminal carbonyl stretches at 2003(\text{s}) and 1992(\text{vs}) in dichloromethane which were identical to those obtained for \([\text{Rh}_2(\mu-\text{Cl})(\text{CO})_2(\mu-\text{dppm})_2]B\text{Ph}_4\) (table 2.1). The solid state spectrum in addition to the terminal carbonyl bands at 1991(\text{s}) and 1972(\text{vs}) \text{cm}^{-1} showed bands at 1231(\text{m}), 1063(\text{m}), and 861(\text{m}) \text{cm}^{-1}. From this, however, nature of the anion associated with either the red-brown or the yellow-orange product was not clear. The most probable choice appeared to be either bisulphite or bisulphate anion with the former being more explicable by a direct combination of hydroxide with sulphur dioxide. The evidence to date, however, suggests that the counterion is, in fact, the bisulphate ion. For example, the extra bands observed in the IR spectrum (1231(\text{m}), 1063(\text{m}), 861(\text{m}) \text{cm}^{-1}) were comparable to those obtained for the free bisulphate ion, which normally exhibits IR maxima between 1180-1160, 1080-1000 and 880-840 \text{cm}^{-1}. The final product \([\text{Rh}_2(\mu-\text{Cl})(\text{CO})_2(\mu-\text{dppm})_2]^+\text{HSO}_4^-\) obtained in the reaction of \([\text{Rh}_2(\mu-\text{OH})(\text{Cl})(\text{CO})_2(\mu-\text{dppm})_2]^+\) with sulphur dioxide could also be prepared by the
reaction of \( \text{Rh}_2(\mu-\text{OH}.\text{Cl})(\text{CO})_2(\mu-\text{dppm})_2 \) with sulphuric acid. A complex with a bridging bisulphate, \([\text{Rh}_2(\mu-\text{HSO}_4)(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4\) was prepared by the reaction of \([\text{Rh}_2(\mu-\text{OH})(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4\) with sulphuric acid. \([\text{Rh}_2(\mu-\text{HSO}_4)(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4\) exhibited terminal carbonyl bands at 1996(s) and 1966(s) cm\(^{-1}\) (2005(s), 1990(vs) cm\(^{-1}\) in dichloromethane) with bands attributable to the bisulphate group being observed at 1269(m) and 935(mw) cm\(^{-1}\). This complex proved very unstable in solution, thereby prohibiting acquisition of \(^{31}\text{P}\) NMR data but the red colour of the product, similar to that seen for carboxylate bridged complexes (Chapter 2), does imply the bidentate bridging mode for the bisulphate ligand.

The formation of the bisulphate ion in the reaction of \( \text{Rh}_2(\mu-\text{OH}.\text{Cl})(\text{CO})_2(\mu-\text{dppm})_2\cdot\text{H}_2\text{O} \) with sulphur dioxide is unusual but not entirely without precedent. Sulphonyl chlorides, \( \text{CH}_3\text{SO}_2\text{Cl} \) are known to react with a variety of \( \text{d}^8 \) osmium complexes gives salts containing sulphonate anions (equation 29).\(^{148}\) This reaction is believed to proceed by

\[
\text{Os(CO)}_2(\text{CNR})(\text{PPh}_3)_2 + \text{CH}_3\text{SO}_2\text{Cl} \rightarrow \text{cis}[\text{OsCl}(\text{CO})_2(\text{CNR})(\text{PPh}_3)_2]\text{CH}_3\text{SO}_3 \quad (29)
\]

a free radical mechanism, with the sulphonate anion being produced via oxidation of the RSQ\(^2\) radical. A radical mechanism seems less likely in the case of...
[\text{Rh}_2(\mu-\text{OH} \cdot \text{Cl}) (\text{CO})_2(\mu-\text{dppm})_2] \cdot \text{H}_2\text{O}

however, since it is conceivable that the dimer itself might function as a catalyst for the oxidation of bisulphite to bisulphate.

Dichloromethane solutions of [\text{Rh}_2(\mu-\text{OR})(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4 \ (R = \text{H, CH}_3, \text{C}_2\text{H}_5)

saturated with sulphur dioxide showed pronounced shifts to higher wavenumbers for the terminal carbonyl frequencies: \(R = \text{H}, \nu(\text{CO}) = 2031(\text{m}), 1993(\text{vs}) \ \text{cm}^{-1};\ R = \text{CH}_3, \nu(\text{CO}) = 2033(\text{m}), 1994(\text{vs}) \ \text{cm}^{-1};\ R = \text{C}_2\text{H}_5, \nu(\text{CO}) = 2033(\text{m}), 1994(\text{s}) \ \text{cm}^{-1}.\) Such values may indicate the formation of bridging sulphur dioxide adducts (cf. [\text{Rh}_2(\mu-X)(\mu-\text{SO}_2)(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4 \ (X = \text{Br, I})

(Table 3.1). The products isolated from these solutions by the addition of diethyl ether, were orange in colour and lost sulphur dioxide in less than 1 h on standing at room temperature or immediately on grinding. Hence no solid

state IR evidence is available for these complexes. Thus the solution IR data indicated that the complexes formed were weak bridging sulphur dioxide adducts. Since all three complexes exhibited similar behaviour with sulphur dioxide, as evident from their solution IR spectra, the \(^{31}\text{P}^{1}\text{H}\) spectrum was recorded only of [\text{Rh}_2(\mu-\text{OC}_2\text{H}_5)(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4

saturated with sulphur dioxide. Surprisingly, the changes observed in the IR spectrum were not reflected in the \(^{31}\text{P}^{1}\text{H}\) NMR spectrum. Thus, the \(^{31}\text{P}^{1}\text{H}\) NMR spectrum exhibited a symmetrical second order pattern at 20.52 ppm,
with \( |^{1}J_{\text{Rh-P}} + xJ_{\text{Rh-P}} | = 126.0 \text{ Hz} \). These values showed only a slight change by comparison to the starting material, 
\([\text{Rh}_{2}(\mu-\text{OC}_{2}H_{5})\text{(CO)}_{2}(\mu-\text{dppm})_{2}]\text{ClO}_{4} \) (20.67 ppm, 
\(|^{1}J_{\text{Rh-P}} + xJ_{\text{Rh-P}} | = 128.2 \text{ Hz} \). This behaviour is in contrast to 
\([\text{Rh}_{2}(\mu-\text{Cl})\text{(CO)}_{2}(\mu-\text{dppm})_{2}]\text{BPh}_{4} \) (16.1 ppm, 
\(|^{1}J_{\text{Rh-P}} + xJ_{\text{Rh-P}} | = 113.3 \text{ Hz} \) ) for example, where significant changes in chemical shift and coupling constant were observed when it formed a genuine sulphur dioxide adduct,

\([\text{Rh}_{2}(\mu-\text{Cl})(\mu-\text{SO}_{2})\text{(CO)}_{2}(\mu-\text{dppm})_{2}]\text{BPh}_{4} \) (24.6 ppm, 
\(|^{1}J_{\text{Rh-P}} + xJ_{\text{Rh-P}} | = 91.3 \text{ Hz} \) ). The \(^{31}\text{P}\{^{1}\text{H}\} \text{NMR data obtained for the reaction between } [\text{Rh}_{2}(\mu-\text{OC}_{2}H_{5})\text{(CO)}_{2}(\mu-\text{dppm})_{2}]\text{ClO}_{4} \) with sulphur dioxide are more in keeping with the formation of a weak Lewis acid-base adduct between sulphur dioxide and the bridging ligand \(\text{(vide infra)}\). As a result, the nature of the products obtained in the reaction of 
\([\text{Rh}_{2}(\mu-\text{OR})\text{(CO)}_{2}(\mu-\text{dppm})_{2}]\text{ClO}_{4} \) (\(R = \text{H, CH}_{3}, \text{C}_{2}\text{H}_{5}\) ) with sulphur dioxide remains unknown.

Another possibility for these sulphur dioxide reactions may be the involvement of the bridging ligand to form 
\([\text{Rh}_{2}(\mu-\text{O}_{2}\text{SOR})\text{(CO)}_{2}(\mu-\text{dppm})_{2}]\text{ClO}_{4} \) (\(R = \text{H, CH}_{3}, \text{C}_{2}\text{H}_{5}\) ). In order to get some further information on this possibility, the \(^{1}\text{H} \text{NMR was recorded for } [\text{Rh}_{2}(\mu-\text{OR})\text{(CO)}_{2}(\mu-\text{dppm})_{2}]\text{ClO}_{4} \) (\(R = \text{H, C}_{2}\text{H}_{5}\) ) before and after saturating with sulphur dioxide. When \(R = \text{H}, \) disappearance of the quintet associated with the hydroxide group was observed. For \(R = \text{C}_{2}\text{H}_{5}\)
triplet signals observed for free ethanol and coordinated ethoxy groups remained, but with new chemical shifts at 0.38 and 0.23 ppm respectively. The quintet, however, due to the hydroxy group of \([\text{Rh}_2(\mu-\text{OH})(\text{CO})_2(\mu\text{-dppm})_2]\text{ClO}_4\) formed by the hydrolysis of \([\text{Rh}_2(\mu-\text{OC}_2\text{H}_5)(\text{CO})_2(\mu\text{-dppm})_2]\text{ClO}_4\) disappeared. The change in chemical shifts could be due to the change in the dielectric constant of the solvent after saturating with sulphur dioxide or due to the formation of a new species. As a result, very little information could be derived regarding the reaction of \([\text{Rh}_2(\mu-\text{OC}_2\text{H}_5)(\text{CO})_2(\mu\text{-dppm})_2]\text{ClO}_4\) and sulphur dioxide. Disappearance of the hydroxide resonance, however, tends to indicate that attack is occurring at the bridgehead ligand in \([\text{Rh}_2(\mu-\text{OH})(\text{CO})_2(\mu\text{-dppm})_2]\text{ClO}_4\). Since all three complexes showed similar solution IR spectra, it would appear that they behave in a similar manner when reacting with sulphur dioxide. Hence, there exists the possibility that sulphur dioxide attacks the bridgehead ligand to form a weak species. This is, however, not the best answer since it is hard to believe that grinding would break down bridging sulphite groups.

The reaction of \([\text{Rh}_2(\mu-X)(\text{CO})_2(\mu\text{-dppm})_2]\text{ClO}_4\) (\(X = I, \text{Br}\)) with sulphur dioxide was similar to that of the chloro analogue, leading to complexes of the type \([\text{Rh}_2(\mu-X)-(\mu-\text{SO}_2)(\text{CO})_2(\mu\text{-dppm})_2]\text{ClO}_4\). These complexes were characterized by the IR spectroscopy which showed two terminal
carbonyl bands and the asymmetric stretch of the bridging sulphur dioxide ligand. The symmetric stretch expected around 1050 cm$^{-1}$ was not observed presumably because of masking by the perchlorate absorption.

When sulphur dioxide was bubbled through a dichloromethane solution of [Rh$_2$(μ-X)(CO)$_2$(μ-dppm)$_2$]ClO$_4$ (X = N$_3$, NCO) the yellow solution turned wine red and deposited red crystalline solids upon the addition of diethyl ether. These solids, when exposed to the atmosphere, lost sulphur dioxide readily (10–15 min) to give back yellow starting material. These complexes, however, were found to be stable at -18 ºC under an atmosphere of SO$_2$ even up to a period of one year. As observed for the alkoxide and hydroxide complexes, sulphur dioxide was lost immediately on grinding and therefore no bands were observed in the solid state IR spectrum that correspond to sulphur dioxide. In order to establish whether these complexes formed genuine sulphur dioxide adducts or weak Lewis acid-base adducts, the solution IR spectra of [Rh$_2$(μ-X)(CO)$_2$(μ-dppm)$_2$]ClO$_4$ (X = N$_3$, NCO) were recorded before and after saturating the solutions with sulphur dioxide. No changes in the ν(CO) frequencies were observed. Similarly, no changes were observed in the $^{31}$P($^1$H) spectra. Despite the lack of spectroscopic evidence, the colour changes observed obviously imply an interaction of some description, either of the Lewis acid-base
or charge transfer type, and it is believed that the site of this interaction is the free end of the pseudohalide ligands. Sulphur dioxide coordinated to pseudohalide ligands in this fashion has been observed in the complexes Pd(PPh$_3$)$_2$X$_2$.SO$_2$ (X = NCO) and Ir(CO)(PPh$_3$)$_2$X.SO$_2$ (X = N$_3$, NCO). Although [Rh$_2$(μ-NCS)(CO)$_2$(μ-dppm)$_2$]ClO$_4$ in dichloromethane formed a red solution with sulphur dioxide, no red complex could be isolated upon the addition of diethyl ether. Instead, a yellow complex precipitated which was identified as the starting material from its IR spectrum. Recording of the IR spectrum in dichloromethane before and after reacting with sulphur dioxide indicated no change in either shape or position of ν(CO) absorption, suggesting that the [Rh$_2$(μ-NCS)(CO)$_2$(μ-dppm)$_2$]ClO$_4$ also forms a weak adduct with sulphur dioxide.

The reaction of [Rh$_2$(SCN)(CO)$_2$(μ-dppm)$_2$]ClO$_4$ with sulphur dioxide was, however, somewhat different. When sulphur dioxide was bubbled through a solution of [Rh$_2$(SCN)-$(CO)_2$(μ-dppm)$_2$]ClO$_4$, a bright red solution was produced. The addition of diethyl ether precipitated a red-orange complex which when recrystallized gave a bright yellow complex. The $^3$P{$^1$H} and $^1$H spectrum of this yellow material was identical to that of [Rh$_2$(μ-NCS)(CO)$_2$(μ-dppm)$_2$]ClO$_4$. Hence, sulphur dioxide caused the isomerization of the tentatively identified [Rh$_2$(SCN)(CO)$_2$(μ-dppm)$_2$]ClO$_4$ to [Rh$_2$(μ-NCS)(CO)$_2$(μ-dppm)$_2$]ClO$_4$. 


### 3.3. Experimental

#### 3.3.1. List of Complexes Synthesized

<table>
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<td>176</td>
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<tr>
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<tr>
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<td>Reaction of Rh$_2$(NCS)$_2$(μ-dppm)$_2$ with carbon monoxide</td>
<td>178</td>
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<td>Reaction of [Rh$_2$(SCN)(CO)$_2$(μ-dppm)$_2$]ClO$_4$ with carbon monoxide</td>
<td>179</td>
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<td>179</td>
</tr>
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</tr>
<tr>
<td>Reaction of [Rh$_2$(μ-OR)(CO)$_2$(μ-dppm)$_2$]ClO$_4$ (R = H, CH$_3$, C$_2$H$_5$) with sulphur dioxide</td>
<td>181</td>
</tr>
<tr>
<td>[Rh$_2$(μ-Br)(μ-SO$_2$)(CO)$_2$(μ-dppm)$_2$]ClO$_4$</td>
<td>181</td>
</tr>
<tr>
<td>[Rh$_2$(μ-I)(μ-SO$_2$)(CO)$_2$(μ-dppm)$_2$]ClO$_4$</td>
<td>182</td>
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<tr>
<td>[Rh$_2$(μ-X·SO$_2$)(CO)$_2$(μ-dppm)$_2$]ClO$_4$ (X = N$_3$, NCO)</td>
<td>182</td>
</tr>
<tr>
<td>Reaction of [Rh$_2$(μ-NCS)(CO)$_2$(μ-dppm)$_2$]ClO$_4$ with sulphur dioxide</td>
<td>183</td>
</tr>
<tr>
<td>Isomerization of [Rh$_2$(SCN)(CO)$_2$(μ-dppm)$_2$]ClO$_4$ to [Rh$_2$(μ-NCS)(CO)$_2$(μ-dppm)$_2$]ClO$_4$</td>
<td>183</td>
</tr>
</tbody>
</table>
3.3.2. Synthetic Procedures

3.3.2(i). Reactions with Carbon Monoxide

\[ \text{Rh}_2(\mu-\text{OH.Cl})(\text{CO})_2(\mu-\text{dppm})_2\text{H}_2\text{O} \] Preparation of \text{trans-Rh}_2\text{Cl}_2(\text{CO})_2(\mu-\text{dppm})_2\text{H}_2\text{O}

\[ \text{Rh}_2(\mu-\text{OH.Cl})(\text{CO})_2(\mu-\text{dppm})_2\text{H}_2\text{O} (0.10 \text{ g}, 0.091 \text{ mmol}) \] was dissolved in 10 mL of dichloromethane and subjected to carbon monoxide under pressure (30 psi) at room temperature. After stirring for 2 h, the reaction vessel was vented and 10 mL of diethyl ether was added to the red-brown solution. An orange solid began to separate from the solution very slowly over a period of 2-3 h. The product was removed by filtration and washed with diethyl ether (0.033 g, 66% based on available chloride).

\[ [\text{Rh}_2(\mu-\text{Br})(\text{CO})_2(\mu-\text{dppm})_2\text{Cl}_2]_4 \] Preparation of \[ [\text{Rh}_2(\mu-\text{Br})(\mu-\text{CO})(\text{CO})_2(\mu-\text{dppm})_2]\text{Cl}_2]_4 \]

Carbon monoxide was bubbled through a solution of \[ [\text{Rh}_2(\mu-\text{Br})(\text{CO})_2(\mu-\text{dppm})_2\text{Cl}_2]_4 (0.10 \text{ g}, 0.083 \text{ mmol}) \] in 10 mL of dichloromethane for 5 min whereupon the orange solution turned yellow. The addition of diethyl ether, while the carbon monoxide flow continued, precipitated a yellow-orange solid. The solid was filtered, washed with diethyl ether and recrystallized from dichloromethane-diethyl ether in an atmosphere of carbon monoxide to give a bright yellow crystalline solid (0.094 g, 92%).
[\textit{Rh}_2(\mu-\textit{I})(\textit{CO})_2(\textit{dppm})_2]\textit{ClO}_4. \text{ Preparation of} \\
[\textit{Rh}_2(\mu-\textit{I})(\mu-\textit{CO})(\textit{CO})_2(\mu-\textit{dppm})_2]\textit{ClO}_4 \\

[\textit{Rh}_2(\mu-\textit{I})(\textit{CO})_2(\textit{dppm})_2]\textit{ClO}_4 \, (0.070 \text{ g}, \, 0.056 \text{ mmol}) \\
was partially dissolved in 5 mL of dichloromethane. Carbon 
monoxide was bubbled through the solution for 5 min. The 
solution became yellow with complete dissolution of the 
solid. Diethyl ether was added to precipitate the product 
as a bright yellow crystalline solid which was filtered, 
washed with diethyl ether and recrystallized from dichloro-
methane-diethyl ether in an atmosphere of carbon monoxide 
(0.056 \text{ g}, 78\%). \\

[\textit{Rh}_2(\mu-\textit{N}_3)(\textit{CO})_2(\textit{dppm})_2]\textit{ClO}_4. \text{ Preparation of} \\
[\textit{Rh}_2(\mu-N\textit{CO})(\textit{CO})_2(\mu-\textit{dppm})_2]\textit{ClO}_4 \\

A solution of [\textit{Rh}_2(\mu-\textit{N}_3)(\textit{CO})_2(\textit{dppm})_2]\textit{ClO}_4 \, (0.10 \text{ g}, 
0.085 \text{ mmol}) in 10 mL of dichloromethane was subjected to 
carbon monoxide pressure (40 psi) for 24 h or one atmosphere 
of carbon monoxide for 72 h. The addition of diethyl ether 
to the resultant yellow-orange solution precipitated bright 
yellow crystals of the product which was filtered, washed 
with diethyl ether and recrystallized from dichloromethane-
diethyl ether (0.075 g, 75\%).
Preparation of \([\text{Rh}_2(\mu-\text{NCS})_2(\mu-\text{dppm})_2]\text{ClO}_4\)

\([\text{Rh}_2(\mu-\text{CN})(\mu-\text{CO})(\mu-\text{dppm})_2] \text{ClO}_4 \cdot \text{CH}_2\text{Cl}_2\)

\([\text{Rh}_2(\mu-\text{NCS})(\mu-\text{CO})_2(\mu-\text{dppm})_2] \text{ClO}_4 \cdot 0.20 \text{ g}, 0.17 \text{ mmol}\)

was dissolved in 10 mL of dichloromethane and carbon monoxide was slowly bubbled through the solution for a period of 10 min. The yellow-orange solution initially turned red-brown and gradually lightened to red-orange. The addition of diethyl ether resulted in the deposition of orange crystals of the complex. The product was removed by filtration and washed with diethyl ether. Recrystallization from dichloromethane-diethyl ether yielded the product as a dichloromethane solvate (0.16 g, 80%).

Analysis Calculated for \(\text{C}_{55}\text{H}_{46}\text{N}_7\text{P}_4\text{Cl}_3\text{Rh}_2\): C, 52.05; H, 3.65; N, 1.11; S, 0.0%. Found: C, 52.84; H, 3.81; N, 1.16; S, <0.2%. \(\lambda_M = 133 \text{ cm}^2 \text{ mol}^{-1} \text{ mol}^{-1}\) (acetone).

Reaction of \(\text{Rh}_2(\text{NCS})_2(\mu-\text{CO})_2(\mu-\text{dppm})_2\) with Carbon Monoxide Under Pressure

\(\text{Rh}_2(\text{NCS})_2(\mu-\text{CO})_2(\mu-\text{dppm})_2\) (0.20 g, 0.18 mmol) was suspended in 20 mL of dichloromethane and subjected to carbon monoxide pressure (25 psi) at room temperature. The solution was stirred for 15 h whereupon the solid dissolved to give a bright red solution. The addition of diethyl ether to this red solution after venting the reaction vessel, precipitated an orange crystalline solid. The product was removed by filtration and recrystallized from
dichloromethane-diethyl ether to give red-orange crystals (0.13 g, 60%). This product has been tentatively identified as Rh$_2$(μ-S)(μ-CO)(CN)$_2$(CO)(μ-dppm)$_2$·1.5 CH$_2$Cl$_2$.

Anal. Calcd for C$_{55.5}$H$_{47}$N$_2$SP$_2$O$_2$Cl$_2$Rh$_2$: C, 53.66; H, 3.78; N, 2.25; S, 2.57%. Found: C, 54.27; H, 3.74; N, 2.28; S, 1.86%. $\Lambda$ = 0 cm$^2$ mol$^{-1}$ l$^{-1}$ (acetone).

Reaction of [Rh$_2$(SCN)(CO)$_2$(μ-dppm)$_2$ClO$_4$] with Carbon Monoxide

[Rh$_2$(SCN)(CO)$_2$(μ-dppm)$_2$ClO$_4$] (90.20 g; 0.17 mmol) was dissolved in 10 mL of dichloromethane. Carbon monoxide was bubbled through the solution for 20 min. The addition of diethyl ether to the brown solution precipitated a greenish-brown solid which was collected by filtration and washed with diethyl ether (0.16 g).

Anal. Found: C, 51.41; H, 4.09; N, 1.76; S, 0.95%.

3.3.2(ii). Reactions with Sulphur Dioxide

Rh$_2$(μ-OH.Cl)(CO)$_2$(μ-dppm)$_2$·H$_2$O. Preparation of

[Rh$_2$(μ-Cl)(CO)$_2$(μ-dppm)$_2$]HSO$_4$·

Sulphur dioxide was slowly bubbled through a solution of Rh$_2$(μ-OH.Cl)(CO)$_2$(μ-dppm)$_2$·H$_2$O (0.12 g; 0.11 mmol) in 10 mL of dichloromethane for 15 min. The solution immediately turned magenta in colour and yielded a red-brown solid upon addition of diethyl ether. The crude material was redissolved in dichloromethane, purged with dinitrogen.
for several minutes. Diethyl ether diffusion to the solution precipitated a yellow-orange solid which was filtered off and washed with diethyl ether (0.07 g, 60%).

Anal. Calcd for C$_{52}$H$_{46}$ClSO$_4$P$_4$Rh$_2$: C, 53.70; H, 3.90; Cl, 3.05; S, 2.76%. Found: C, 54.06; H, 3.90; Cl, 4.72; S, 2.97%. $\lambda_M = 93 \text{ cm}^2 \text{ mol}^{-1} \text{ cm}^{-1}$ (acetone).

Reaction of Rh$_2$(µ-OH.Cl)(CO)$_2$(µ-dppm)$_2$.H$_2$O with Sulphuric Acid

To Rh$_2$(µ-OH.Cl)(CO)$_2$(µ-dppm)$_2$.H$_2$O (0.15 g, 0.14 mmol) dissolved in 10 mL of dichloromethane was added 0.03 mL of concentrated sulphuric acid dissolved in 1 mL of ethanol. After stirring the mixture for 10 min, diethyl ether was added to precipitate the product as a yellow-orange crystalline solid which was recrystallized from dichloromethane-diethyl ether (0.15 g, 92%). IR spectroscopy established the product as being identical to that obtained in the preceding reaction.

$[\text{Rh}_2(\mu-\text{HSO}_4)(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4$

$[\text{Rh}_2(\mu-\text{OC}_2\text{H}_5)(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4$ (0.10 g, 0.085 mmol) was dissolved in 10 mL of dichloromethane to which was added 0.03 mL concentrated sulphuric acid dissolved in 1 mL of ethanol. The addition of diethyl ether precipitated a red-orange crystalline solid which was filtered off and recrystallized from dichloromethane-diethyl
ether in the presence of 1 or 2 drops of concentrated sulphuric acid (0.092 g, 91%). Anal. Calcd for C_{52}H_{44}P_{4}SO_{10}ClRh_{2}: C, 50.90; H, 3.70; P, 10.10; S, 2.61%. Found: C, 51.14; H, 4.09; P, 10.13; S, 3.29%. 

\[ \Lambda_{M} = 118 \text{ cm}^{-2} \text{ mol}^{-1} \text{ (acetone)} \]

Reaction of $[\text{Rh}_2(\mu-\text{OR})(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4$ ($R = \text{H, CH}_3, \text{C}_2\text{H}_5$) with Sulphur Dioxide

Sulphur dioxide was bubbled through a solution of the appropriate complex (0.10 g, ca. 0.085 mmol) in 10 mL of dichloromethane for 10 min. The addition of diethyl ether saturated with sulphur dioxide to the resultant red solutions gave orange products which were collected by filtration and washed with diethyl ether (ca. 0.085 g, 85%). When ground or exposed to the atmosphere for 1 h, loss of sulphur dioxide occurred resulting in regeneration of yellow starting material.

$[\text{Rh}_2(\mu-\text{Br})(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4$. Preparation of $[\text{Rh}_2(\mu-\text{Br})(\mu-\text{SO}_2)(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4$

Sulphur dioxide was bubbled through a solution of $[\text{Rh}_2(\mu-\text{Br})(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4$ (0.10 g, 0.078 mmol) in 10 mL of dichloromethane for a period of 10 min. No colour change was observed. The addition of diethyl ether saturated with sulphur dioxide precipitated an orange, crystalline solid. The product was removed by filtration and
recrystallized from dichloromethane-diethyl ether saturated with sulphur dioxide (0.087 g, 83%).

\[ \text{[Rh}_2(\mu-\text{I})(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4 \]. Preparation of \[ \text{[Rh}_2(\mu-\text{I})(\mu-\text{SO}_2)(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4 \]

\[ \text{[Rh}_2(\mu-\text{I})(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4 \] (0.070 g, 0.056 mmol) was partially dissolved in 5 mL of dichloromethane to give a red-orange solution. Sulphur dioxide was bubbled through the solution for a period of 10 min. The solid completely dissolved to give an orange solution. The addition of diethyl ether saturated with sulphur dioxide gave a yellow-orange crystalline solid which was recrystallized in the presence of sulphur dioxide (0.061 g, 83%).

\[ \text{[Rh}_2(\mu-X)(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4 \] (X = N\textsubscript{3}, NCO). Preparation of \[ \text{[Rh}_2(\mu-X.\text{SO}_2)(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4 \]

A solution of \[ \text{[Rh}_2(\mu-X)(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4 \] (X = N\textsubscript{3}, NCO) (0.10 g, 0.085 mmol) in 10 mL of dichloromethane was treated with sulphur dioxide for 10 min. The solution immediately turned wine red. The addition of diethyl ether, while sulphur dioxide flow was continued, precipitated a bright red crystalline solid (ca. 0.09 g, 90%). The complexes were stable only in an atmosphere of sulphur dioxide and lost sulphur dioxide immediately on grinding or on standing 10-15 min in air.
Bubbling sulphur dioxide through a solution of 
\[ \text{[Rh}_2(\mu\text{-NCS})(\text{CO})_2(\mu\text{-dppm})_2]\text{ClO}_4 \] 
(0.085 g, 0.072 mmol) in 10 mL of dichloromethane resulted in a colour change to a bright red-orange. The slow addition of diethyl ether to this solution, even while sulphur dioxide was still being passed, resulted in a gradual lightening of colour and the deposition of yellow crystals of the starting material (0.071 g, 83%).

\[ \text{[Rh}_2(\text{SCN})(\text{CO})_2(\mu\text{-dppm})_2]\text{ClO}_4 \] Isomerization to 
\[ \text{[Rh}_2(\mu\text{-NCS})(\text{CO})_2(\mu\text{-dppm})_2]\text{ClO}_4 \]

was dissolved in 10 mL of dichloromethane and sulphur dioxide was bubbled through the solution for 15 min. The addition of sulphur dioxide saturated diethyl ether to the wine red solution resulted in the deposition of a crude orange solid. Recrystallization of the crude material from dichloromethane-diethyl ether yielded yellow crystals of 
\[ \text{[Rh}_2(\mu\text{-NCS})(\text{CO})_2(\mu\text{-dppm})_2]\text{ClO}_4 \] (0.080 g, 73%).
Table 3.1. IR Data of the Products Obtained by the Reaction of \([\text{Rh}_2(\mu-X)(\mu-CO)(\mu-dppm)_2]ClO_4\) (\(X = \text{OH, Cl, Br, I and NCS}\)) and \([\text{Rh}_2(\mu-NCS_2)(\mu-CO)_2(\mu-dppm)_2]\) with Carbon Monoxide and Sulphur Dioxide

<table>
<thead>
<tr>
<th>Compound</th>
<th>(\nu(CO)^a), cm(^{-1})</th>
<th>(\nu(CO)^b), cm(^{-1})</th>
<th>Others, (^b) cm(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trans-(\text{Rh}_2\text{Cl}_2(\mu-CO)\text{CO}_2(\mu-dppm)_2)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>([\text{Rh}_2(\mu-\text{Br})(\mu-CO)(\mu-CO)_2(\mu-dppm)_2]ClO_4)</td>
<td>1993(vs), 2004(sh), 1871(m)</td>
<td>1976(vs), 1937(sh)</td>
<td></td>
</tr>
<tr>
<td>([\text{Rh}_2(\mu-\text{I})(\mu-CO)(\mu-CO)_2(\mu-dppm)_2]ClO_4)</td>
<td>1987(m), 1974(vs), 1856(m), 1844(m)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>([\text{Rh}_2(\mu-CN)(\mu-CO)(\mu-CO)_2(\mu-dppm)_2]ClO_4\cdot\text{CH}_2\text{Cl}_2)</td>
<td>1983(vs), 1975(vs), 1859(m)</td>
<td>1978(vs), 1969(vs), 1840(s)</td>
<td></td>
</tr>
<tr>
<td>([\text{Rh}_2(\mu-CN)(\mu-CO)(\mu-CO)_2(\mu-dppm)_2]ClO_4\cdot\text{CH}_2\text{Cl}_2)</td>
<td>1983(vs), 1840(s)</td>
<td>1978(vs), 1969(vs), 1840(s)</td>
<td></td>
</tr>
<tr>
<td>([\text{Rh}_2(\mu-CN)(\mu-CO)(\mu-CO)_2(\mu-dppm)_2]ClO_4\cdot\text{CH}_2\text{Cl}_2)</td>
<td>1983(vs), 1840(s)</td>
<td>1978(vs), 1969(vs), 1840(s)</td>
<td></td>
</tr>
<tr>
<td>([\text{Rh}_2(\mu-CN)(\mu-CO)(\mu-CO)_2(\mu-dppm)_2]ClO_4\cdot\text{CH}_2\text{Cl}_2)</td>
<td>1983(vs), 1840(s)</td>
<td>1978(vs), 1969(vs), 1840(s)</td>
<td></td>
</tr>
</tbody>
</table>

(a) Recorded in dichloromethane solution.
(b) Recorded as nujol mulls on potassium bromide plates.
(c) Obscured by terminal carbonyl bands.
Table 3.2. NMR ($^1$H, $^{13}$C, $^{31}$P) Data of the Products Obtained by the Reaction of 

$[\text{Rh}_2(u-X)(CO)_2(u-dppm)_2]ClO_4$ ($X = \text{Br, I and NCS}$) and $\text{Rh}_2(\text{NCS})_2(\text{CO})_2(u-dppm)_2$ with Carbon Monoxide

<table>
<thead>
<tr>
<th>Compound</th>
<th>$^{31}$P</th>
<th>$^{1}$H</th>
<th>$^{13}$C</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{Rh}_2(u-\text{Br})(u-CO)(CO)_2(u-dppm)_2]ClO_4$</td>
<td>31.15 (m, dppm)</td>
<td>29.32 (m, dppm)</td>
<td>188.6 (m, dppm)</td>
</tr>
<tr>
<td>$[\text{Rh}_2(u-\text{I})(u-CO)(CO)_2(u-dppm)_2]ClO_4$</td>
<td>26.32 (m, dppm)</td>
<td>30.36 (m, dppm)</td>
<td>203.4 (ttq, dppm)</td>
</tr>
<tr>
<td>$[\text{Rh}_2(u-\text{NCS})(u-CO)(CO)_2(u-dppm)_2]ClO_4$</td>
<td>20.07 (m, dppm)</td>
<td>7.71 (m, dppm)</td>
<td>189.7 (dt, dppm)</td>
</tr>
</tbody>
</table>

Abbreviations: $C_e$ = Carbon of the terminal carbonyl group, $C_B$ = Carbon of the bridging carbonyl group.

(a) Chemical shifts (in ppm) relative to tetramethylsilane ($^1$H and $^{13}$C) and 85% phosphoric acid ($^{31}$P) in dichloromethane.
(b) $^1$H NMR spectra were recorded in dichloromethane-d$_2$.
(c) The degree of dichloromethane solvate was determined by recording the spectrum in acetone-d$_6$ (5.69, s, 2H).
(d) Degree of dichloromethane solvation could not be determined by $^1$H NMR because of its poor solubility.
(e) 360 MHz at -40°C. At room temperature, dppm methylene protons appeared as a barely resolved broad peak centred at 3.72 ppm.
4.1. Introduction

The discussion in Chapter 3 revealed that majority of the binuclear A-frame complexes described in Chapter 2 were either inert to carbon monoxide at one atmosphere or reacted at the bridgehead ligand. In an attempt to determine the behaviour of these inert complexes at higher pressures, the complexes \([\text{Rh}_2(\mu-\text{OR})(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4\) \((R = \text{H, CH}_3\text{ and } \text{C}_2\text{H}_5)\) were subjected to carbon monoxide at 30 psi pressure at room temperature. This led to the serendipitous isolation of an orange product, identified as an unusual trinuclear cluster, \([\text{Rh}_3(\text{CO})_3(\mu-\text{CO})_3(\mu-1,2-\text{dppm})_2]\text{ClO}_4\cdot\text{CH}_2\text{Cl}_2\) (92) whose structure resembles that of a doubly bridged A-frame complex with \(\text{Rh} \cdot \text{(CO)}_3\) as the bridgehead ligand and carbon monoxide in the endo pocket. This cluster is unusual because of its unsaturation. It has a total electron count of 46, two electrons short of the effective atomic number rule, according to which 48 electrons are required to form a stable triangular cluster. The present chapter deals with the synthesis and characterization of \([\text{Rh}_3(\mu-\text{CO})_3(\text{CO})_3(\mu-1,2-\text{dppm})_2]\text{ClO}_4\cdot\text{CH}_2\text{Cl}_2\) and its reactivity with tertiary phosphines.
As far as can be determined, \([\text{Rh}_3(\mu-\text{CO})_3(\text{CO})_3(\mu-1,2-\text{dppm})_2]\)ClO_4·CH_2Cl_2 appears to be the only trinuclear cluster of rhodium with dppm bridging ligands to be synthesized and structurally characterized. Other examples of dppm bridged cluster include \(\text{Ru}_3(\text{CO})_{10}(\mu-\text{dppm})\), \(\text{Ru}_3(\text{CO})_8(\mu-\text{dppm})_2\), \(\text{Pd}_2\text{CO}_2(\text{CO})_7(\mu-\text{dppm})_2\), \(\text{Rh}_6(\mu_3-\text{CO})_4(\text{CO})_6(\mu-\text{dppm})_3\), and \(\text{Pt}_4(\mu-\text{CO})_2(\mu-\text{dppm})_3(\text{PPh}_2\text{CH}_2\text{POPPh}_2)\).

4.2. Results and Discussion

IR and NMR \(^1\text{H}, \text{ }^{31}\text{P}\{^1\text{H}\}, \text{ and } ^{13}\text{C}\{^1\text{H}\}\) data of the complexes are given in table 4.1 and table 4.2 respectively, and all other physical data are given immediately after each synthetic procedure.
4.2.1. The Synthesis and Characterization of Rh$_3$(μ-CO)$_3$(CO)$_3$(μ-1,2-dppm)$_2$ClO$_4$.CH$_2$Cl$_2$

When a dichloromethane solution of [Rh$_2$(μ-OR)(CO)$_2$(μ-dppm)$_2$]ClO$_4$ (R = H, CH$_3$, and C$_2$H$_5$) was subjected to carbon monoxide pressure (30 psi) at room temperature for 2 h, a red-brown solution resulted. The addition of diethyl ether to this solution precipitated an orange crystalline solid which, on recrystallizing from dichloromethane-diethyl ether, gave bright orange needles, identified as the trimeric cluster, [Rh$_3$(μ-CO)$_3$(CO)$_3$(μ-1,2-dppm)$_2$]ClO$_4$.CH$_2$Cl$_2$ from analytical, spectroscopic and X-ray crystallographic results. The yields were in the range 32-34% (based upon available rhodium) and increased up to 52% when the reaction was carried out in the presence of a small amount of the appropriate alcohol. [Rh$_3$(μ-CO)$_3$(CO)$_3$(μ-1,2-dppm)$_2$]ClO$_4$.CH$_2$Cl$_2$ was found to be stable in the solid state even up to 3 weeks and was either partially soluble or insoluble in most commonly used organic solvents. Conductivity data in acetone showed that this trimer behaves as a 1:1 electrolyte ($\Lambda_M = 132$ cm$^2$ Ω$^{-1}$ mol$^{-1}$).

An X-ray crystallographic study of [Rh$_3$(μ-CO)$_3$(CO)$_3$(μ-1,2-dppm)$_2$]ClO$_4$.CH$_2$Cl$_2$ was performed by Prof. T.S. Cameron. Figure 4.1 shows the equatorial plane of the molecule with some relevant bond distances. The long needles used in the X-ray diffraction were of poor diffracting
Figure 4.1. The Equatorial Plane of the Cation, 
\[ \text{[Rh}_3(\mu-\text{CO})_3(\text{CO})_3(\mu-1,2-\text{dppm})_2]^{\text{2}+} \]

Esd's of bond lengths are indicated by subscripts.
ability. Despite this problem, an X-ray crystallographic analysis was performed which established with some reliability that the complex is trimeric, with trans dppm ligands bridging Rh(1) and Rh(2) and each rhodium atom carrying one terminal carbonyl group. In addition, three bridging carbonyl groups were identified, one on each edge. The triangle formed by the three rhodium atoms has two short edges (Rh(2)-Rh(3) = 2.781(9) Å, Rh(1)-Rh(3) = 2.763(7) Å), one long edge (Rh(1)-Rh(2) = 2.827(6) Å). These values fall in the range (2.7566(9)-2.855(7) Å) normally observed in binuclear and trinuclear rhodium complexes with rhodium-rhodium single bonds. Of the three bridging carbonyl groups, that bridging Rh(1) and Rh(2) is symmetrical. The other two bridging Rh(1), Rh(3) and Rh(2), Rh(3), however, are asymmetric, and are associated with asymmetry parameters of 0.14 and 0.16 respectively. These values, when plotted versus the large-MCO angle θ, lie on the curve obtained by Curtis et al. for normal two electron bridging carbonyls. The large esu's associated with the parameters of both bridging and terminal Rh-C-O moieties preclude any meaningful comparison of these with other reported values. As mentioned earlier, the cluster, \([\text{Rh}_3(\mu-\text{CO})_3(\mu-\text{CO}_3(\mu-1,2-\text{dppm})_2\text{ClO}_4\cdot\text{CH}_2\text{Cl}_2\) can also be visualized as a binuclear A-frame with a Rh(CO)_3 fragment as the bridgehead ligand and carbon monoxide in the endo pocket. As observed in many other structurally
characterized doubly bridged A-frames, the dpmp methylenes are folded cis and bent towards the bulky Rh(CO)₃ group (figure III.1, Appendix III). The spectroscopic data obtained for [Rh₃(μ-CO)₃(CO)₃(μ-dppm)₃]ClO₄·CH₂Cl₂ to be discussed below, are quite consistent with the structural characterization. The IR spectrum of this complex in the solid state showed bands at 2035 (m), 2000 (sh), 1998 (vs), 1924 (w), 1869 (sh) and 1858 (s) cm⁻¹. The number of bands observed, although not well resolved, is consistent with approximate $C_2v$ symmetry of the cluster. The most reasonable assignment of the terminal carbonyls would have the 2035 cm⁻¹ band attributed to $ν$(CO) of the unique carbonyl attached to the bridging rhodium (vide infra) and the 2000 and 1998 cm⁻¹ pair due to the symmetric and antisymmetric stretch of the remaining terminal carbonyl groups. Very little can be said about the bridging carbonyls except that the weak band at 1924 cm⁻¹ appears to be the symmetric stretch of the two equivalent bridging carbonyls. In dichloromethane solutions, the high frequency shoulder at 2000 cm⁻¹ could not be identified and the absorptions appeared at 2032 (m), 1929 (w), 1872 (sh) and 1869 (s) cm⁻¹.

[Rh₃(μ-CO)₃(CO)₃(μ-1,2-dppm)₃]ClO₄·CH₂Cl₂, when subjected to ¹³-carbon monoxide (¹³CO, 90%, 20 mg, 5 mL; dichloromethane, 5 min) underwent rapid exchange of the
terminal carbonyl attached to the bridging Rh(CO)$_3$ group. This behaviour was evident from both IR and $^{13}$C{$^1$H} NMR spectra. The solution IR spectrum of the cluster after exchange, with labelled carbon monoxide ($^{13}$CO) showed the appearance of a medium to strong band at 1980 cm$^{-1}$ along with the complete disappearance of the band at 2032 cm$^{-1}$. The $^{13}$C{$^1$H} NMR spectrum of the labelled cluster, [Rh$_3$(μ-CO)$_3$(CO)$_2$(μ-$^{13}$CO)(μ-1,2-dppm)$_2$]ClO$_4$ showed a simple doublet centred at 185.73 ppm ($^{1}J_{Rh_b-C} = 90.0$ Hz) (Rh$_b =$ bridging rhodium atom) which confirmed that it is the unique terminal carbonyl attached to the bridging rhodium that underwent exchange. No coupling due to other rhodium atoms on phosphorus was observed. The chemical shift and the coupling constant observed for this doublet compares favourably with other terminal carbonyls attached to rhodium centres.

The solution of the labelled complex when left for ca. 12 h showed evidence that the label was being slowly introduced to the two adjacent bridging carbonyl groups. This became evident from both the solution IR spectrum as well as the $^{13}$C{$^1$H} spectrum. The solution IR spectrum of the aged sample, for example, showed a distinct high energy shoulder (2035 cm$^{-1}$) on the 2008 cm$^{-1}$ band and a low energy shoulder (ca. 1820 cm$^{-1}$) on the 1869 cm$^{-1}$ band along with a decrease in the intensity of the 1980 cm$^{-1}$ band. The $^{13}$C{$^1$H} NMR spectrum of the aged sample (after 12 h), in addition to the doublet at 185.73 ppm,
showed a complex second order doublet, centred at 242.2 ppm (separation ca. 54 Hz) probably arising from coupling with non-equivalent rhodium and phosphorus atoms. This type of ligand mobility is a commonly observed phenomenon in transition metal clusters, which are now frequently regarded as simple models for comprehending ligand mobility on metal surfaces.

The $^1$H NMR spectrum of $[\text{Rh}_3(\mu-\text{CO})_3(\text{CO})_3(\mu-1,2-\text{dppm})_2]\text{ClO}_4 \cdot \text{CH}_2\text{Cl}_2$ showed that the dppm methylene protons cannot be resolved at 80 MHz. However, at 360 MHz they became completely resolved with the resonances appearing at 3.36 and 3.65 ppm. Furthermore, the spectrum was silent up to ca. -50 ppm, indicating the absence of bridging and terminal hydrides. The $^{31}$P($^1$H) NMR spectrum showed a symmetric second order pattern characteristic of a doubly bridged A-frame with a metal-metal bond. This confirmed the equivalent environment of the four phosphorus atoms. The most striking feature of this spectrum was the apparently uniform splitting of both the major and minor lines into doublets. The spectrum has been successfully analyzed as an AA'AA'MXX' spin system which gives rise to the typical A-frame pattern in which each line is split into a doublet by coupling with nucleus M, the bridging rhodium. Figure 4.2 shows the observed $^{31}$P spectrum of $[\text{Rh}_3(\mu-\text{CO})_3(\text{CO})_3(\mu-\text{dppm})_2]\text{ClO}_4$, along with the simulated spectrum and the
Figure 4.2. $^{31}P{[^1H]}$ NMR Spectra of $[\text{Rh}_3(\mu-\text{CO})_3(\text{CO})_3(\mu-1,2\text{-dppm})_2]\text{ClO}_4\cdot\text{CH}_2\text{Cl}_2$

(a) calculated  (b) observed

Derived Coupling Constants at Bottom

$J_{P_1P_2} = 429.6$ Hz

$J_{Rh_3P_1} = 95.2$ Hz

$J_{P_2P_3} = 81.5$ Hz

$J_{Rh_3P_2} = 1.5$ Hz

$J_{P_3P_4} = 33.8$ Hz

$J_{Rh_3P_3} = 2.5$ Hz

$J_{Rh_3Rh_3} = 0$
derived coupling constants. The observed constants are given in table 4.2.

The steps involved in the formation of the cluster appear to be complex. Whatever steps may be involved, at some point it is necessary to involve a reduction step to explain the 1/3 formal oxidation state of the rhodium atoms in the cluster. A tentative reaction scheme for the formation of the cluster is shown below (equation 30 to 33).

\[
{\text{[Rh}_2(\mu-\text{OH})(\text{CO})_2(\mu-\text{dppm})_2]^+ + 2 \text{CO}} \xrightarrow{\text{or}} \text{[Rh}_2(\mu-\text{H})(\mu-\text{CO})(\text{CO})_2(\mu-\text{dppm})_2]^+ + \text{CO}_2
\]

\[
{\text{[Rh}_2(\mu-\text{OR})(\text{CO})_2(\mu-\text{dppm})_2]^+ + \text{CO}} \qquad \text{(R = CH}_3, \text{C}_2\text{H}_5)
\]

\[
{\text{[Rh}_2(\mu-\text{H})(\mu-\text{CO})(\text{CO})_2(\mu-\text{dppm})_2]^+ + \text{R'CHO}} \quad \text{(R' = H, CH}_3) \text{)} \quad \text{(30)}
\]

\[
{\text{[Rh}_2(\mu-\text{OR})(\text{CO})_2(\mu-\text{dppm})_2]^+ + [Rh}_2(\mu-\text{H})(\mu-\text{CO})(\text{CO})_2(\mu-\text{dppm})_2]^2+ \quad \text{(R = H, CH}_3, \text{C}_2\text{H}_5)} \xrightarrow{\text{CO}} \text{Rh}_2(\mu-\text{CO})(\text{CO})_2(\mu-\text{dppm})_2 + [\text{Rh}_2(\mu-\text{CO})(\text{CO})_2(\mu-\text{dppm})_2]^2+ + \text{ROH} \quad \text{(31)}
\]

\[
{\text{[Rh}_2(\mu-\text{CO})(\text{CO})_2(\mu-\text{dppm})_2]^+ + \text{CO}} \xrightarrow{\text{Rh}(\text{CO})_3^+} \text{"monomer"} \quad \text{(32)}
\]

\[
\text{Rh}(\text{CO})_3^+ + \text{Rh}_2(\mu-\text{CO})(\text{CO})_2(\mu-\text{dppm})_2 \xrightarrow{\text{or}} \text{[Rh}_2(\mu-\text{CO})(\text{CO})_3(\mu-\text{dppm})_2]^+ \quad \text{(33)}
\]
The first step of this reaction (equation 30) may involve reaction of the \([\text{Rh}_2(\mu-\text{OH})(\text{CO})_2(\mu-\text{dppm})_2]^+\) with carbon monoxide to form a bridging metallocarboxylate which on elimination of carbon dioxide could give \([\text{Rh}_2(\mu-\text{H})(\mu-\text{CO})(\text{CO})_2(\mu-\text{dppm})_2]^+\) as postulated for the reaction of \(\text{Rh}_2(\mu-\text{OH}.\text{Cl})(\text{CO})_2(\mu-\text{dppm})_2\) with carbon monoxide (vide supra). In the case of alkoxide complexes, a similar starting point can be reached by assuming an \(\alpha\)- or \(\beta\)-hydride elimination to give formaldehyde and acetaldehyde respectively, together with \([\text{Rh}_2(\mu-\text{H})(\mu-\text{CO})(\text{CO})_2(\mu-\text{dppm})_2]^+\). This species could then conceivably react with another molecule of \([\text{Rh}_2(\mu-\text{OR})(\text{CO})_2(\mu-\text{dppm})_2]^+\) to produce \(\text{ROH} \cdot (R = \text{H}, \text{CH}_3, \text{C}_2\text{H}_5)\), the neutral dimer \(\text{Rh}_2(\mu-\text{CO})(\text{CO})_2(\mu-\text{dppm})_2\) and \([\text{Rh}_2(\mu-\text{CO})(\text{CO})_2(\mu-\text{dppm})_2]^2+\) (equation 31). The latter may then break down to give a monomer of some description and a source of \(\text{Rh}(\text{CO})_3^+\), which can then combine with \(\text{Rh}_2(\mu-\text{CO})(\text{CO})_2(\mu-\text{dppm})_2\) to form the cluster; \([\text{Rh}_3(\mu-\text{CO})_3(\text{CO})_2(\mu-\text{dppm})_2]^+\) (equation 32 and 33). In order to test the validity of this reaction scheme equimolar amounts of \([\text{Rh}_2(\mu-\text{OC}_2\text{H}_5)(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4\) and \(\text{Rh}_2(\mu-\text{H})(\mu-\text{CO})(\text{CO})_2(\mu-\text{dppm})_2\text{ClO}_4\) were mixed and subjected to carbon monoxide pressure (30 psi) in dichloromethane for 2 h. IR spectrum of the product isolated showed that this is in fact a mixture of \([\text{Rh}_3(\mu-\text{CO})_3(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4\text{CH}_2\text{Cl}_2\) and \([\text{Rh}_2(\mu-\text{H})(\mu-\text{CO})(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4\) with the latter as the major product. Hence this observation indicated that the steps involved in the formation of
[Rh$_3$(μ-CO)$_3$(CO)$_3$(μ-1,2-dppm)$_2$]ClO$_4$ are much more complex than proposed in equations 30 to 33 and [Rh$_2$(μ-μ)$(μ$-CO)(CO)$_2$(μ-dppm)$_2$]ClO$_4$ does not intermediate in the reaction.

In an attempt to find the fate of the remaining rhodium in the reaction of [Rh$_2$(μ-OR)(CO)$_2$(μ-dppm)$_2$]ClO$_4$ (R = H, CH$_3$, C$_2$H$_5$), the filtrate was evaporated to dryness after isolating the cluster, [Rh$_3$(μ-CO)$_3$(CO)$_3$(μ-1,2-dppm)$_2$]ClO$_4$. This yielded an ionic, mustard coloured material (80-90 mg), the IR spectrum of which showed a single carbonyl absorption at 1991 cm$^{-1}$, which suggested that the complex in fact contains Rh(l). This material could not be recrystallized to give a pure crystalline sample and as a result analytical data were not obtained. The $^{31}$P($^1$H)NMR spectrum of this material, however, appeared to be somewhat clean, showing a doublet of triplets at 48.48 ppm ($J = 16.8$ and $1.3$ Hz respectively) and triplets at 28.30 and 25.15 ppm ($J = 16.9$ Hz for both). The $^1$H NMR spectrum did not indicate the presence of hydrides since the region up to -50 ppm was clear. To date, the assignment of a single reasonable structure for this material that conforms to physical data obtained has not been possible. Attempts to improve the yields of [Rh$_3$(μ-CO)$_3$(CO)$_3$(μ-1,2-dppm)$_2$]ClO$_4$ by performing the carbonylation in the presence of stoichiometric amounts of various monomers and monomer precursors such as Rh$_2$Cl$_2$(CO)$_4$, Rh(COD)(acac), and [Rh(COD)(PPh$_3$)$_2$]ClO$_4$ were not successful. Rh$_2$Cl$_2$(CO)$_4$ gave [Rh$_2$(μ-Cl)(μ-CO)(CO)$_2$-
(\(\mu\)-dppm\)_2]ClO_4 whereas the latter two monomers merely gave [Rh_3(\(\mu\)-CO)_3(CO)_3(\(\mu\)-1,2-dppm)_2]ClO_4·CH_2Cl_2 with no improvement in the yield. These observations underscore the complex nature of the reactions leading to the formation of [Rh_3(\(\mu\)-CO)_3(CO)_3(\(\mu\)-1,2-dppm)_2]ClO_4·CH_2Cl_2.

The most conspicuous structural feature of [Rh_3(\(\mu\)-CO)_3(CO)_3(\(\mu\)-dppm)_2]ClO_4·CH_2Cl_2 is the presence of the Rh(CO)_3 bridging moiety rather than Rh(CO)_4, which is favoured on the basis of electron-counting techniques. Furthermore, the structure is also unusual in contrast to the predictions made by Hoffman and Hoffmann in which they employed the isolobal analogy between methylene and the C_2v metal fragments, d'\(^{10}\)M'L_2' and d'\(^{8}\)M'L_4' to predict the existence of trimetallic clusters based upon the A-frame structure with bridging M'L_\(n\)' (n = 2, 4) groups, i.e. M_2L_6(\(\mu\)-M'L_\(n\)'). In their study concerning the electronic structure of A-frame complexes, these authors generated the orbitals of an M_2L_6 fragment by combining two planar T-shaped ML_3 fragments to form a planar M_2L_6 framework which was then bent in such a way as to give the M_2L_6 fragment a geometry appropriate to that of an A-frame as shown in scheme 10.

Ignoring the bridging carbonyl group attached to two equivalent rhodium centres in [Rh_3(\(\mu\)-CO)_3(CO)_3(\(\mu\)-1,2-dppm)_2]ClO_4·CH_2Cl_2 the formation of [Rh_2(\(\mu\)-Rh(CO)_3)(CO)_2-
Scheme 10
(u-dppm)$_2$]ClO$_4$ can be considered to result from interaction of the molecular orbitals of the d$^9$-d$^9$ M$_2$L$_6$ (Rh$_2$(CO)$_2$- (u-dppm)$_2$ fragment in this case) with the frontier orbitals of the d$^8$ Rh(CO)$_3^+$ and d$^8$ Rh(CO)$_4^+$ moieties. The frontier orbitals of d$^8$ Rh(CO)$_3^+$ and d$^8$ Rh(CO)$_4^+$ fragments are analogous to those obtained for the d$^9$ PtCl$_3^-$ and d$^9$ Fe(CO)$_4$ species of the same symmetry respectively. For the bridging ligand Rh(CO)$_3^+$, the main bonding interaction is between the filled M$_2$L$_6$ 3a$_1$ and empty 2a$_1$ of the Rh(CO)$_3^+$ group (figure 4.3). Hence, a T-shaped geometry is expected at the bridging rhodium together with approximate coplanarity of the Rh$_3$ triangle with the carbonyl groups. In this geometry the carbonyls directly opposite to each other in the Rh(CO)$_3^+$ group can also be bridged to the other two rhodium centres. This has been observed in the structural characterization of [Rh$_3$(u-CO)$_3$(CO)$_3$(u-1,2-dppm)$_2$]ClO$_4$. When Rh(CO)$_4^+$ is considered as the bridging group, however, there will be two important bonding interactions between the filled 3a$_1$ and empty 3b$_2$ orbitals of M$_2$L$_6$ and the empty 2a$_1$ and filled b$_2$ orbitals of Rh(CO)$_4^+$ group. The b$_2$ orbital is highly directional and the interaction with the M$_2$L$_6$ 3b$_2$ orbital depends upon the way in which the Rh(CO)$_4^+$ group is oriented with respect to the M$_2$L$_6$ framework. When both bonding interactions are effective, as shown in 93, two of the carbonyl groups lie on a plane parallel to the Rh$_2$P$_4$ plane directly opposite to each other and directed towards the methylene
Figure 4.3. Molecular Orbitals of the Fragments

$\text{Rh}_2(\text{CO})_2 \mu$-dppm $\rightarrow \text{Rh(CO)}_4^+$ and $\text{Rh(CO)}_3^+$
groups of the dppm ligands. When Rh(CO)$_4$ interacts with the M$_2$L$_6$ fragments as shown in 94, the only dominant bonding interaction is between the $3a_1$ orbital of M$_2$L$_6$ and the $2a_1$ orbital of the Rh(CO)$_4$ group, and in this case the carbonyls extending towards the methylene of the dppm are not trans but inclined at an angle, of 9° to one another.

A typical feature of the structure of doubly bridging rhodium A-frame complexes, including this example, is the occurrence of the cis folding of the dppm methylene groups towards the bulky bridgehead ligand. Hence, with Rh(CO)$_4$ as the bridgehead ligand there would be considerable steric interaction between the methylene of the dppm ligands and the carbonyls directed towards the methylene groups. This interaction will be far greater in 93 than in 94. Another point to note here is that whereas in 93, the
formation of bridging carbonyl interactions with the other rhodium atoms is not possible, it is so in 94. Hence, overall, 93 will generate two bonding interactions, but will suffer from severe steric strain between the trans carbonyls and the dppm methylene groups, whereas 94, although only generating one bonding interaction, will have the added advantages of decreased steric interaction and the possibility of further stabilization from the formation of carbonyl bridges. Hence, qualitatively, 94 might be expected to be more energetically favourable than 93. The inability to isolate the cluster with the Rh(CO)$_4$ fragment in either orientation, however, indicates that destabilization due to steric interactions predominates. Further support for a severe non-bonding interaction between the methylene and the carbonyl groups of Rh(CO)$_4$ fragment can be obtained by considering a typical A-frame complex, [Rh$_2$(μ-Cl)(CO)$_2$-(μ-dppm)$_2$]ClO$_4$ in which cis folding of the methylene groups results in non-bonded contacts of 2.85 and 2.90 Å between the equatorial methylene protons and the bridgehead chloride. It is quite apparent from these distances that severe interactions would result if the bridging rhodium atoms carried carbonyl groups of approximately 3.0 Å in length perpendicular to the Rh$_3$ plane. No such interactions are possible in the case of Rh(CO)$_3$ fragment since all carbonyl groups lie in the Rh$_3$ plane.
4.2.2. Reactivity with Phosphines

Since the unique terminal carbonyl attached to the bridging rhodium of \([\text{Rh}_3(\mu-\text{CO})_3(\mu-1,2-\text{dppm})_2]\text{ClO}_4\cdot\text{CH}_2\text{Cl}_2\) underwent rapid exchange with \(^{13}\text{CO}\), the possibility of the ligand being substituted by other ligands such as tertiary phosphines was explored. As anticipated, the reactions were found to proceed with the displacement of this group to give complexes; \([\text{Rh}_2(\mu-\text{CO})_3(\text{CO})_2(3-\text{L})-(\mu-1,2-\text{dppm})_2]\text{ClO}_4\) (95) \((L = \text{PPh}_3, \text{PMePh}_2, \text{PET}_3, \eta^1-\text{dppm})\) which have been characterized by IR and NMR \((^1\text{H}, ^{13}\text{C}, ^1\text{H})\) and \(^{31}\text{P} (^1\text{H})\) spectroscopy (equation 34).

When a suspension of the parent cluster, \([\text{Rh}_3(\mu-\text{CO})_3-(\text{CO})_3(\mu-1,2-\text{dppm})_2]\text{ClO}_4\cdot\text{CH}_2\text{Cl}_2\) in dichloromethane was treated with slight excess of methylidiphenylphosphine, the solution immediately turned red with complete dissolution.
of the cluster along with gas evolution. The addition of diethyl ether to this red solution gave an orange solid which on recrystallizing with dichloromethane-diethyl ether yielded red-orange crystals, $[\text{Rh}_3(\mu-\text{CO})_3(\text{CO})_2(3\text{-PMePh}_2)(\mu-1,2\text{-dppm})_2\text{ClO}_4]$. This complex exhibited IR bands in the solid state at 1992 (m), 1982 (sh), 1975 (vs), 1919 (m), 1855 (s), 1837 (sh) whereas in dichloromethane at 2003 (sh), 1993 (vs), 1920 (mw), 1853 (s) and 1845 (sh). The origin of the high energy shoulder on the most intense band in the solid state spectrum is not clear but may arise from some solid state effect. The $^{31}\text{P}[^{1}\text{H}]$ NMR spectrum in dichloromethane (figure 4.4) showed a symmetrical second order pattern for the dppm ligands similar to that observed for the parent cluster, except that each line of the doublet was further split (ca. 1 Hz) as a result of coupling with the phosphorus of methyldiphenylphosphine. The lines were, however, not always resolved. The phosphorus resonance of the coordinated methyldiphenylphosphine appeared as a doublet of triplets centred at 17.11 ppm with $^1J_{\text{Rh}^\text{b}-\text{P}^\text{D}} = 200.8$ Hz and $^2J_{\text{Rh}^\text{b}-\text{P}^\text{D}} = 6.9$ Hz ($\text{Rh}^\text{b}$ = bridging rhodium atom, $\text{P}^\text{D}$ = phosphorus attached to bridging rhodium). These observations established that the position of phosphine substitution is at the bridging rhodium atom. Both IR and $^{13}\text{C}[^{1}\text{H}]$ NMR studies confirmed that the attack of phosphine at the bridging group takes place with displacement of carbon monoxide. Recording of the solution IR of the labelled
Figure 4.4. $^{31}\text{P}^1\text{H}$ NMR Spectrum of $\left[\text{Rh}_3(\mu-\text{CO})_3(\text{CO})_2(3\text{-PMePh}_2)(\mu-1,2\text{-dppm})_2\right]\text{ClO}_4$ in Dichloromethane (40.5 MHz)
cluster, $[\text{Rh}_3(\mu-\text{CO})_3(\text{CO})_2(3-^{13}\text{CO})(\mu-1,2-\text{dppm})_2]\text{ClO}_4\cdot\text{CH}_2\text{Cl}_2$ after addition of one mole of methyldiphenylphosphine showed the complete disappearance of the 1980 cm$^{-1}$ band with the appearance of absorptions at 2003 (sh), 1993 (vs), 1920 (mw), 1853 (s), 1845 (sh), identical to those observed for $[\text{Rh}_3(\mu-\text{CO})_3(\text{CO})_2(3-\text{PMePh}_2)(\mu-1,2-\text{dppm})_2]\text{ClO}_4$. The red-orange complex isolated from the solution also had an identical IR spectrum to that obtained by the reaction of the unlabelled cluster with methyldiphenylphosphine. As mentioned earlier, the $^{13}\text{C}$$^1\text{H}$ NMR spectrum of the labelled cluster showed a simple doublet at 185.73 ppm. The addition of methyldiphenylphosphine caused the complete disappearance of the doublet and the region between 150-300 ppm was silent. The $^1\text{H}$ NMR spectrum of $[\text{Rh}_3(\mu-\text{CO})_3(\text{CO})_2(3-\text{PMePh}_2)(\mu-\text{dppm})_2]\text{ClO}_4$ showed a doublet of doublets at 1.92 ppm for the methyl signal of the methyldiphenylphosphine with $^2J_{\text{P}-\text{H}} = 8.0$ Hz and $^3J_{\text{Rh}-\text{H}} = 1.8$ Hz. The coupling constants have been assigned by comparison with the data quoted for trans-RhCl(CO)(PMe$_2$)$_2$ ($^3J_{\text{Rh-H}} = 1.3$ Hz, $^2J_{\text{P-H}} = 6.2$ Hz) $^{185}$ The methylene protons of the bridging dppm ligands, as observed for the parent cluster, could not be resolved at 80 MHz. Similar behaviour was exhibited by both complexes, $[\text{Rh}_3(\mu-\text{CO})_3(\text{CO})_2(3-\text{L})(\mu-1,2-\text{dppm})_2]\text{ClO}_4$ ($\text{L} = \text{PMe}_3$, $\eta^1$-dppm). The pattern of the multiplet, however, indicated that they could be separated at a higher field strength. This has
been demonstrated for the complex with \( L = \eta^1\text{-dppm} \) (vide infra).

The preparation of \([\text{Rh}_2(\mu-\text{CO})_3(\text{CO})_2(3-\text{PET}_3)(\mu-\text{l,2-dppm})_2]\text{ClO}_4\) was similar to that of the other phosphine complexes. The IR spectrum in the solid state showed bands at 1990(s), 1974(vs), 1920(mw), 1840(vs) and 1827(s) which in \(\text{CH}_2\text{Cl}_2\) solution appeared at 2002(sh), 1991(vs), 1919(mw), 1850(s) and 1841(sh). The \(^{31}\text{P}(\text{^1H})\) spectrum in \(\text{CH}_2\text{Cl}_2\) showed a symmetric second order pattern centred at \( \delta = 23.31 \) ppm with \( |J_{\text{Rh-P}} + XJ_{\text{Rh-P}}| = 101.2 \) Hz. The signal due to triethyl phosphine appeared as a doublet of triplets with \( J_{\text{Rh-P}} = 185.6 \) Hz and \( J_{\text{Rh-P}} = 6.2 \) Hz. In the \(^1\text{H}\) NMR spectrum, the methyl and methylene groups of the triethylphosphine ligand appeared as complex multiplets at 1.13 and 1.68 ppm in the approximate ratio of 3:2 respectively. The reaction complex, \([\text{Rh}_3(\mu-\text{CO})_3(\text{CO})_2(3\text{-PPh}_3)(\mu-\text{dppm})_2]\text{ClO}_4\) was synthesized by the reaction of \([\text{Rh}_3(\mu-\text{CO})_3(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4\) with triphenylphosphine. The IR spectrum of this complex showed carbonyl stretches at 1993(m), 1977(vs), 1934(mw), 1840(s), and 1840(s) consistent with the removal of the unique terminal carbonyl group. \([\text{Rh}_3(\mu-\text{CO})_3(\text{CO})_2(3\text{-PPh}_3)(\mu-\text{dppm})_2]\text{ClO}_4\) was found to be extremely insoluble in most commonly used organic solvents and as a result its characterization was limited. The close similarity, however, of the IR frequencies observed for these cluster-phosphine complexes

(table 4.1) which are well characterized, and the method of synthesis, leave little doubt as to its formulation. The reaction of the parent cluster \([\text{Rh}_3(\mu-\text{CO})_3(\text{CO})_3(\mu-1,2-dppm)]_2\text{ClO}_4 \cdot \text{CH}_2\text{Cl}_2\) with one equivalent of dppm in dichloromethane solution gave a dark red solution from which red crystals could be isolated by the addition of diethyl ether. This complex has been identified as \([\text{Rh}_3(\mu-\text{CO})_3(\text{CO})_2(3-n^1-dppm)]_2\text{ClO}_4 \cdot 0.5\text{CH}_2\text{Cl}_2\). The IR spectrum of this complex in the solid state showed bands at 1995(sh), 1978(vs), 1921(mw), 1849(sh) and 1844(s) cm\(^{-1}\) which in solution appeared at 2003(sh), 1995(vs), 1918(mw), 1850(s) and 1845(sh) cm\(^{-1}\). These bands compared very closely with those observed for \([\text{Rh}_3(\mu-\text{CO})_3(\text{CO})_2(3-L)(\mu-1,2-dppm)]_2\text{ClO}_4 \cdot L = \text{PPh}_3, \text{PMePh}_2, \text{PET}_3\) (table 4.1). This suggested that the dppm appears to be coordinated to the bridging Rh atom through one phosphorus atom only. This has been confirmed by \(^1\text{H}\) and \(^{31}\text{P}\{^1\text{H}\}\) NMR spectroscopy. This complex was found to be fluxional as indicated by variable temperature \(^{31}\text{P}\{^1\text{H}\}\) and \(^1\text{H}\) NMR spectroscopy. The \(^{31}\text{P}\{^1\text{H}\}\) NMR spectrum of \([\text{Rh}_3(\mu-\text{CO})_3(\text{CO})_2(3-n^1-dppm)(\mu-1,2-dppm)]_2\text{ClO}_4 \cdot 0.5\text{CH}_2\text{Cl}_2\) at room temperature in \text{CH}_2\text{Cl}_2 showed a well-resolved symmetrical second order pattern \((\delta_p = 24.87 \text{ ppm, } |^{1}\text{J}_{\text{Rh-P}} + ^{4}\text{J}_{\text{Rh-P}}| = 99.9 \text{ Hz})\), similar to that observed for the parent cluster. The most perturbing feature of the spectrum was the absence of resonance attributable to the dppm ligand attached to the bridging rhodium atom, even when the spectrum was recorded...
with a spectral window of ±5000 Hz (-125 ppm to +125 ppm). On cooling down to -40 °C, however, new peaks emerged at -25.25 ppm (d, $^2J_{Pa-Pb} = 102$ Hz) and 27.23 ppm (dd, $^1J_{Rh_b-Pb} = 201.68$ Hz, $^2J_{Pa-Pb} = 103$ Hz) which corresponds to the free (Pa) and coordinated ends (Pb) of the monodentate dppm ligand attached to the bridging rhodium atom. The latter peaks were somewhat broad with unresolved coupling imposed, probably arising from coupling with the equivalent rhodium atoms. The poor resolution obtained seemed to originate from precipitation of the complex at the low temperature limit (-40 °C). The room temperature and low temperature and $^{31}P$($^1H$) spectrum of $[\text{Rh}_3(\mu-\text{CO})_3(\text{CO})_2(3-\eta^1-\text{dppm})(\mu-1,2-\text{dppm})]\text{ClO}_4 \cdot 0.5\text{CH}_2\text{Cl}_2$ can be rationalized by invoking an intramolecular exchange process as shown in equation 35, in which the free end of the
monodentate dppm exchanges position with the coordinated end. The coalescence temperature for this process appears to lie at room temperature or very close to room temperature since resonances that could be attributed to the $\eta^1$-dppm ligand are absent. The chemical shifts observed for monodentate dppm ligand, in $[\text{Rh}_3(\mu-\text{CO})_3(\text{CO})_2(3-\eta^1\text{-dppm})(\mu-1,2\text{-dppm})_2\text{ClO}_4]^+0.5\text{CH}_2\text{Cl}_2$ are in good agreement with those observed in $\text{fac-Mo(}CO)_3(\eta^2\text{-dppm})(\eta^1\text{-dppm})^+ (\delta_{P_A} = -25.2$ and $\delta_{P_B} = 30.0$ ppm (85% $\text{H}_3\text{PO}_4$). Three other complexes with monodentate dppm ligands are known which are believed to exhibit similar intramolecular exchange processes. These include $[\text{Pt}_2\text{H}(\eta^1\text{-dppm})(\mu\text{-dppm})_2]^+, [\text{Pd(CN}^+\text{Bu})_2(\eta^1\text{-dppm})]^+, [\text{Pt}(C\equiv\text{CPh})(\eta^1\text{-dppm})]^+)$. The $^1\text{H}$ NMR spectrum of $[\text{Rh}_3(\mu-\text{CO})_3(\text{CO})_2(\eta^1\text{-dppm})(\mu-1,2\text{-dppm})_2\text{ClO}_4]^+0.5\text{CH}_2\text{Cl}_2$ also supported the fluxional nature of the $\eta^1$-dppm ligand. At room temperature the methylene protons of the monodentate ligand appeared as 1:2:1 triplet ($J_{P_AH} = J_{P_BH} =$...
5.1 Hz) which on cooling collapsed to give a complex multiplet. The triplet at room temperature arises as a result of the phosphorus atoms possessing an average environment caused by the rapid intra-molecular exchange process. On cooling, (-35 °C), however, this motion is frozen and the phosphorus atoms no longer are equivalent. As a result, the methylene protons appear as a complex multiplet due to coupling with both the non-equivalent phosphorus atoms of the dpdm and the rhodium. The resolution of the complex multiplet was somewhat poor as a result of precipitation. The conductivity data of all the cluster-phosphine complexes showed that they behaved as 1:1 electrolytes in solution.

The cluster-phosphine complexes, $[\text{Rh}_3(\mu\text{-CO})_3\text{(CO)}_2(3\text{-L})(\mu-1,2\text{-dpdm})_2]\text{ClO}_4$ (L = PMePh$_{2}$, PEt$_3$ and $\eta^1$-dpdm) when treated with 13-carbon monoxide underwent exchange of the equivalent bridging carbonyls (equation 36). No evidence was seen for replacement of the phosphine ligand and, in fact, carbonylation of the $\text{Rh}_3(\mu\text{-CO})_3\text{(CO)}_2(3\text{-PMe-PPh}_2)(\mu-1,2\text{-dpdm})_2]\text{ClO}_4$ to regenerate the parent cluster was found to take 80 h at room temperature under 30 psi of carbon monoxide. A dichloromethane solution of $[\text{Rh}_3(\mu\text{-CO})_3\text{(CO)}_2(3\text{-PMePh}_2)(\mu-1,2\text{-dpdm})_2]\text{ClO}_4$ when made to react with 13-carbon monoxide (90%) (20 mg, 15 mL of dichloromethane, 10 min) showed new IR bands at 2003(sh), 1993(vs), 1877(mw),
The intensity of the bridging carbonyl absorptions were approximately in the ratio of 2:1, indicating that both equivalent carbonyls have undergone exchange. Similar behaviour was observed for \([\text{Rh}_3(\mu-CO)_3\text{CO}_2(3-L)(\mu-1,2-\text{dppm})_2]\text{ClO}_4 \) \((L = \text{PET}_3, \eta^1-\text{dppm})\), although longer reaction times were required, and the approximate IR values are given in table 4.1. The \(^{13}\text{C}\{^1\text{H}\}\) NMR of the
complexes, \([\text{Rh}_3(\mu-\text{CO})_3(\text{CO})_2(3-\text{L})(\mu-1,2-\text{dppm})_2]^+\text{ClO}_4^- (\text{L} = \text{PMePh}_2, \text{PET}_3 \text{ and } \eta^1-\text{dppm})\) in dichloromethane showed complex doublets in the region 245-250 ppm and no change was apparent in these signals when cooled down to -40 °C. The complex doublets observed for the bridging carbonyls confirmed that the labelling took place at the equivalent bridging carbonyl groups since exchange at the unique bridging carbonyl should give rise to a triplet of quintets.

It is quite obvious that two different carbonyl exchange mechanisms are operative for the parent cluster \([\text{Rh}_3(\mu-\text{CO})_3(\text{CO})_3(\mu-1,2-\text{dppm})_2]^+\text{ClO}_4^- \cdot \text{CH}_2\text{Cl}_2\) and its phosphine derivatives. Although it is not certain for sure what these mechanisms are, one possible mechanism (associative type) by which the parent cluster exhibits facile exchange of the unique terminal carbonyl is shown in equation 37 (dppm ligands omitted for clarity). The first step of this mechanism probably involves the coordination of a 13-carbon monoxide molecule to give a 48 electron species identical to 94 (vide supra) which then expels the unlabelled carbonyl group to give the enriched cluster. This type of mechanism is likely to be operative provided that the energy difference between the intermediate and the product is relatively small. If such a mechanism is operative, the absence of labelled carbonyl on the adjacent bridging carbonyls tends to indicate that there is no pseudorotation of the \(\text{Rh}(\text{CO})_4\)
fragment before carbon monoxide is lost. Alternatively, the bridging carbonyls may remain bridging in the intermediate such as to gain stabilization. Another possibility for the exchange of the unique carbonyl group is to invoke an interchange type mechanism where the unique terminal carbonyl group begins to leave as the incoming 13-labelled carbon monoxide molecule approaches the bridging rhodium centre.
If a similar associative mechanism (scheme 11) is to be invoked for the cluster phosphine complexes, it is necessary to assume that the phosphine should exert a labilizing influence on the bridging carbonyl groups. It has been observed, however, that phosphine substitution in clusters favour the formation of bridging carbonyl groups.\textsuperscript{173,187}

Hence, a dissociative mechanism seems more appropriate for the exchange of the equivalent bridging carbonyls in cluster-phosphine complexes, $\text{Rh}_3(\mu-\text{CO})_3(\text{CO})_2(\mu-\text{L})(\mu-1,2-\text{dppm})_2\text{ClO}_4$ ($\text{L} = \text{PMePh}_2$, $\text{PET}_3$ and $\eta^2$-dppm) (scheme 12).

As a result of the unsaturation of $\text{[Rh}_3(\mu-\text{CO})_3(\text{CO})_2(\mu-1,2-\text{dppm})_2\text{ClO}_4 \cdot \text{CH}_2\text{Cl}_2$ it was believed that this complex may act as an efficient homogeneous catalyst. Hence, the ability of this complex to catalyze the hydrogenation of terminal olefins (1-hexene and 1-octene) was investigated at one atmosphere of dihydrogen at room temperature in dichloromethane. No catalysis was observed during the initial 5 h. On stirring for a period of up to 24 h, however, the initial orange solutions became red-brown with deposition of a black film on the walls of the reaction vessel. Analysis of the samples (column: 25% Carbowax on Chromosorb W; column temperature; hexane/hexene, 80 °C, octane/octene, 90 °C) showed that ca. 90% of 1-octene and 70% of 1-hexene had been converted to their corresponding alkanes. The black deposit is presumably rhodium metal formed by the decomposition of the
Scheme 11
cluster which was probably responsible for the catalytic activity observed. The catalytic activity of the complexes, \( \text{Rh}_3(\mu\text{-CO})_3(\text{CO})_2(3\text{-L})(\mu\text{-l,2-dppm})_2\text{ClO}_4 \) \((L = \text{PMePh}_2, \text{PET}_3, \eta^1\text{-dppm})\) has not yet been investigated.
4.3. Experimental

4.3.1. List of Complexes Synthesized

<table>
<thead>
<tr>
<th>Complex</th>
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</tr>
</thead>
<tbody>
<tr>
<td>$[\text{Rh}_3(\mu-\text{CO})_3(\mu-1,2-\text{dppm})_2]\text{ClO}_4\cdot\text{CH}_2\text{Cl}_2$</td>
<td>221</td>
</tr>
<tr>
<td>$[\text{Rh}_3(\mu-\text{CO})_3(\mu-\text{dppm})_2]2\text{ClO}_4$</td>
<td>222</td>
</tr>
<tr>
<td>$[\text{Rh}_3(\mu-\text{CO})_3(3-\text{PPh}_3)(\mu-1,2-\text{dppm})_2]\text{ClO}_4$</td>
<td>222</td>
</tr>
<tr>
<td>$[\text{Rh}_3(\mu-\text{CO})_3(3-\text{PMePh}_2)(\mu-1,2-\text{dppm})_2]\text{ClO}_4$</td>
<td>222</td>
</tr>
<tr>
<td>$[\text{Rh}_3(\mu-\text{CO})_3(3-\text{PET}_3)(\mu-1,2-\text{dppm})_2]\text{ClO}_4$</td>
<td>223</td>
</tr>
<tr>
<td>$[\text{Rh}_3(\mu-\text{CO})_3(3-\text{dppm})(\mu-1,2-\text{dppm})_2]\text{ClO}_4\cdot0.5\text{CH}_2\text{Cl}_2$</td>
<td>223</td>
</tr>
</tbody>
</table>

Reaction of $[\text{Rh}_2(\mu-\text{OC}_2\text{H}_5)(\mu-\text{dppm})_2]\text{ClO}_4$ with $\text{Rh}_2\text{Cl}_2(\text{CO})_4$ under carbon monoxide pressure.
4.3.2. Synthetic Procedures

Preparation of \([\text{Rh}_3(\mu-\text{CO})_3(\text{CO})_3(\mu-1,2\text{-dppm})_2]\text{ClO}_4\cdot\text{CH}_2\text{Cl}_2\)

A solution containing \([\text{Rh}_2(\mu-\text{OC}_2\text{H}_5)(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4\) (0.20 g, 0.17 mmol) dissolved in 5 mL of dichloromethane and 0.5 mL of ethanol, was subjected to carbon monoxide pressure (30 psi) for 2 h. During the course of the reaction a colour change from yellow to red-brown was observed and an orange precipitate developed. After venting the reaction vessel, diethyl ether was added dropwise to complete the precipitation. The product was collected by filtration, washed with diethyl ether, and recrystallized from dichloromethane-diethyl ether to give fine orange needles (0.085 g, 52% based on available rhodium).

Identical product could also be obtained by using the methoxy analogue with similar yields (0.083 g, 51% based on available rhodium). The reaction could also be carried out in the absence of added alcohol but the yields were found to be somewhat low (\(R = \text{CH}_3\); 0.058 g, 35%; \(R = \text{C}_2\text{H}_5\); 0.052 g, 32% based on available rhodium). \([\text{Rh}_2(\mu-\text{OH})(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4\) also gave the identical product when subjected to conditions analogous to that described for \([\text{Rh}_2(\mu-\text{OC}_2\text{H}_5)(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4\), but without added alcohol (0.055 g, 34% based on available rhodium). In the presence of added alcohol (methanol or ethanol), however, the yields became comparable with those obtained from \([\text{Rh}_2(\mu-\text{OR})(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4\).
Preparation of \([\text{Rh}_3(\mu-\text{CO})_3(\text{CO})_2(3\text{-PPh}_3)(\mu-1,2\text{-dppm})_2]\text{ClO}_4\)

To \([\text{Rh}_3(\mu-\text{CO})_3(\text{CO})_2(\mu-1,2\text{-dppm})_2]\text{ClO}_4\cdot\text{CH}_2\text{Cl}_2\) (0.05 g; 0.035 mmol) suspended in 5 mL of dichloromethane was added one mole of triphenylphosphine (0.0092 g; 0.035 mmol) with stirring. The suspended solid immediately went into solution to give a red solution with gas evolution and precipitated an orange solid almost quantitatively. The product was removed by filtration, and washed with diethyl ether (0.052 g, 94%). Anal. Calcd for \(\text{C}_{73}\text{H}_{59}\text{P}_9\text{O}_9\text{ClRh}_2\): C, 55.52; H, 3.77; P, 9.81%. Found: C, 55.17; H, 3.59; P, 8.90%.

Preparation of \([\text{Rh}_3(\mu-\text{CO})_3(\text{CO})_2(3\text{-PMcPh}_2)(\mu-1,2\text{-dppm})_2]\text{ClO}_4\)

\([\text{Rh}_3(\mu-\text{CO})_3(\text{CO})_2(\mu-1,2\text{-dppm})_2]\text{ClO}_4\cdot\text{CH}_2\text{Cl}_2\) (0.10 g, 0.070 mmol) was suspended in 5 mL of dichloromethane to which was added a slight excess of methyldiphenylphosphine (0.015 mL, 0.075 mmol). The suspended solid immediately dissolved to give a red solution with gas evolution. After stirring for 10 min, diethyl ether was added to the red solution to precipitate an orange solid. Filtration followed by recrystallization with dichloromethane-diethyl
ether gave the product as red-orange crystals (0.091 g, 86%).

Anal. Calcd for $C_{68}H_{57}P_{5}O_{9}ClRh_3$: C, 53.83; H, 3.79;
P, 10.20%. Found: C, 52.81; H, 3.62; P, 10.07%.

$\lambda_M = 128 \text{ cm}^2 \text{ mol}^{-1} \text{ mol}^{-1}$ (acetone).

Similar procedures employing triethylphosphine
(0.011 g, 0.074 mmol) and bis(diphenylphosphino)methane
(0.0269 g, 0.070 mmol) also gave analogous products as
orange (0.073 g, 73%) and red (0.11 g, 90%) crystals
respectively, latter being isolated as a dichloromethane
hemi-solvate.

$$[\text{Rh}_3(\mu-\text{CO})_2(3-P(\text{Et})_3)(\mu-1,2\text{-dppm})_2]\text{ClO}_4$$

Anal. Calcd for $C_{61}H_{59}P_{7}O_{9}ClRh_3$: C, 51.04; H, 4.15;
P, 10.79%. Found: C, 49.99; H, 3.93; P, 9.40%.

$\lambda_M = 128 \text{ cm}^2 \text{ mol}^{-1}$ (acetone).

$$[\text{Rh}_3(\mu-\text{CO})_2(3-\eta^{-1}\text{-dppm})(\mu-1,2\text{-dppm})_2]\text{ClO}_4\cdot0.5\text{CH}_2\text{Cl}_2$$

Anal. Calcd for $C_{80.5}H_{67}P_{6}O_{9}Cl_2\text{Rh}_3$: C, 55.41; H, 3.87;
P, 10.65%. Found: C, 55.04; H, 3.73; P, 11.42%.

$\lambda_M = 124 \text{ cm}^2 \text{ mol}^{-1}$ (acetone).

Reaction of $[\text{Rh}_2(\mu-\text{OC}_2\text{H}_5)(\text{CO})_2(\mu\text{-dppm})_2]\text{ClO}_4$ with
$\text{Rh}_2\text{Cl}_2(\text{CO})_4$ under carbon monoxide pressure

$$[\text{Rh}_2(\mu-\text{OC}_2\text{H}_5)(\text{CO})_2(\mu\text{-dppm})_2]\text{ClO}_4 (0.1 \text{ g}, 0.085 \text{ mmol}),$$
and $\text{Rh}_2\text{Cl}_2(\text{CO})_4 (0.017 \text{ g}, 0.043 \text{ mmol})$ was dissolved in 5 mL
of dichloromethane and subjected to carbon monoxide pressure
(30 psi) for 2 h. After venting the reaction vessel, diethyl ether was added to precipitate an orange crystalline product. The product was filtered and recrystallized with dichloromethane-diethyl ether in an atmosphere of carbon monoxide (0.075 g, 74%). This product was identified as 

\[ \text{[Rh}_2(\mu-\text{Cl})(\mu-\text{CO})(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4 \]

from its IR spectrum (\(\nu(\text{CO})\), 2006 (sh), 1991 (vs) and 1874 (m) cm\(^{-1}\) in dichloromethane). When the reaction was carried out using Rh(COD)-(acac) or [Rh(COD)(PPh\(_3\))\(_2\)]ClO\(_4\) instead of Rh\(_2\)(C\(_2\))\(_2\)(CO)\(_4\), [Rh\(_3\)(\mu-\text{CO})_3(\text{CO})_3(\mu-1,2\text{-dppm})_2]\text{ClO}_4\cdot\text{CH}_2\text{Cl}_2 could be isolated (0.030 g, 37% based on available rhodium). Rh\(_2\)(C\(_2\))\(_2\)(CO)\(_4\)\(^{188}\), [Rh(COD)(PPh\(_3\))\(_2\)]ClO\(_4\)\(^{189}\) and Rh(COD)(acac)\(^{190}\) were prepared using published procedures.
<table>
<thead>
<tr>
<th>Compound</th>
<th>$\nu$(CO)$_a$, cm$^{-1}$</th>
<th>$\nu$(CO)$_b$, cm$^{-1}$</th>
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<tbody>
<tr>
<td>[Rh$_3$(u-CO)$_3$(CO)$_3$(u-1,2-dppm)$_2$]ClO$_4$-CH$_2$Cl$_2$</td>
<td>2032 (m), 2008 (vs), 1929 (w), 1872 (sh), 1869 (s)</td>
<td>2035 (m), 2000 (sh), 1998 (vs), 1924 (w), 1869 (sh), 1858 (s)</td>
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<tr>
<td>[Rh$_3$(u-CO)$_3$(CO)$_3$(3-13CO) (u-1,2-dppm)$_2$]ClO$_4$-CH$_2$Cl$_2$</td>
<td>2008 (vs), 1980 (m), 1929 (w), 1872 (sh), 1869 (s)</td>
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<tr>
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<td>1993 (m), 1977 (vs), 1934 (mw), 1849 (s), 1640 (s)</td>
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<tr>
<td>[Rh$_3$(u-CO)$_3$(CO)$_3$(3-PMePh$_2$) (u-1,2-dppm)$_2$]ClO$_4$</td>
<td>2003 (sh), 1993 (vs), 1920 (mw), 1853 (s), 1845 (sh)</td>
<td>1992 (m), 1982 (sh), 1975 (vs), 1919 (mw), 1855 (s), 1837 (sh)</td>
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<tr>
<td>[Rh$_3$(u-CO)$_3$(CO)$_3$(3-PMePh$_2$) (u-1,2-dppm)$_2$]ClO$_4$</td>
<td>2003 (sh), 1993 (vs), 1977 (mw), 1853 (m), 1811 (s)</td>
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<tr>
<td>[Rh$_3$(u-CO)$_3$(CO)$_3$(3-PEt$_3$) (u-1,2-dppm)$_2$]ClO$_4$</td>
<td>2002 (sh), 1991 (vs), 1919 (mw), 1850 (s), 1841 (sh)</td>
<td>1980 (s), 1974 (vs), 1920 (mw), 1844 (vs), 1827 (s)</td>
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<td>[Rh$_3$(u-CO)$_3$(CO)$_3$(3-PEt$_3$) (u-1,2-dppm)$_2$]ClO$_4$</td>
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<tr>
<td>[Rh$_3$(u-CO)$_3$(CO)$_3$(3-n$_1$-dppm) (u-1,2-dppm)$_2$]ClO$_4$-0.5CH$_2$Cl$_2$</td>
<td>2003 (sh), 1995 (vs), 1918 (mw), 1850 (s), 1845 (sh)</td>
<td>1955 (sh), 1978 (vs), 1921 (mw), 1849 (sh), 1844 (s)</td>
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<tr>
<td>[Rh$_3$(u-CO)$_3$(CO)$_3$(3-n$_1$-dppm) (u-1,2-dppm)$_2$]ClO$_4$-0.5CH$_2$Cl$_2$</td>
<td>2003 (sh), 1995 (vs), 1980 (sh), 1850 (m), 1810 (s)</td>
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</tr>
</tbody>
</table>

(a) Recorded in dichloromethane solution.

(b) Recorded as nujol mulls on potassium bromide plates.
Table 4.2. NMR ($^1$H, $^{31}$P($^1$H) and $^{13}$C($^1$H)) Data of [Rh$_3$(μ-CO)$_3$(μ-1,2-dppm)$_2$]ClO$_4$.CH$_2$Cl$_2$ and Its Phosphine Derivatives

<table>
<thead>
<tr>
<th>Compound</th>
<th>NMR $^a,b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Rh$_3$(μ-CO)$_3$(μ-1,2-dppm)$_2$]ClO$_4$.CH$_2$Cl$_2$</td>
<td>$^{31}$P: 25.60 (m, dppm, $^1$J$<em>{Rh-P}$ + $^3$J$</em>{Rh-P}$ = 93.7 Hz, $^2$J$_{Rh-P}$ = 2.5 Hz)</td>
</tr>
<tr>
<td></td>
<td>$^1$H: 7.37 (m, 40H, Phenyl), 5.32 (s, CH$_2$Cl$_2$); 3.40 (m, 4H, CH$_2$-dppm)</td>
</tr>
<tr>
<td>[Rh$_3$(μ-CO)$_3$(CO)$_2$(3-$^{13}$CO)(μ-1,2-dppm)$_2$]ClO$_4$.CH$_2$Cl$_2$</td>
<td>$^{13}$C: 185.7 (d, $^1$J$_{Rh-C}$ = 90.0 Hz)</td>
</tr>
<tr>
<td>[Rh$_3$(μ-CO)$_3$(CO)$_2$(3-PMePh$_2$)(μ-1,2-dppm)$_2$]ClO$_4$</td>
<td>$^{31}$P: 24.52 (m, dppm, $^1$J$<em>{Rh-P}$ + $^3$J$</em>{Rh-P}$ = 100.6 Hz)</td>
</tr>
<tr>
<td></td>
<td>$^{17}$C: 111 (dt, PMePh$<em>2$), $^1$J$</em>{Rh-P}$ = 200.8 Hz, $^2$J$_{Rh-P}$ = 6.9 Hz)</td>
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<tr>
<td></td>
<td>$^1$H: 7.21 (m, 50H, Phenyl); 3.65 (m, 4H, CH$_2$-dppm); 1.92 (dd, 3H, PMePh$_2$)</td>
</tr>
<tr>
<td></td>
<td>$^2$J$<em>{P-N}$ = 8.0 Hz, $^3$J$</em>{Rh-H}$ = 1.8 Hz)</td>
</tr>
<tr>
<td>[Rh$_3$(μ-CO)$_3$(13CO)$_2$(3-PMePh$_2$)(μ-1,2-dppm)$_2$]ClO$_4$</td>
<td>$^{13}$C: 245.7 (dm, 55 Hz)</td>
</tr>
<tr>
<td>[Rh$_3$(μ-CO)$_3$(13CO)$_2$(3-PMePh$_2$)(μ-1,2-dppm)$_2$]ClO$_4$</td>
<td>$^{31}$P: 23.31 (m, dppm, $^1$J$<em>{Rh-P}$ + $^3$J$</em>{Rh-P}$ = 101.2 Hz)</td>
</tr>
<tr>
<td></td>
<td>$^{17}$C: 111 (dt, PMePh$<em>2$), $^1$J$</em>{Rh-P}$ = 200.8 Hz, $^2$J$_{Rh-P}$ = 6.9 Hz)</td>
</tr>
<tr>
<td></td>
<td>$^1$H: 7.26 (m, 50H, Phenyl); 3.71 (m, 4H, CH$_2$-dppm)</td>
</tr>
<tr>
<td></td>
<td>$^2$J$<em>{P-N}$ = 8.0 Hz, $^3$J$</em>{Rh-H}$ = 1.8 Hz)</td>
</tr>
</tbody>
</table>

(continued)
Table 4.2. (continued)

<table>
<thead>
<tr>
<th>Compound</th>
<th>NMR (^{\text{a},b})</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Rh}_3(\mu-\text{CO})_3(\text{CO})_2(\mu-1,2-\text{dppm})_2]\text{ClO}_4\cdot 0.5\text{CH}_2\text{Cl}_2)</td>
<td>(^{13}\text{C} : 247.0(\text{dm}, 53 \text{ Hz}))</td>
</tr>
<tr>
<td>([\text{Rh}_3(\mu-\text{CO})_3(\text{CO})_2(\mu-1,2-\text{dppm})_2]\text{ClO}_4\cdot 0.5\text{CH}_2\text{Cl}_2)</td>
<td>(^{31}\text{P} : 24.87(\text{m}, \text{dppm}), \left</td>
</tr>
<tr>
<td>([\text{Rh}_3(\mu-\text{CO})_3(\text{CO})_2(\mu-1,2-\text{dppm})_2]\text{ClO}_4\cdot 0.5\text{CH}_2\text{Cl}_2)</td>
<td>(^{1}H : 7.17(\text{m}, 6 \text{H}, \text{Phenyl}); 5.32(\text{s}, \text{CH}_2\text{Cl}_2); 3.90, 3.61(\text{m}, 4 \text{H}, \text{CH}<em>2\text{-dppm}); 3.17(\text{t}, 2 \text{H}, \text{n-dppm}, 2\text{J}</em>{\text{P-H}} = 5.1 \text{ Hz}))</td>
</tr>
</tbody>
</table>

Abbreviations: \(\text{Rh}_b\) = bridging rhodium atom; \(\text{P}_b\) = phosphorus attached to bridging rhodium atom.

(a) Chemical shifts (in ppm) relative to tetramethylsilane \(^1\text{H}\) and \(^{13}\text{C}\) and 85% phosphoric acid \(^{31}\text{P}\).

(b) \(^1\text{H}\) NMR spectra recorded in dichloromethane-\(d_2\).

(c) These could be resolved at 360 MHz \((3.36, 3.65, \text{m}, 4 \text{H})\).

(d) The degree of solvation was determined by recording the \(^1\text{H}\) NMR spectrum in acetone-\(d_6\) \((5.60, \text{s}, 2 \text{H})\).

(e) Multiplet separation is given in Hz.

(f) The degree of solvation was determined by recording the \(^1\text{H}\) NMR spectrum in acetone-\(d_6\) \((5.60, \text{s}, 1 \text{H})\).

(g) At -40°C. Broad lines with width at half height approximately equal to 40 Hz.

(h) At 360 MHz.
CHAPTER 5

THE REACTIVITY OF CARBOXYLATE BRIDGED COMPLEXES

5.1. Introduction

This chapter discusses the reactivity of the carboxylate complexes, \[ \text{[Rh}_2(\mu-O_2CR)(CO)_2(\mu-dppm)_2]ClO}_4 \] (R = H, CH₃, CH₂Cl, CHCl₂, CCl₃ and CF₃) described in Chapter 3 with carbon monoxide and a 1:1 mixture of dihydrogen/carbon monoxide. In addition, the oxidative addition of halogens (Cl₂, Br₂ and I₂) to some members (R = H, CH₃ and CF₃) of this carboxylate family will be discussed. The previous work on carboxylate bridged rhodium-dppm complexes and their reactivity has been discussed in section 1.2.3.

5.2. Results and Discussion

IR data of complexes described in sections 5.2.1 and 5.2.2 are given in table 5.1 whereas \(^3\text{P}[^1\text{H}]\) and \(^1\text{H} \) NMR data are tabulated in table 5.2. All other physical data are given after each experimental procedure.

5.2.1. Reactions with Carbon Monoxide

\[ \text{[Rh}_2(\mu-O_2CCH}_₃)(CO)_2(\mu-dppm)_2]ClO}_4 \] did not form a stable adduct with carbon monoxide at room temperature.
Magae et al., however, have investigated the binding of carbon monoxide to [Rh$_2$(μ-O$_2$CR)(CO)$_2$L]PF$_6$ (R = CH$_3$, L = dppm, dpam; R = C$_2$H$_5$, L = dppm) at -70 °C. This investigation has revealed that only [Rh$_2$(μ-O$_2$CCH$_3$)(CO)$_2$(μ-dppm)$_2$]PF$_6$ forms a carbon monoxide adduct, Rh$_2$(μ-CO)(μ-O$_2$CCH$_3$)-(CO)$_2$(μ-dppm)$_2$]PF$_6$, which reverts to the starting material on warming.

In contrast, all the halide-bridged complexes, [Rh$_2$(μ-O$_2$CR)(CO)$_2$(μ-dppm)$_2$]ClO$_4$ (R = CH$_2$Cl, CHCl$_2$, CCl$_3$ and CF$_3$) were found to bind carbon monoxide between the metal centres at room temperature to give stable isolable complexes (equation 38). These complexes have been characterized as [Rh$_2$(μ-CO)(μ-O$_2$CR)(CO)$_2$(μ-dppm)$_2$]ClO$_4$ (97) by IR and $^{31}$P NMR spectroscopy. One member of the series (R = CF$_3$)

\[
\begin{align*}
\text{Rh} & \quad \text{C} \quad \text{O} \\
\text{O} & \quad \text{R} \\
\text{Rh} & \quad \text{C} \quad \text{O} \\
\text{O} & \quad \text{R} \\
\end{align*}
\]

\[\text{CO} \quad \text{Rh} \quad \text{C} \quad \text{O} \quad \text{Rh} \quad \text{CO} \]

\[\text{(38)}\]

has also been structurally characterized and shown to possess a bridging carbonyl group with the carboxylate group bridging the two metal centres in a bidentate fashion.
The $^{31}\text{P}^{1}\text{H}$ NMR spectra of these complexes, at -35 °C under one atmosphere of carbon monoxide exhibited a typical AA'X'XX' pattern, in keeping with the structural assignments. A representative example of the $^{31}\text{P}^{1}\text{H}$ NMR spectra obtained for these complexes is shown in figure 5.1 for $\text{[Rh}_2(\mu-\text{CO})(\mu-\text{O}_2\text{CCHCl}_2)(\text{CO})_2(\mu-\text{dppm})_2\text{]}\text{ClO}_4$. These spectra were recorded at low temperatures in order to eliminate intermolecular exchange of carbonyl ligands. The $^{31}\text{P}$ chemical shifts and coupling constants range from 31-34 ppm and 93-94 Hz respectively (table 5.2). These values are similar to those previously observed for $\text{Rh}_2(\mu-\text{CO})(\mu-\text{O}_2\text{CCH}_2)(\text{CO})_2(\mu-\text{dppm})_2\text{]}\text{PF}_6$ (30.0 ppm, $|J_{\text{Rh-P}} + xJ_{\text{Rh-P}}| = 93.2$ Hz).

The IR spectra (table 5.1) of these carbon monoxide adducts contained bands that could be assigned to both terminal and bridging carbonyl groups as well as carboxylate functions. Inspection of the carboxylate frequencies of the carbon monoxide adducts indicates that they are shifted to lower frequencies upon carbon monoxide uptake, by comparison to the parent complexes (table 2.1, Chapter 2). This suggests that the carboxylate function of the carbon monoxide adducts remain bidentate since a monodentate bridging mode would give rise to a large shift in the opposite direction as a result of the increased double bond character of the carboxylate carbonyl group. This has been confirmed by an X-ray structural determination of $\text{Rh}_2(\mu-\text{CO})(\mu-\text{O}_2\text{CCF}_3)(\text{CO})_2(\mu-\text{dppm})_2\text{]}\text{ClO}_4\cdot\text{CH}_2\text{Cl}_2$, performed by Prof. T.S. Cameron.
Figure 5.1. $^{31}$P$^{1}$H NMR Spectrum of $[\text{Rh}_2(\mu-\text{CO})(\mu-\text{O}_2\text{CCHCl}_2)-(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4$ in Dichloromethane at $-35 \, ^\circ\text{C}$.
The equatorial plane of the complex with some relevant bond distances are given in figure 5.2. Some relevant bond angles and the perspective view of the cation are given in Appendix IV. The equatorial plane of the complex is comprised of a bridging carbonyl group, trifluoroacetate group and two terminal carbonyl groups attached to each metal. Additionally, the rhodium-rhodium distance of 2.784(2) Å indicates that these two atoms are joined by a single bond. This value falls within the range (2.8415(7) - 2.7566(8) Å)\(^{20,42,43}\) normally encountered for rhodium-rhodium single bonds in similar complexes. Excluding the rhodium-rhodium single bond, each metal centre exhibits a distorted trigonal-bipyramidal geometry with the two coordination spheres sharing a common edge at C(7) belonging to the bridging carbon.

Both terminal carbonyl groups are oriented approximately trans to the rhodium-rhodium single bond \((\text{Rh}(1)-\text{Rh}(2)-\text{C}(6) = 156.9(5)°, \text{Rh}(2)-\text{Rh}(1)-\text{C}(5) = 156.5(5)°)\) and are bent towards the bridging carbonyl group by about 24°. A similar arrangement has been observed in [Rh\(_2(\mu-\text{Cl})-(\mu-\text{CO})(\text{CO})_2(\mu-\text{dppm})_2]B\text{Ph}_4\).\(^{20}\) The Rh-C-O angles of 172(1)° and 173(1)° indicate a slight deviation from linearity which may be a result of crystal packing. The Rh-C-(av) distance of 1.83(3) Å falls within the range usually observed for Rh(1) complexes (typically 1.80-1.84 Å).\(^{20,29,30}\)
Figure 5.2: The Equatorial Plane of the Cation,

\[ \text{[Rh}_2(\mu-\text{CO})(\mu-O_2\text{CCF}_3)(\text{CO})_2(\mu-\text{dppm})_2]^+ \]

Esd's of the bond lengths are indicated by subscripts.
The bridging carbonyl group is symmetrically bound to the two rhodium atoms. As usual the Rh-C distances associated with the bridging carbonyl group (1.98(1) and 2.00(1) Å) are longer than those to the terminal carbonyl groups (1.80(2) and 1.85(2) Å). These Rh-C distances are not unusual and compare favourably with other determinations. For example, \( \text{Rh}_2(\mu-\text{CO})(\mu-\text{DMAD})\text{Cl}_2(\mu-\text{dppm})_2 \) \(^{79}\) [\( \text{Rh}_2(\mu-\text{CO})[\text{CO}_2\text{OH}]_3(\mu-\text{dppm})_2 \)]PF\(_5\) 0.5(CH\(_3\))\(_2\)CO, \(^{112}\) and [\( \text{Rh}_2(\mu-\text{CO})(\mu-\text{CO})(\text{CO})_2(\mu-\text{dppm})_2 \)]BPh\(_4\) \(^{20}\) all have Rh-C (bridging) distances in the range 1.977(4) to 2.104(7) Å. The Rh-C-Rh angle of 89.1(5)° is comparable to those exhibited by other groups bridging rhodium-rhodium single bonds. The trifluoroacetate group is asymmetrically connected to the rhodium atom and more tightly bound to the Rh(1) centre in preference to the Rh(2) (Rh(1)-O(2) = 2.30(1) and Rh(2)-O(1) = 2.39(1) Å). The asymmetry of the bridging trifluoroacetate group probably arises to avoid some non-bonded contacts since a chemical difference cannot be expected between the two rhodium atoms. The Rh-O distances of the present complex are significantly longer than those observed for the parent complex [\( \text{Rh}_2(\mu-\text{OCCF}_3)(\text{CO})_2(\text{CO})_2\)Cl\(_4\) \( (2.09(1), 2.15(1) \) Å\)] \(^{\text{vide infra}}\) as well as those in some typical Rh(1) complexes. For example, Rh(acac)(CO)(PPh\(_3\)) has Rh(1)-O distances of 2.029 and 2.087 Å. \(^{191}\) Somewhat similar behaviour has been observed for Rh-Cl distances in [\( \text{Rh}_2(\mu-\text{Cl})(\mu-\text{CO})(\text{CO})_2(\text{CO})_2(\mu-\text{dppm})_2 \)]BPh\(_4\) \(^{20}\) and [\( \text{Rh}_2(\mu-\text{Cl})(\text{CO})_2(\mu-\text{dppm})_2 \)].
The Rh-Cl distances are significantly longer in the former compound than in the latter.

The bond distances and angles are not unusual within the trifluoroacetate group (Appendix IV). These distances and angles compare favourably with other dimeric complexes bridged by the trifluoroacetate group such as Mo$_2$(O$_2$CCF$_3$)$_4$ and Rh$_2$(O$_2$CCF$_3$)$_4$(PPh$_3$)$_2$. As observed in [Rh$_2$(μ-Cl)(μ-CO)(CO)$_2$(μ^-dppm)$_2$]BF$_4$ and in many other complexes with bridging ligands, the methylene groups of the dppm in the present complex are cis folded and tipped towards the bulky trifluoroacetate group.

All the carbon monoxide adducts, [Rh$_2$(μ-CO)(μ-O$_2$CR)(CO)$_2$(μ^-dppm)$_2$]ClO$_4$ (R = CH$_2$Cl, CHCl$_2$, CCl$_3$ and CF$_3$) are either yellow or yellow-orange in the solid state. On exposure to the atmosphere, however, they became red within a period of 24-48 h. Although the red colour may imply reversion to the starting material, it appears to be only a surface phenomenon for most complexes. The times taken for the complexes to lose carbon monoxide completely and revert to starting material are as follows; R = CH$_2$Cl, 4 days; R = CHCl$_2$, 10 days; R = CCl$_3$, 24 h; R = CF$_3$, >6 months. The bridging carbon monoxide group, however, can be removed from all complexes by heating under vacuum at 100 °C for 30-45 min or by dissolution in dichloromethane. At the beginning of this discussion, it was mentioned that...
[Rh$_2$(μ-O$_2$CCH$_3$)(CO)$_2$(μ-dppm)$_2$]ClO$_4$ showed the binding of carbon monoxide at -75 °C whereas the other complexes.

[Rh$_2$(μ-O$_2$C$^R$)(CO)$_2$(μ-dppm)$_2$]ClO$_4$ ($R = CH_2Cl, CHCl_2, CCl_3$ and $CF_3$) reacted with carbon monoxide at room temperature. This difference in behaviour is certainly thermodynamic in origin. It is not clear, however, as to how electronegative substituents attached to the carboxylate group facilitate the binding of carbon monoxide at room temperature.

In contrast to the carboxylate dimer, [Rh$_2$(μ-O$_2$CR)-(CO)$_2$(μ-dppm)$_2$]ClO$_4$ ($R = CH_2Cl, CHCl_2, CCl_3$ and $CF_3$), the reaction of [Rh$_2$(μ-O$_2$CH)(CO)$_2$(μ-dppm)$_2$]ClO$_4$ with carbon monoxide took an alternate path. The reaction occurred with decomposition of the formate group to produce red-brown [Rh$_2$(μ-H)(μ-CO)(CO)$_2$(μ-dppm)$_2$]ClO$_4$ (98) (equation 39).

While this work was in progress, Eisenberg and coworkers$^{46}$ reported the synthesis of [Rh$_2$(μ-H)(μ-CO)(CO)$_2$(μ-dppm)$_2$]$^+$ by two methods which involve either the reaction of the neutral dimer Rh$_2$(CO)$_2$(μ-dppm)$_2$ with acid (H$^+$) followed by
carbon monoxide or the reaction of \([\text{Rh}_2(\mu-OCH)(CO)_2(\mu-dppm)_2]\)PF₆ with carbon monoxide. They obtained the hydride species as a purple dichloromethane solvate or toluene solvated hexafluorophosphate salt, depending on the solvent used in the reaction or as a dark green tetrahydrofuran solvated p-toluene sulphonate salt.

IR spectrum of the red-brown \([\text{Rh}_2(\mu-H)(\mu-CO)(CO)_2(\mu-dppm)_2]\)ClO₄ in the solid state showed two terminal carbonyl bands (2002(s), 1989(vs) cm⁻¹) and one bridging carbonyl group (1898(s) cm⁻¹) and no bands attributable to the formate group were present. In solution the carbonyl bands were at 2003(sh), 1992(vs) and 1902(m) cm⁻¹. The \(^1H\) NMR spectrum in dichloromethane-d₂ (360 MHz) exhibited a broad featureless hydride resonance at -9.76 ppm confirming the presence of a bridging hydride. The \(^{31}P\)\(^{1H}\) NMR spectrum showed a symmetric second order pattern (28.65 ppm, \(|J_{\text{Rh-P}} + XJ_{\text{Rh-P}}| = 109 \text{ Hz}\)) belonging to the AA'"A"XX' spin system. The preparation of this complex as the hexafluorophosphate was also performed. The dark red solution obtained by the reaction of \([\text{Rh}_2(\mu-OCH)(CO)_2(\mu-dppm)_2]\)PF₆ with carbon monoxide showed IR bands at 2003(sh), 1992(vs) and 1902(m) cm⁻¹ which were markedly different from those reported by Eisenberg et al. (1980(s), 1963(vs) and 1870(s) cm⁻¹). Furthermore, no purple product could be isolated from the solution upon addition of diethyl ether.
Instead, only a brown crystalline solid could be obtained. The IR spectrum of this complex in the solid state was slightly different from that of the perchlorate salt in that two bands (1873(m), 1898(m) cm\(^{-1}\)) in the bridging carbonyl region were observed. This seems, however, to arise from a solid state effect, since the solution IR spectrum had only one band in the bridging region and was identical to that of the perchlorate salt. Purple crystals, however, could be isolated by storing the solution at -18 °C for ca. 15 h. IR spectrum of these purple crystals in the solid state showed bands at 1995(sh), 1984(vs) and 1874(m) cm\(^{-1}\) and in dichloromethane they appeared at 2003(sh), 1992(vs) and 1902(m) cm\(^{-1}\). The \(^1\)H NMR spectrum indicated that the purple crystals are dichloromethane solvated (5.60 ppm, acetone-d\(_6\), 2H) similar to that observed by Eisenberg. Although the IR data observed for the purple crystals are different to those reported by Eisenberg, it does appear that these complexes are one and the same.

One possible mechanism by which the bridging formate breaks down in the presence of carbon monoxide is shown in scheme 13 (dppm bridges are not shown). The first step may involve the coordination of carbon monoxide between the metal centres as observed for other carboxylate complexes. The second step may involve the change in the formate coordination from bridging bidentate to monodentate which may then
Rh(I') + CO → Rh-CO

Scheme 13

undergo β-hydride elimination to form the rhodium-hydride and carbon dioxide. Precedent for this type of reaction has been reported by Masters. This involves the rapid elimination of carbon monoxide from IrH(Cl)(CO)(CH₂)L₂, formed by the oxidative addition of formic acid to IrCl(CO)L₂, to give the dihydro species IrH₂Cl(CO)L₂ (L = PPh₃). In fact, the decomposition of formate groups is a commonly used route to metal 'hydride' complexes.
As mentioned in Chapter 1, the binding of carbon monoxide in the endo pocket of the A-frame takes place via the initial attack of carbon monoxide at one rhodium centre only, with the previously ligated carbon monoxide group moving simultaneously into the bridging position. A similar mechanism was found to be operative in the binding of carbon monoxide to the carboxylate complexes. This was established through solution IR spectroscopy by reacting $[\text{Rh}_2(\mu-O_2\text{CCF}_3)(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4$ with one equivalent of 13-carbon monoxide in dichloromethane at -78 °C. The unlabelled complex, $[\text{Rh}_2(\mu-\text{CO})(\mu-O_2\text{CCF}_3)(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4$ is known to exhibit terminal carbonyl absorptions at 2009(sh), 1977(vs) cm$^{-1}$ and a bridging carbonyl stretch at 1841(m) cm$^{-1}$ in dichloromethane (table 5.1). When a dichloromethane solution of $[\text{Rh}_2(\mu-O_2\text{CCF}_3)(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4$ ($\nu(\text{CO}) = 2007(s), 1995(\text{sh})$ cm$^{-1}$) was treated with one equivalent of 13-carbon monoxide at -78 °C, new carbonyl bands appeared at 2006(s), 1957(m) and 1841(m) cm$^{-1}$ establishing that the label was appearing in the terminal rather than the bridging position.

The structure of $[\text{Rh}_2(\mu-O_2\text{CCF}_3)(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4$ in the solid state would seem to have relevance to this mechanism (vide infra). The structure of $[\text{Rh}_2(\mu-O_2\text{CCF}_3)(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4$ was initially undertaken to confirm the bidentate bridging behaviour of the carboxylate group as
evident from UV spectra, and also in an attempt to get information regarding the extreme lability of the trifluoroacetate group.

The structure determination of \( \text{Rh}_2(\mu-\text{O}_2\text{CCF}_3)(\text{CO})_2(\mu-\text{dppm})_2\text{ClO}_4 \) was performed by Prof. T.S. Cameron, establishing the bidentate mode of the trifluoroacetate group. Figure 5.3 depicts the ligand in the equatorial plane with some relevant bond distances. Some data relevant to this structure including the perspective view of the cation are given in Appendix V.

The coordination about each of the two rhodium atoms exhibits distorted square planar geometry and involves bonding to trans dppm ligands, terminal carbonyl group and one oxygen of the bridging trifluoroacetate. The rhodium-rhodium distance of 2.982(2) Å is intermediate between non-bonding rhodium-rhodium distances (3.34-3.15 Å)\(^{29,30,112}\) and bonding rhodium-rhodium distances (2.84-2.75 Å)\(^{20,42,43}\). Conventional electron counting techniques do not require a formal rhodium-rhodium single bond in this compound and each metal atom has a sixteen electron configuration. This suggests that although no formal rhodium-rhodium single bond is present, there is significant rhodium-rhodium interaction as observed in the UV spectrum (\textit{vide supra}). The shortening of the metal-metal distance may also have its origin in the bite size of the trifluoroacetate group which may not be
Figure 5.3. The Equatorial Plane of the Cation, $[\text{Rh}_2(\mu-O_2\text{CCF}_3)(\text{CO})_2(\mu-\text{dppm})_2]^+$

Esd's of bond lengths are indicated by subscripts.
capable of spanning the range of rhodium-rhodium separation that is found in dimeric dppm bridged rhodium complexes without metal-metal bonds.

The Rh-C distances (1.68(2), 1.74(3) Å) of the terminal carbonyl groups are significantly shorter than other terminal Rh-C distances. Comparative distances are 1.807(7), 1.799(7) Å in [Rh₂(µ-Cl)(CO)₂(µ-dppm)₂]BF₄, 1.814(4) Å in trans-Rh₂Cl₂(CO)₂(µ-dppm)₂²² and 1.831(7), 1.836(7) Å in [Rh₂(µ-Cl)(µ-CO)(CO)₂(µ-dppm)₂]BPh₄.²⁰ This suggests that there is extensive π-bonding from metal to ligand causing the shortening of the Rh-C distances. This effect is not, however, reflected in the IR spectrum since the ν(CO) values are comparable with those in other cationic A-frames whose structures are known to exhibit typical Rh-C distances. The carbonyl groups attached to the Rh(2) is bent away from the rhodium-rhodium vector whereas the carbonyl group joined to Rh(1) is tipped towards the bridging site of the metal-metal centres. The observed structure of [Rh₂(µ-O₂CCF₃)(CO)₂(µ-dppm)₂]Clo₄ bears some relevance to the mechanism of carbon monoxide adduct formation in the sense that if one imagines an incoming ligand beginning to associate with Rh(1), then the observed structure represents a point well along the reaction coordinate, assuming, of course, that the structure of [Rh₂(µ-O₂CCF₃)ₐ(CO)₂(µ-dppm)₂]Clo₄ is quite symmetrical in solution. It
would appear, however, that steric factors are most likely responsible for the unusual geometry observed since no close contacts with Rh(1) could be identified.

In \([\text{Rh}_2(\mu-O_2CCF_3)(\text{CO})_2(\mu-dppm)_2]ClO_4\) the trifluoroacetate group bridges in an unsymmetrical fashion between the metal centres. This is evident from the Rh-0 distances (2.09(1), 2.15(1) Å) and the angles, Rh(1)-O(4)-C(53) = 119(1)° and Rh(2)-O(3)-C(53) = 135(1)°. The Rh-0 distances are somewhat longer than normal Rh(l)-O (typically 2.0-2.1 Å) distances. This could possibly be one factor that makes the trifluoroacetate group extremely labile in the present complex.

5.2.2. Reactions with a Hydrogen/Carbon Monoxide Mixture

\([\text{Rh}_2(\mu-O_2CR)(\text{CO})_2(\mu-dppm)_2]ClO_4\) (R = CH_2Cl, CHCl_2, CCl_3 and CF_3) reacted with a mixture of dihydrogen/carbon monoxide (1:1) to give a red-brown crystalline product identified as \([\text{Rh}_2(\mu-H)(\mu-CO)(\text{CO})_2(\mu-dppm)_2]ClO_4\). This product had identical chemical and physical properties to those obtained from the reaction of \([\text{Rh}_2(\mu-O_2CH)(\text{CO})_2(\mu-dppm)_2]ClO_4\) with carbon monoxide. No reaction, however, was observed with \([\text{Rh}_2(\mu-O_2CCH_3)(\text{CO})_2(\mu-dppm)_2]ClO_4\). The reaction of \([\text{Rh}_2(\mu-OCCH_2Cl)(\text{CO})_2(\mu-dppm)_2]ClO_4\) was slower than the other carboxylates and required 3 h to go to
completion. Reaction rates of the remaining carboxylates were moderate, with a reaction time up to 45 min being required.

Carboxylate bridged complexes are known to react with carbon monoxide very rapidly. Therefore, the carbon monoxide adduct should be formed first in the reaction between $\text{Rh}_2(\mu-\text{O}_2\text{CR})(\text{CO})_2(\mu-\text{dppm})_2\text{ClO}_4$ and dihydrogen/carbon monoxide mixture. The carbon monoxide adduct may then react with dihydrogen to form the final product. Some support for this statement is provided by the following experimental observations.

(a) The reaction of $[\text{Rh}_2(\mu-\text{O}_2\text{CCF}_3)(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4$ with a mixture of dihydrogen/carbon monoxide was monitored with slow addition of the gas. This was performed by bubbling a mixture of dihydrogen/carbon monoxide (1:1) very slowly (bubble at a time) through a dichloromethane (5 mL) solution of $[\text{Rh}_2(\mu-\text{O}_2\text{CCF}_3)(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4$ (20 mg). Recording of the IR spectrum after the first 30 seconds had elapsed showed the presence of a medium band at 1841 cm$^{-1}$ and a weak band at 1898 cm$^{-1}$. As the amount of dihydrogen/carbon monoxide was increased the band at 1898 cm$^{-1}$ began to grow in intensity with the expense of the band at 1841 cm$^{-1}$. This continued until the band at 1841 cm$^{-1}$ completely disappeared and no further change in 1898 cm$^{-1}$ band was observed. The bands at 1841 and 1898 cm$^{-1}$ are due to the formation of
(b) The formation of $[\text{Rh}_2(\mu-H)(\mu-CO)(\mu-CO)_2(\mu-dppm)_2]\text{ClO}_4$ by the reaction $[\text{Rh}_2(\mu-H)(\mu-CO)(\mu-dppm)_2]\text{ClO}_4$ or any other species with carbon monoxide could be eliminated since no reaction was observed between carboxylate complexes and dihydrogen. This was verified by recording the $^1\text{H}$ NMR spectrum (360 MHz) of the carboxylate complexes after reacting with dihydrogen for 2 h in dichloromethane-d$_2$. No peaks attributable to metal hydrides could be found up to -40 ppm.

These observations suggest that the formation of $[\text{Rh}_2(\mu-CO)(\mu-O_2CR)(\mu-dppm)_2]\text{ClO}_4$ is essential to the removal of the carboxylate function. This may be related to the fact that the trifluoroacetate ligand appears to be more weakly bound in $[\text{Rh}_2(\mu-CO)(\mu-O_2CR)(\mu-dppm)_2]\text{ClO}_4$ than in the parent complex.

The reaction of $[\text{Rh}_2(\mu-OH)(\mu-dppm)_2]\text{ClO}_4$ with dihydrogen/carbon monoxide mixture also gave $[\text{Rh}_2(\mu-H)(\mu-CO)(\mu-dppm)_2]\text{ClO}_4$, and the reaction was found to be complete within a period of 1.5 h. In contrast, the reaction with $[\text{Rh}_2(\mu-OC_2H_5)(\mu-dppm)_2]\text{ClO}_4$ was extremely slow and after a period of 2 h only a small quantity of $[\text{Rh}_2(\mu-H)(\mu-CO)(\mu-dppm)_2]\text{ClO}_4$ was formed. When $[\text{Rh}_2(\mu-OC_2H_5)(\mu-dppm)_2]\text{ClO}_4$, however, was subjected to the mixture under pressure (30 psi) at room temperature, a
mixture of the trinuclear cluster, \( \text{Rh}_3(\mu-\text{CO})_3(\mu-1,2\text{-dppm})_2\text{ClO}_4 \) and \( \text{[Rh}_2(\mu-\text{H})(\mu-\text{CO})(\mu-\text{dppm})_2]\text{ClO}_4 \) was formed. This was evident from the IR spectrum of the solid isolated which showed bands corresponding to both species.

The reactions of \( \text{[Rh}_2(\mu-\text{O}_2\text{CR})(\mu-\text{dppm})_2]\text{ClO}_4 \) and \( \text{[Rh}_2(\mu-\text{OH})(\mu-\text{dppm})_2]\text{ClO}_4 \) with dihydrogen and carbon monoxide to give \( \text{[Rh}_2(\mu-\text{H})(\mu-\text{CO})(\mu-\text{dppm})_2]\text{ClO}_4 \) can be considered as examples of the heterolytic activation of dihydrogen. In general, this reaction is thought to involve oxidative addition of dihydrogen to form the dihydride intermediate which undergoes reductive elimination in the presence of a base to give a metal-hydride complex and the protonated base as shown by equation 40.

\[
M + H_2 \rightarrow M + H \quad \rightarrow M - H + BH
\]

(40)

An example of this type of behaviour is shown in equation 41. There are examples, however, where dihydrogen activation does not require added base. These are exemplified by equations 42 and 43 in which an alkyl or aryl ligand performs the role of the base.

\[
\text{RuCl}_2(\text{PPh}_3)_3 + \text{NEt}_3 + H_2 \rightarrow \text{RuCl}(\text{PPh}_3)_3 + (\text{NEt}_3)\text{Cl} \quad \text{(41)}
\]

\[
\text{RhR}(\text{PPh}_3)_3 \rightarrow \text{RhH}(\text{PPh}_3)_3 + \text{RH} \quad \text{(42)}
\]

\[
\text{PtCl}(\text{Ph})(\text{PPh}_3)_2 \rightarrow \text{PtH(Cl)(PPh}_3)_2 + C_6H_6 \quad \text{(43)}
\]
It should be noted, however, that no attempt has been made to detect any intermediate formed in the reaction of carboxylate bridged dimers with the dihydrogen/carbon monoxide mixture. One possible mechanism by which \([\text{Rh}_2(\mu-O_2CR)(CO)_2^{-}(\mu-dppm)_2]\) reacts with the dihydrogen/carbon monoxide mixture is shown in scheme 14 (dppm ligands not shown).
5.2.3. Oxidative Addition Reactions

The term "oxidative addition" is used to define a class of reactions of transition metal complexes in which an increase in formal oxidation state of the metal is accompanied by an increase in the coordination number. This transformation can generally be represented for mononuclear complexes using equation 44 \((L = \text{ligands}, M = \text{metal} \text{ and } X-Y = \text{addendum})\) in which, the oxidation state of the metal has increased by two units. Oxidative addition to mononuclear systems has had a dominant position in the field of organometallic chemistry and their scope and application have been well reviewed.\(^{198,199}\)

Although there are ample examples detailing the oxidative addition of mononuclear complexes in the literature, parallel studies on binuclear systems are still in their infancy. These limited studies led to the discovery of the transannular oxidative addition reactions (equation 45) for binuclear complexes with bridging ligands. This type of conversion results in a one electron oxidation of each metal and the formation of metal-metal bond which
results in the complex being diamagnetic. Examples of this
type include the oxidative addition of halogens \((X_2)\) to face
to face dimers, \(\text{Rh}_2\text{Br}_2(\text{CO})_2(\mu-\text{dpam})_2\) \(^{72}\) and \([\text{Rh}_2(\text{CN}R)_2L_2](\text{BPh}_4)_2\)
\((L = \text{dpam, dppm; } R = \text{CH}_3, \text{n-C}_4\text{H}_9, \text{C}_6\text{H}_{11})\) \(^{72,73}\) to yield
\(\text{Rh}_2X_2\text{Br}_2(\text{CO})_2(\mu-\text{dpam})_2\) \((X = \text{Br, I})\) and \([\text{Rh}_2X_2(\text{CN}R)_2(\mu-\text{L})_2](\text{BPh}_4)_2\) \((X = \text{I})\) respectively (see section 1.2.1). Transannular
oxidative addition reactions are not confined to transition
metal complexes. The oxidative addition of halogens and
methyl iodide to cyclic gold(I) complexes, \(\text{Au}_2((\text{CH}_3)_2\text{PR}_2)_2\)
\((R = \text{CH}_3, \text{C}_2\text{H}_5)\) to give a gold(II) complex has been reported
by Schmidbaur. \(^{200}\)

Another type of reaction identified in binuclear
systems is the cleavage of metal-metal bonds by mild oxi-
dizing agents as shown in equation 46. Such reactions

\[
\begin{align*}
M + X-Y & \rightarrow M \text{M} \quad \text{(46)}
\end{align*}
\]
closely resemble the transannular oxidative addition reac-
tion despite the fact that they do not formally result in
an increase in coordination number. An example of this type
of reaction is afforded by the addition of halogens to the
palladium(I) complexes \(\text{Pd}_2X_2(\mu-\text{dppm})_2\) \((X = \text{I, Br})\), to form
transient palladium(II) species by the rupture of palladium-
palladium bond (equation 2, section 1.2.1).
Another interesting class of transannular oxidative addition reactions has been observed in the addition of organic dihalides (X-Y-X) to the palladium(0) complex Pd₂(dppm)₃. Unlike the above mentioned transannular additions, these reactions result in a +2 change in oxidation state yielding, in this case, A-frame palladium(II) dimers via a two centre, three fragment oxidative addition (equation 47).

\[
Pd₂(dppm)₃ + X-Y-X \rightarrow Pd(Pd-Y)₂(dppm)₂ + 2dppm
\]

(47)

\[
Pd₂(dppm)₃ + X-Y-X \rightarrow Pd(Pd-Y)₂(dppm)₂ + 2dppm
\]

(47)

X = Cl, Br, I, X = I
Y = CH₂, Y = \[\text{O} or C₆H₄

The work described in this section involves the oxidative addition of halogens (X = Cl₂, Br₂ and I₂) to the carboxylate complexes, \([\text{Rh}_2(\mu-O₂CR)(CO)_2(\mu-dppm)_2]ClO₄\) (R = H, CH₃ or CF₃). As anticipated, transannular oxidative addition did occur to give complexes of the type \([\text{Rh}_2(\mu-O₂CR)X₂(CO)_2(\mu-dppm)_2]ClO₄\) (99) (equation 48). Although the reactions of X₂ with \([\text{Rh}_2(\mu-O₂CR)(CO)_2(\mu-dppm)_2]ClO₄\) (R = H, CH₃) gave exclusively the transannular addition product, \([\text{Rh}_2(\mu-O₂CCF₃)(CO)_2(\mu-dppm)_2]ClO₄\) gave mixtures, with \([\text{Rh}_2(\mu-O₂CCF₃)X₂(CO)_2(\mu-dppm)_2]ClO₄\) as the major product.
IR data of oxidative addition products are presented in table 5.3 whereas NMR data (\(^1\text{H}\) and \(^{31}\text{P}\{\(^1\text{H}\})\) are given in table 5.4.

The addition of one mole of halogens (\(X_2 = \text{Cl}_2, \text{Br}_2\) and \(\text{I}_2\)) to \([\text{Rh}_2(\mu-O_2CR)(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4\) (\(R = \text{H}, \text{CH}_3\)) in dichloromethane, gave \([\text{Rh}_2(\mu-O_2CR)X_2(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4\) as the sole product in good yields. The reactions were almost instantaneous and the air-stable products were isolated by the addition of diethyl ether. The dichlorides and dibromides \([\text{Rh}_2(\mu-O_2CR)X_2(\mu-\text{dppm})_2]\text{ClO}_4\) (\(X = \text{Cl}, \text{Br}; R = \text{H}, \text{CH}_3\)) crystallized as a dichloromethane and diethyl ether hemisolvates. These solvents were found to be tenaciously held in the crystal lattice, since they could not be removed even after heating to 100 °C under vacuum for 24 h. The iodide did not contain any solvent molecules occluded in the crystals and were found to be very soluble in most organic
solvents. In contrast, dichlorides and dibromides were less soluble. All complexes exhibited electrical conductivities characteristic of 1:1 electrolytes in acetone solution. The stoichiometry of the oxidation reactions was established by the titration of $[\text{Rh}_2(\mu-O_2C\text{CH}_3)(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4$ with bromine and $[\text{Rh}_2(\mu-O_2\text{CH})(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4$ with iodine. IR spectroscopy was used ($2300$-$1900$ cm$^{-1}$ region) to monitor the appearance of new carbonyl bands in the higher frequency region. This increase in frequency is caused by the decrease in the extent of metal to ligand $\pi$-bonding as a result of the increase in the formal oxidation state of the metals. The addition of one mole of bromine in small aliquots (0.25 mol of bromine at a time) to a dichloro-methane solution of $[\text{Rh}_2(\mu-O_2C\text{CH}_3)(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4$ (0.05 g) resulted in a decrease in the intensity of the carbonyl frequencies of $[\text{Rh}_2(\mu-O_2C\text{CH}_3)(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4$ ($v(\text{CO}) = 2001$ (s) and $1985$ (vs) cm$^{-1}$, table 5,3) and the appearance of new bands at $2056$ and $2028$ cm$^{-1}$. This continued until the mole ratio reached one, at which stage the $v(\text{CO})$ bands of $[\text{Rh}_2(\mu-O_2C\text{CH}_3)(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4$ had completely disappeared. No further changes were observed in the region studied with further addition of bromine. This clearly established the stoichiometry of the oxidation to be 1:1. The product of this reaction was isolated as orange crystals. The microanalytical data of this complex were in good agreement with the titration results. Similar
behaviour was observed for the iodine/[Rh₂(u-O₂CH)(CO)₂(u-dppm)₂]ClO₄ titration.

The IR spectrum of all complexes (table 5.1) showed an increase in their carbonyl frequencies by about 40-60 cm⁻¹, relative to the starting material (table 5.1). This indicates the formation of a rhodium(II) dimer since similar shifts are observed in the oxidation of Rh₂Br₂(CO)₂(u-dpam)₂, with iodine and bromine to give the rhodium(II) dimer. The frequency shift of 40-60 cm⁻¹ observed for these transannular rhodium(I) to rhodium(II) oxidations is in marked contrast to the approximately 100 cm⁻¹ increase observed in the oxidation of the monomeric rhodium(I) complex, RhCl(CO)(PPh₃)₂ with iodine to give the rhodium(III) complex, RhI₂Cl(CO)(PPh₃)₂.¹⁴

The ³¹P[¹H] NMR spectra of all these complexes showed symmetric second order patterns of the AA' 'A''XX' confirming that all four phosphorus atoms are in an equivalent environment. At 80 MHz, it proved impossible to resolve the methylene proton resonances in the ¹H NMR spectrum of [Rh₂(u-O₂CR)Cl₂(CO)₂(u-dppm)₂]ClO₄ (R = H, CH₃). When the spectrum for the acetate derivative was obtained at 360 MHz, however, the non-equivalent protons were clearly separated. For the complex Rh₂(u-O₂CH)Br₂(CO)₂(u-dppm)₂ ClO₄ the methylene resonances were barely resolved at 80 MHz and no separate chemical shift could be assigned whereas
for \( \text{Rh}_2(\mu-\text{O}_2\text{CCH}_3)\text{Br}_2(\text{CO})_2(\mu-\text{dppm})_2\text{ClO}_4 \) they were resolved but still lie quite close to one another. In contrast for

\[ \text{[Rh}_2(\mu-\text{O}_2\text{CR})\text{II}_2(\text{CO})_2(\mu-\text{dppm})_2\text{ClO}_4 \ (R = \text{H, CH}_3) \]

the methylene resonances were well separated, as observed for other A-frame complexes. The reason for this behaviour is not at all clear but could involve anomalous shielding resulting from the \( \pi \)-system of the carboxylate function. The dependence of this phenomenon on the nature of the halide would probably therefore represent conformational changes in the \( \text{Rh}_2(\mu-\text{dppm})_2 \) framework occurring as a result of the increasing bulk of the halide. The methyl resonances for the acetate complexes appeared as singlets whereas the hydrogen of the formate group in \( \text{[Rh}_2(\mu-\text{O}_2\text{CH})\text{X}_2(\text{CO})_2(\mu-\text{dppm})_2\text{ClO}_4 \ (X = \text{Cl, Br and I}) \) appeared as a complex multiplet. \(^1\text{H NMR spectra also indicated that these complexes are diamagnetic, confirming the presence of a metal-metal interaction.}\

Inspection of tables 5.3 and 5.4 reveals a number of identical trends for every carboxylate complex when it forms addition products with the halogens. These include

(a) an increase in the carbonyl stretching frequency with an increase in the electronegativity of the halogen. This is to be expected as a result of the decrease in metal to ligand back donation with the increase in electronegativity of halogen,

(b) A downfield shift of the \(^{31}\text{P} \) resonances was observed
with an increase in the electronegativity of the halogen (table 5.4). A slight but similar trend has been observed for Rh₂(μ-X)(μ-CO)(CO)₂(μ-dppm)₂⁺ (X = Cl, 29.6; X = Br, 28.7; X = I, 26.6)²² where the halogen is bridging the two metal centres in this case.

(c) The principal coupling constants of the ³¹P spectra (|¹Jₚₚ + ³¹Jₚₚ|) decreases with increasing electronegativity of the halogen. This change is not very significant, however, and since the coupling constant is a two component system, it is not certain which of the two components (or both) is responsible for this trend.

Unlike [Rh₂(μ-O₂CR)(CO)₂(μ-dppm)₂]ClO₄ (R = H, CH₃), the reaction of [Rh₂(μ-O₂CCF₃)(CO)₂(μ-dppm)₂]ClO₄ with halogens gave more than one product. The major product in these reactions was, however, the symmetrical Rh(II) dimer, [Rh₂(μ-O₂CCF₃)X₂(CO)₂(μ-dppm)₂]ClO₄ (X = Cl, Br and I), as obtained for [Rh₂(μ-O₂CR)(CO)₂(μ-dppm)₂]ClO₄ (R = H, CH₃).

When a dichloromethane solution of [Rh₂(μ-O₂CCF₃)-(CO)₂(μ-dppm)₂]ClO₄ was treated with chlorine, the colour of the solution immediately turned from red to orange. From this solution a yellow-orange solid was isolated by the addition of diethyl ether. Recording of the ³¹P{¹H} NMR spectrum of [Rh₂(μ-O₂CCF₃)(CO)₂(μ-dppm)₂]ClO₄ after reacting with chlorine showed a symmetric second order pattern (15.94 ppm, \(|¹Jₚₚ + ³¹Jₚₚ| = 78.5 \text{ Hz}) and an asymmetric
multiplet centred approximately at 0.3 ppm. The symmetric multiplet belongs to the rhodium(II) dimer, 

\[ \text{[Rh}_2(\mu-O_2CCF_3)\text{Cl}_2(\text{CO})_2(\mu-dppm)_2]ClO}_4 \]

whose formation was also evident from its IR spectrum. The IR spectrum of the solid isolated from the reaction mixture had bands at 2123(mw), 2064(m), 2035(mw), 1792(w), 1688(w) and 1646(mw) cm\(^{-1}\). The band profile of the peaks 2064(m) and 2035(mw) cm\(^{-1}\) was virtually identical to those obtained for the other rhodium(II) dimers \[ \text{[Rh}_2(\mu-O_2CR)\text{X}_2(\text{CO})_2(\mu-dppm)_2]ClO}_4 \] (X = Cl, Br; R = H, CH\(_3\)). Furthermore, the band maxima also compare favourably with these rhodium(II) dimers (table 5.3). The band at 1646(mw) cm\(^{-1}\) was assigned to the antisymmetric stretch of the trifluoroacetate group of \[ \text{[Rh}_2(\mu-O_2CCF_3)\text{Cl}_2(\text{CO})_2(\mu-dppm)_2]ClO}_4 \]. The remaining bands presumably belong to the asymmetric product. The band at 2123(w) cm\(^{-1}\) was indicative of a terminal carbonyl group attached to a rhodium(III) centre (vide supra) whereas the peak at 1792(w) cm\(^{-1}\) suggested the presence of a bridging carbonyl group. The absorption of 1688(w) cm\(^{-1}\) may at first sight favour a monodentate trifluoroacetate. It should be noted, however, that a shift to higher frequencies has been observed in the conversion of a carboxylate group from a bridging bidentate mode to a chelating bidentate mode. Based on the foregoing data, the most plausible structure for this asymmetric complex is shown in 100. The formulation gives the complex a total of 36 electrons thereby obviating the need for a formal rhodium-rhodium bond. This
classifies the bridging carbonyl group as a ketonic type. The frequency associated with this ketonic carbonyl group is somewhat high by comparison to those found in other rhodium-dppm complexes (typically 1756-1700 cm\(^{-1}\)). This may not be that surprising, however, since in this instance the two rhodium centres are in a higher formal oxidation state than those so far reported.

The reaction of bromine with \([\text{Rh}_2(\mu-O_2\text{CCF}_3)(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4\) also produced a mixture of products. This was evident from both the \(^3\text{P}{^1}\text{H}\) NMR and IR spectra. The \(^3\text{P}{^1}\text{H}\) NMR spectrum of \([\text{Rh}_2(\mu-O_2\text{CCF}_3)(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4\) in dichloromethane solution containing one mole of bromine showed the presence of a second order symmetric multiplet (13.9 ppm, \(\mid J_{\text{Rh-P}} + xJ_{\text{Rh-P}} \mid = 79.5 \text{ Hz}\)) and two other minor asymmetric patterns centred at 10.26 and 18.37 ppm. The product associated with the multiplet at 18.37 ppm was formed only in small quantities compared to the other two
products. The symmetric species at 13.91 ppm has been assigned to the formation of \([\text{Rh}_2(\mu-O_2\text{CCF}_3)\text{Br}_2(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4\). The IR spectrum of the solid isolated from the reaction mixture by adding diethyl ether showed bands at 2106(w), 2071(sh), 2062(s), 2039(sh), 1781(w), 1705(w), 1680(w) and 1646(mw) cm\(^{-1}\). The bands at 2062(s), 2039(sh) and 1646(mw) cm\(^{-1}\) have been assigned to the rhodium(II) dimer, \([\text{Rh}_2(\mu-O_2\text{CCF}_3)\text{Br}_2(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4\), by comparison with other rhodium(II) dimers (table 5.3). The bands at 2106(w), 1781(w) and 1680(w) cm\(^{-1}\) can be attributed to a product 101 similar to that formed in the reaction of the chlorine and \([\text{Rh}_2(\mu-O_2\text{CCF}_3)(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4\). The remaining bands have been assigned to a complex having the structure 102 based on the results obtained for the reaction of iodine and \([\text{Rh}_2(\mu-O_2\text{CCF}_3)(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4\).

The reaction of iodine with \([\text{Rh}_2(\mu-O_2\text{CCF}_3)(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4\) also gave more than one product. The \(^{31}\text{P}^{1}\text{H}\) NMR spectrum of the product obtained by the reaction of
[\text{Rh}_2(\mu-O_2CCF_3)(\text{CO})_2(\mu-dppm)_2]ClO_4 with one mole of iodine showed the presence of only two products. Since the peaks associated with these two products were overlapping, very little could be said about the exact nature of these species. IR spectrum, however, indicated that the major product was the normal rhodium(II) dimer, [\text{Rh}_2(\mu-O_2CCF_3)\text{I}_2(\text{CO})_2(\mu-dppm)_2]ClO_4. Thus, the two major $^{31}$P peaks corresponding to this species could be identified. The IR spectrum of the solid isolated showed bands at 2069 (m), 2055 (s), 2031 (mw), 1701 (w), 1680 (w) and 1647 (m) cm$^{-1}$. The bands at 2055 (s), 2031 (mw) and 1647 (mw) cm$^{-1}$ could be easily ascribed to [\text{Rh}_2(\mu-O_2CCF_3)\text{I}_2(\text{CO})_2(\mu-dppm)_2]ClO_4. Of the remaining bands, that at 2069 (m) cm$^{-1}$ was suggestive of a carbonyl group coordinated to a rhodium(II) centre. The band at 1701 (w) cm$^{-1}$ indicated the presence of a ketonic type bridging carbonyl group whereas the absorption at 1680 (w) cm$^{-1}$, as mentioned earlier, may suggest a terminal.
monodentate or bidentate carboxylate group. The structure shown below (103) would appear to explain these data satisfactorily. This has a total of 32 electrons and does not contain a rhodium-rhodium single bond.

The interpretation of the IR and $^{31}$P NMR data used to assign structures to the by-products obtained in the reaction of $[\text{Rh}_2(\mu-O_2\text{CCF}_3)(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4$ with halogen is by no means unambiguous. To confirm these assignments, further work is required. Preliminary attempts to separate these products in this laboratory have so far been unsuccessful.

The unusual behaviour shown by the complex, $[\text{Rh}_2(\mu-O_2\text{CCF}_3)(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4$ in the reaction of chlorine, bromine and iodine may be attributed to the extreme lability of the trifluoroacetate group and the difference in behaviour observed for different halogens may be associated with the steric bulk of the halogen.
5.3. Experimental

5.3.1. List of Complexes Synthesized

<table>
<thead>
<tr>
<th>Complex</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{Rh}_2(\mu-\text{CO})(\mu-\text{O}_2\text{CR})(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4$</td>
<td>263</td>
</tr>
<tr>
<td>$(R = \text{CH}_2\text{Cl}, \text{CHCl}_2, \text{CCl}_3, \text{CF}_3)$</td>
<td></td>
</tr>
<tr>
<td>$[\text{Rh}_2(\mu-\text{H})(\mu-\text{CO})(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4$</td>
<td>264</td>
</tr>
<tr>
<td>$[\text{Rh}_2(\mu-\text{OC}_2\text{H}_5)(\text{CO})_2(\mu-\text{dppm})_2]\text{PF}_6$</td>
<td>265</td>
</tr>
<tr>
<td>$[\text{Rh}_2(\mu-\text{O}_2\text{CH})(\text{CO})_2(\mu-\text{dppm})_2]\text{PF}_6$</td>
<td>266</td>
</tr>
<tr>
<td>$[\text{Rh}_2(\mu-\text{H})(\mu-\text{CO})(\text{CO})_2(\mu-\text{dppm})_2]\text{PF}_6$</td>
<td>266</td>
</tr>
<tr>
<td>$[\text{Rh}_2(\mu-\text{O}_2\text{CH})\text{Cl}_2(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4 \cdot 0.5\text{CH}_2\text{Cl}_2 \cdot 0.5\text{C}_4\text{H}_10\text{O}$</td>
<td>266</td>
</tr>
<tr>
<td>$[\text{Rh}_2(\mu-\text{O}_2\text{CCH}_3)(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4 \cdot 0.5\text{CH}_2\text{Cl}_2 \cdot 0.5\text{C}_4\text{H}_10\text{O}$</td>
<td>267</td>
</tr>
<tr>
<td><strong>Reaction of $[\text{Rh}_2(\mu-\text{O}_2\text{CCF}_3)(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4$ with chlorine</strong></td>
<td>267</td>
</tr>
<tr>
<td>$[\text{Rh}_2(\mu-\text{O}_2\text{CH})\text{Br}_2(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4 \cdot 0.5\text{CH}_2\text{Cl}_2 \cdot 0.5\text{C}_4\text{H}_10\text{O}$</td>
<td>268</td>
</tr>
<tr>
<td>$[\text{Rh}_2(\mu-\text{O}_2\text{CCH}_3)\text{Br}_2(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4 \cdot 0.5\text{CH}_2\text{Cl}_2 \cdot 0.5\text{C}_4\text{H}_10\text{O}$</td>
<td>268</td>
</tr>
<tr>
<td><strong>Reaction of $[\text{Rh}_2(\mu-\text{O}_2\text{CCF}_3)(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4$ with bromine</strong></td>
<td>268</td>
</tr>
<tr>
<td>$[\text{Rh}_2(\mu-\text{O}_2\text{CH})\text{I}_2(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4$</td>
<td>269</td>
</tr>
<tr>
<td>$[\text{Rh}_2(\mu-\text{O}_2\text{CCH}_3)\text{I}_2(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4$</td>
<td>269</td>
</tr>
<tr>
<td><strong>Reaction of $[\text{Rh}_2(\mu-\text{O}_2\text{CCF}_3)(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4$ with iodine</strong></td>
<td>270</td>
</tr>
</tbody>
</table>
5.3.2. Synthetic Procedures

Preparation of \([\text{Rh}_2(\mu-\text{CO})(\mu-\text{O}_2\text{CR})(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4\) 
\((R = \text{CH}_2\text{Cl}, \text{CHCl}_2, \text{CCl}_3, \text{CF}_3)\)

In a typical experiment, carbon monoxide was bubbled through a solution of \([\text{Rh}_2(\mu-\text{O}_2\text{CR})(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4\) 
\((R = \text{CH}_2\text{Cl}, \text{CHCl}_2, \text{CCl}_3, \text{CF}_3)\) for 10 min. The red solution turned red-orange, orange, yellow and pale yellow-orange for 
\(R = \text{CH}_2\text{Cl}, \text{CHCl}_2, \text{CCl}_3\) and \(\text{CF}_3\) respectively. The addition of diethyl ether while the carbon monoxide flow was main­tained precipitated the product, which was filtered off, washed with diethyl ether and dried in air. Recrystalliza­tion was achieved from dichloromethane-diethyl ether in the presence of an atmosphere of carbon monoxide.

<table>
<thead>
<tr>
<th>R</th>
<th>Colour and appearance</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{CH}_2\text{Cl})</td>
<td>yellow-orange crystalline solid</td>
<td>(0.089 g, 87%)</td>
</tr>
<tr>
<td>(\text{CHCl}_2)</td>
<td>bright yellow crystalline solid</td>
<td>(0.090 g, 88%)</td>
</tr>
<tr>
<td>(\text{CCl}_3)</td>
<td>yellow crystalline solid which became red-orange immediately on filtering. This could be minimized by filtering under an atmosphere of carbon monoxide.</td>
<td>(0.082 g, 80%)</td>
</tr>
<tr>
<td>(\text{CF}_3)</td>
<td>bright crystalline solid, which was obtained as a dichloromethane solvate</td>
<td>(0.090 g, 83%)</td>
</tr>
</tbody>
</table>

\(R = \text{CF}_3\): Anal. Calcd for \(\text{C}_{55.46}\text{F}_{3.46}\text{O}_{9.13}\text{Cl}_3\text{Rh}_2\): C, 49.60; H, 3.42; F, 4.20; P, 9.13%. Found: C, 49.86; H, 3.38; F, 2.95; P, 9.52%.
Preparation of $\text{[Rh}_2(\mu-\text{H})(\mu-\text{CO})(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4$

**Method A:** $\text{[Rh}_2(\mu-\text{O}_2\text{CR})(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4$ ($R = \text{CF}_3$: 0.01 g; $R = \text{CH}_2\text{Cl}$, $\text{CHCl}_2$, $\text{CCl}_3$: 0.05 g) was dissolved in 10 mL of dichloromethane in a two necked flask. A mixture of carbon monoxide/dihydrogen (1:1) was bubbled through this solution for a period of 5 min. The colour changes were as follows; $R = \text{CH}_2\text{Cl}$: red to red-orange; $R = \text{CHCl}_2$: red, red-orange and red-brown; $R = \text{CCl}_3$: red, yellow, red-brown and wine; $R = \text{CF}_3$: red, red-brown and wine-red. The flask was then capped under an atmosphere of carbon monoxide/dihydrogen and stirred for a period of time 't' h ($R = \text{CH}_2\text{Cl}$: $t = 3$ h; $R = \text{CHCl}_2$, $\text{CCl}_3$: $t = 0.75$ h; $R = \text{CF}_3$: $t = 0.5$ h) during which time all solutions were wine-red in colour. The addition of diethyl ether in an atmosphere of carbon monoxide/dihydrogen precipitated a red-brown solid almost quantitatively. This was filtered and recrystallized with dichloromethane-diethyl ether in the presence of carbon monoxide/dihydrogen to give a red-brown crystalline solid ($R = \text{CH}_2\text{Cl}$: 0.037 g, 78%; $R = \text{CHCl}_2$: 0.039 g, 85%; $R = \text{CCl}_3$: 0.032 g, 71%; $R = \text{CF}_3$: 0.082 g, 88%).

**Method B:** $\text{[Rh}_2(\mu-\text{O}_2\text{CH})(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4$ (0.10 g; 0.085 mmol) was dissolved in 5 mL of dichloromethane in a 10 mL flask and sealed with a rubber septum. Carbon monoxide (2 mL, 1 mol) was injected into this reaction flask using a gas syringe. Solution was stirred for 1 h during which time
the red solution had become wine-red. The addition of diethyl ether precipitated a red-brown crystalline product. Recrystallization was from dichloromethane-diethyl ether in an atmosphere of carbon monoxide (0.085 g, 86%).

Method C: A mixture of carbon monoxide-dihydrogen was passed through a solution of 

\[ \text{[Rh}_2(\mu-\text{OH})(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4 \]

(0.10 g, 0.087 mmol) in 10 mL of dichloromethane for 3 min. The yellow solution turned yellow-brown during this period. The flask was sealed at this stage under an atmosphere of carbon monoxide/dihydrogen and stirred for 1.5 h during which time solution had become wine-red. The addition of diethyl ether in an atmosphere of carbon monoxide/dihydrogen precipitated the product almost quantitatively (0.095 g, 94%). Recrystallization was achieved by dichloromethane-diethyl ether in an atmosphere of carbon monoxide/dihydrogen to give a red-brown crystalline solid (0.078 g, 77%).

Preparation of \([\text{Rh}_2(\mu-\text{OC}_2\text{H}_5)(\text{CO})_2(\mu-\text{dppm})_2]\text{PF}_6\)

To a solution of \([\text{Rh}_2(\mu-\text{OC}_2\text{H}_5)(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4 \)

(0.20 g, 0.17 mmol) was added a filtered solution of ten fold excess sodium hexafluorophosphate (0.30 g, 1.79 mmol) dissolved in 15 mL of ethanol. A yellow crystalline solid precipitated on stirring. The product was filtered, washed with water, ethanol and hexane. Recrystallization from dichloromethane-ethanol gave the product as bright yellow.
crystals (0.17 g, 82%).

Preparation of \([\text{Rh}_2(\mu-O_2\text{CH})(\text{CO})_2(\mu-dppm)_2\text{]}\text{PF}_6\)

This complex was obtained as red crystals by a method analogous (section 2.4) to that used to obtain the perchlorate salt using \([\text{Rh}_2(\mu-\text{OC}_2\text{H}_5)(\text{CO})_2(\mu-dppm)_2\text{]}\text{PF}_6\) (0.15 g, 0.12 mmol) instead of \([\text{Rh}_2(\mu-\text{OC}_2\text{H}_5)(\text{CO})_2(\mu-dppm)_2\text{]}\text{ClO}_4\) (0.14 g, 93%).

Preparation of \([\text{Rh}_2(\mu-H)(\mu-\text{CO})(\text{CO})_2(\mu-dppm)_2\text{]}\text{PF}_6\)

\([\text{Rh}_2(\mu-O_2\text{CH})(\text{CO})_2(\mu-dppm)_2\text{]}\text{PF}_6\) (0.05 g, 0.041 mmol) was dissolved in 5 mL of dichloromethane in a 10 mL flask. The flask was then sealed with a rubber septum and carbon monoxide was introduced (1 mL, ca. 0.04 mmol) using a gas syringe. The solution was stirred for 1 h during which time the solution had become dark red in colour. The addition of diethyl ether precipitated a brown crystalline solid which was filtered off and recrystallized in an atmosphere of carbon monoxide with dichloromethane-diethyl ether (0.035 g, 71%).

Preparation of \([\text{Rh}_2(\mu-O_2\text{CH})\text{Cl}_2(\text{CO})_2(\mu-dppm)_2\text{]}\text{ClO}_4\cdot 0.5\text{CH}_2\text{Cl}_2\cdot 0.5\text{C}_4\text{H}_10\text{O}\)

\([\text{Rh}_2(\mu-O_2\text{CH})(\text{CO})_2(\mu-dppm)_2\text{]}\text{ClO}_4\) (0.10 g, 0.085 mmol) was dissolved in 5 mL of dichloromethane and to it added dropwise with stirring a dichloromethane solution saturated
with chlorine gas until the red colour of the solution had turned completely orange. The addition of diethyl ether to the orange solution precipitated a yellow orange solid. The product was filtered off, washed with diethyl ether and recrystallized with dichloromethane-diethyl ether to give yellow-orange crystals (0.091 g, 81%).

Anal. Calcd for \( \text{C}_{55.5}\text{H}_{51}\text{Cl}_{4.8}\text{P}_{4}\text{Rh}_{2} \): C, 50.25; H, 3.87; Cl, 10.69%. Found: C, 50.35; H, 3.77; Cl, 10.68%. 
\( \Lambda_{M} = 130 \text{ cm}^{2} \text{ mol}^{-1} \text{ cm}^{-1} \) (acetone).

Preparation of \([\text{Rh}_{2}(\mu-\text{O}_{2}\text{CCH}_{3})\text{Cl}_{2}(\text{CO})_{2}(\mu-\text{dppm})_{2}]\text{ClO}_{4} \cdot 0.5\text{C}_{4}\text{H}_{10}\text{O}\)

This was prepared by an analogous method described for the previous complex and the product was obtained as yellow-orange crystals (0.081 g, 71%).

Anal. Calcd for \( \text{C}_{56.5}\text{H}_{53}\text{O}_{8.5}\text{P}_{4}\text{Cl}_{4}\text{Rh}_{2} \): C, 50.62; H, 3.98%. Found: C, 50.39; H, 3.89%. \( \Lambda_{M} = 131 \text{ cm}^{2} \text{ mol}^{-1} \text{ cm}^{-1} \) (acetone).

Reaction of \([\text{Rh}_{2}(\mu-\text{O}_{2}\text{CCF}_{3})\text{Cl}_{2}(\text{CO})_{2}(\mu-\text{dppm})_{2}]\text{ClO}_{4} \) with Chlorine

The reaction procedure was similar to those of formate and acetate and the yield of the orange crude material was 0.062 g. Spectroscopic data indicated the presence of a mixture of compounds (see text).
Preparation of \([\text{Rh}_2(\mu-\text{O}_2\text{CH})\text{Br}_2(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4 \cdot 0.5\text{CH}_2\text{Cl}_2 \cdot 0.5\text{C}_4\text{H}_10\)  

To a solution of \([\text{Rh}_2(\mu-\text{O}_2\text{CH})(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4 \) (0.10 g, 0.092 mmol) in 5 mL of dichloromethane added one mole of bromine with stirring. The red solution immediately turned orange-brown. The addition of diethyl ether precipitated an orange solid which on filtration, followed by recrystallization from dichloromethane-diethyl ether gave orange crystals (0.085 g, 71%).  

Anal. Calcd for \(\text{C}_{55.5}\text{H}_{51.0}\text{O}_{8.5}\text{P}_4\text{Cl}_2\text{Br}_2\text{Rh}_2\): C, 47.09; H, 3.63%. Found: C, 47.88; H, 3.52%. \(\lambda_M = 126 \text{ cm}^2 \text{ mol}^{-1} \text{ mol}^{-1}\) (acetone).  

Preparation of \([\text{Rh}_2(\mu-\text{O}_2\text{CCH}_3)\text{Br}_2(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4 \cdot 0.5\text{CH}_2\text{Cl}_2 \cdot 0.5\text{C}_4\text{H}_10\)  

This was prepared in an analogous fashion to the previous complex. The colour change was from red to orange and the recrystallized product was isolated as orange crystals (0.090 g, 75%).  

Anal. Calcd for \(\text{C}_{56.5}\text{H}_{53.0}\text{Br}_2\text{O}_{8.5}\text{P}_4\text{Cl}_2\text{Rh}_2\): C, 47.46; H, 3.71; Br, 11.20%. Found: C, 47.41; H, 3.57; Br, 11.54%. \(\lambda_M = 125 \text{ cm}^2 \text{ mol}^{-1} \text{ mol}^{-1}\) (acetone).  

Reaction of \([\text{Rh}_2(\mu-\text{O}_2\text{CF}_3)(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4\) with Bromine  

Reaction procedure was similar to those of formate and acetate. The colour change was from red to dark brown.
from which was isolated a brown solid by the addition of diethyl ether (0.080 g). Spectroscopic data indicated the presence of a mixture of products (see text).

Preparation of $[\text{Rh}_2(\mu-O_2\text{CH})_2(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4$

To a solution of $[\text{Rh}_2(\mu-O_2\text{CH})(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4$ (0.10 g, 0.085 mmol) in 5 mL of dichloromethane added one mole of iodine with stirring. The red solution immediately turned red-brown from which a black crystalline solid was isolated upon addition of diethyl ether. The product was filtered and recrystallized from dichloromethane-diethyl ether to give black crystals with a green lustre (0.098 g, 81%).

Anal. Calcd for $C_{53}H_{45}O_8P_4\text{ClI}_2\text{Rh}_2$: C, 44.55; H, 3.18%. Found: C, 43.88; H, 3.08%. $\Lambda_M = 129 \text{ cm}^2 \text{ mol}^{-1} \text{ mol}^{-1}$ (acetone).

Preparation of $[\text{Rh}_2(\mu-O_2\text{CCH}_3)_2\text{I}_2(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4$

This was prepared by analogous fashion to the previous complex and the product was obtained as a brown amorphous solid (0.091 g, 75%).

Anal. Calcd for $C_{54}H_{47}O_8P_4\text{ClI}_2\text{Rh}_2$: C, 44.95; H, 3.74%. Found: C, 44.40; H, 3.06%. $\Lambda_M = 123 \text{ cm}^2 \text{ mol}^{-1} \text{ mol}^{-1}$ (acetone).
Reaction of $[\text{Rh}_2(\mu-O_2\text{CCF}_3)(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4$ with Iodine

The procedure was similar to that of acetate and formate. A brown crystalline solid was obtained by the addition of diethyl ether (0.084 g). Spectroscopic data indicated the formation of a mixture of products (see text).

Anal. Calcd for $C_{54}H_{44}O_8F_3P_4\text{Cl}_2\text{Rh}_2$: C, 43.33; H, 2.96%.

Found: C, 43.14; H, 2.75%.
Table 5.1. IR Data of the Products Obtained by the Reaction of Carboxylate Bridged Dimers with Carbon Monoxide

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\nu$(CO)$^a$, cm$^{-1}$</th>
<th>$\nu$(CO)$^b$, cm$^{-1}$</th>
<th>Others$^b$, cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Rh$_2$(µ-CO)(µ-O$_2$CCH$_2$Cl)(CO)$_2$(µ-dppm)$_2$]ClO$_4$</td>
<td>2001(sh), 1996(vs), 1836(m)</td>
<td>1992(s), 1977(vs), 1821(m)</td>
<td>$\nu_{as}$(CO$<em>2$), 1561(m); $\nu</em>{vs}$(CO$_2$), 1376(m)</td>
</tr>
<tr>
<td>[Rh$_2$(µ-CO)(µ-O$_2$CCHCl$_2$)(CO)$_2$(µ-dppm)$_2$]ClO$_4$</td>
<td>1997(vs), 1839(m)</td>
<td>1996(s), 1982(vs), 1824(m)</td>
<td>$\nu_{as}$(CO$<em>2$), 1595(m); $\nu</em>{vs}$(CO$_2$), 1402(mw)</td>
</tr>
<tr>
<td>[Rh$_2$(µ-CO)(µ-O$_2$CCCl$_3$)(CO)$_2$(µ-dppm)$_2$]ClO$_4$</td>
<td>1999(vs), 1840(m)</td>
<td>1996(sh), 1988(vs), 1820(mw)</td>
<td>$\nu_{as}$(CO$<em>2$), 1614(m); $\nu</em>{vs}$(CO$_2$), 1335(mw)</td>
</tr>
<tr>
<td>[Rh$_2$(µ-CO)(µ-O$_2$CCF$_3$)(CO)$_2$(µ-dppm)$_2$]ClO$_4$</td>
<td>2009(sh), 1997(vs), 1841(m)</td>
<td>1997(s), 1988(vs), 1824(m)</td>
<td>$\nu_{as}$(CO$_2$), 1623(s)</td>
</tr>
<tr>
<td>[Rh$_2$(µ-H)(µ-CO)(CO)$_2$(µ-dppm)$_2$]ClO$_4$</td>
<td>2003(sh), 1992(vs), 1902(m)</td>
<td>2002(s), 1989(vs), 1898(s)</td>
<td>---</td>
</tr>
<tr>
<td>[Rh$_2$(µ-H)(µ-CO)(CO)$_2$(µ-dppm)$_2$]PF$_6$,CH$_2$Cl$_2$</td>
<td>2003(sh), 1992(vs), 1902(m)</td>
<td>1995(sh), 1984(vs), 1874(m)</td>
<td>---</td>
</tr>
<tr>
<td>[Rh$_2$(µ-H)(µ-CO)(CO)$_2$(µ-dppm)$_2$]PF$_6$</td>
<td>2003(sh), 1992(vs), 1902(m)</td>
<td>2002(sh), 1988(vs), 1898(m), 1873(m)</td>
<td>---</td>
</tr>
<tr>
<td>[Rh$_2$(µ-O$_2$CH)(CO)$_2$(µ-dppm)$_2$]PF$_6$</td>
<td>2002(vs), 1991(s)</td>
<td>1995(s), 1961(s)</td>
<td>$\nu_{as}$(CO$_2$), 1561(s)</td>
</tr>
<tr>
<td>[Rh$_2$(µ-OC$_2$H$_5$)(CO)$_2$(µ-dppm)$_2$]PF$_6$</td>
<td>1992(sh), 1981(vs)</td>
<td>1989(s), 1977(vs)</td>
<td>---</td>
</tr>
</tbody>
</table>

(a) In dichloromethane.
(b) Recorded as nujol mulls on potassium bromide plates.
(c) Purple crystals.
(d) Brown crystalline solid.
Table 5.2. IR and NMR ($^1$H and $^{31}$P($^1$H)) Data of the Products Obtained by the Reactions of Carboxylate Bridged Dimers with Carbon Monoxide

<table>
<thead>
<tr>
<th>Compound</th>
<th>NMR $^{a,b}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{[}$Rh$_2$(μ-CO)(μ-0$_2$CCH$_2$Cl)(CO)$_2$(μ-dppm)$_2$]$ClO_4$</td>
<td>$^{31}$P: 33.80 (m, dppm, $^1$J$<em>{Rh-P}$, $^3$J$</em>{Rh-P}$) = 93.4 Hz $^d$</td>
</tr>
<tr>
<td>$^{[}$Rh$_2$(μ-CO)(μ-0$_2$CCHCl$_2$)(CO)$_2$(μ-dppm)$_2$]$ClO_4$</td>
<td>$^{31}$P: 32.78 (m, dppm, $^1$J$<em>{Rh-P}$, $^3$J$</em>{Rh-P}$) = 93.2 Hz $^d$</td>
</tr>
<tr>
<td>$^{[}$Rh$_2$(μ-CO)(μ-0$_2$CCl$_3$)(CO)$_2$(μ-dppm)$_2$]$ClO_4$</td>
<td>$^{31}$P: 32.70 (m, dppm, $^1$J$<em>{Rh-P}$, $^3$J$</em>{Rh-P}$) = 93.1 Hz $^d$</td>
</tr>
<tr>
<td>$^{[}$Rh$_2$(μ-CO)(μ-0$_2$CCF$_3$)(CO)$_2$(μ-dppm)$_2$]$ClO_4$.CH$_2$Cl$_2$</td>
<td>$^{31}$P: 32.62 (m, dppm, $^1$J$<em>{Rh-P}$, $^3$J$</em>{Rh-P}$) = 93.8 Hz $^d$</td>
</tr>
<tr>
<td>$^{[}$Rh$_2$(μ-H)(μ-CO)(CO)$_2$(μ-dppm)$_2$]$ClO_4$</td>
<td>$^{31}$P: 28.65 (m, dppm, $^1$J$<em>{Rh-P}$, $^3$J$</em>{Rh-P}$) = 109.0 Hz $^{1}$H: 7.56 (m, 40H, Phenyl); 4.11, 4.11 (m, 4H, CH$_2$-dppm)</td>
</tr>
</tbody>
</table>

(a) Chemical shifts (in ppm) relative to tetramethylsilane ($^1$H) and 85% phosphoric acid ($^{31}$P).

(b) $^1$H NMR spectra in dichloromethane-d$_2$.

(c) The degree of solvation was determined by recording the $^1$H NMR in acetone-d$_6$ (5.60, s, 2H).

(d) At -35°C.

(e) 360 MHz.
Table 5.3. IR data of the Complexes, \([\text{Rh}_2(\mu-\text{O}_2\text{CFX}_2)(\text{CO})_2(\mu-\text{dppm})_2]^{2}\text{ClO}_4\) (R = H, CH\(_3\) and CF\(_3\); X = Cl, Br and I)

<table>
<thead>
<tr>
<th>Compound</th>
<th>(v(\text{CO})^a) cm(^{-1})</th>
<th>(v(\text{CO})^b) cm(^{-1})</th>
<th>Others(^b), cm(^{-1})</th>
</tr>
</thead>
</table>
| \([\text{Rh}_2(\mu-\text{O}_2\text{CH})\text{Cl}_2(\text{CO})_2(\mu-\text{dppm})_2]^{2}\text{ClO}_4\cdot0.5\text{CH}_2\text{Cl}_2\cdot0.5\text{C}_4\text{H}_10^0\) | 2060 (vs), 2032 (m) | 2051 (vs), 2022 (m) | \(v\_\text{as}(\text{CO}_2), 1555 (m);\) 
| \(\delta(\text{CH}), 1353 (m)\) |
| \([\text{Rh}_2(\mu-\text{O}_2\text{CH})\text{Br}_2(\text{CO})_2(\mu-\text{dppm})_2]^{2}\text{ClO}_4\cdot0.5\text{CH}_2\text{Cl}_2\cdot0.5\text{C}_4\text{H}_10^0\) | 2057 (vs), 2030 (m) | 2048 (vs), 2019 (m) | \(v\_\text{as}(\text{CO}_2), 1555 (s);\) 
| \(\delta(\text{CH}), 1352 (m)\) |
| \([\text{Rh}_2(\mu-\text{O}_2\text{CH})\text{I}_2(\text{CO})_2(\mu-\text{dppm})_2]^{2}\text{ClO}_4\cdot0.5\text{CH}_2\text{Cl}_2\cdot0.5\text{C}_4\text{H}_10^0\) | 2058 (vs), 2031 (m) | 2050 (vs), 2021 (m) | \(v\_\text{as}(\text{CO}_2), 1538 (mw)\) |
| \([\text{Rh}_2(\mu-\text{O}_2\text{CH}_3)\text{Cl}_2(\text{CO})_2(\mu-\text{dppm})_2]^{2}\text{ClO}_4\cdot0.5\text{CH}_2\text{Cl}_2\cdot0.5\text{C}_4\text{H}_10^0\) | 2056 (vs), 2028 (m) | 2047 (vs), 2029 (m) | \(v\_\text{as}(\text{CO}_2), 1537 (mw)\) |
| \([\text{Rh}_2(\mu-\text{O}_2\text{CH}_3)\text{Br}_2(\text{CO})_2(\mu-\text{dppm})_2]^{2}\text{ClO}_4\cdot0.5\text{CH}_2\text{Cl}_2\cdot0.5\text{C}_4\text{H}_10^0\) | 2047 (vs), 2021 (m) | 2046 (vs), 2021 (m) | \(v\_\text{as}(\text{CO}_2), 1539 (mw)\) |
| \([\text{Rh}_2(\mu-\text{O}_2\text{CF}_3)\text{Cl}_2(\text{CO})_2(\mu-\text{dppm})_2]^{2}\text{ClO}_4\cdot0.5\text{CH}_2\text{Cl}_2\cdot0.5\text{C}_4\text{H}_10^0\) | 2063 (m), 2\,231 (sh) | 2064 (m), 2035 (mw) | \(v\_\text{as}(\text{CO}_2), 1645 (mw)\) |
| \([\text{Rh}_2(\mu-\text{O}_2\text{CF}_3)\text{Br}_2(\text{CO})_2(\mu-\text{dppm})_2]^{2}\text{ClO}_4\cdot0.5\text{CH}_2\text{Cl}_2\cdot0.5\text{C}_4\text{H}_10^0\) | 2060 (m), 2\,230 (sh) | 2062 (m), 2030 (mw) | \(v\_\text{as}(\text{CO}_2), 1646 (mw)\) |
| \([\text{Rh}_2(\mu-\text{O}_2\text{CF}_3)\text{I}_2(\text{CO})_2(\mu-\text{dppm})_2]^{2}\text{ClO}_4\cdot0.5\text{CH}_2\text{Cl}_2\cdot0.5\text{C}_4\text{H}_10^0\) | 2051 (m), 2\,231 (mw) | 2055 (m), 2031 (mw) | \(v\_\text{as}(\text{CO}_2), 1647 (m)\) |

(a) Recorded in dichloromethane solution.
(b) Recorded as nujol mulls on potassium bromide plates.
Table 5.4. NMR Data \(^{1}H\) and \(^{31}P\) of the Complexes \([\text{Rh}_{2}(\mu-O_{2}CR)\text{X}_{2}(\text{CO})_{2}(\mu-\text{dppm})]^{2}\text{ClO}_{4}\)  
\(R = H, \text{CH}_3\) and \(\text{CF}_3\); \(X = \text{Cl}, \text{Br}\) and \(\text{I}\) 

<table>
<thead>
<tr>
<th>Compound</th>
<th>NMR (a,b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Rh}<em>{2}(\mu-\text{O}CH)\text{Cl}</em>{2}(\text{CO})<em>{2}(\mu-\text{dppm})]^{2}\text{ClO}</em>{4})</td>
<td>(^{31}P: 16.10\text{ (m, dppm, } 1\text{H}<em>{\text{Rh-P}} \cdot X\text{H}</em>{\text{Rh-P}} = 80.8\text{ Hz}))</td>
</tr>
<tr>
<td>([\text{Rh}<em>{2}(\mu-\text{O}CH)\text{Br}</em>{2}(\text{CO})<em>{2}(\mu-\text{dppm})]^{2}\text{ClO}</em>{4})</td>
<td>(^{31}P: 13.70\text{ (m, dppm, } 1\text{H}<em>{\text{Rh-P}} \cdot X\text{H}</em>{\text{Rh-P}} = 81.2\text{ Hz}))</td>
</tr>
<tr>
<td>([\text{Rh}<em>{2}(\mu-\text{O}CH)\text{I}</em>{2}(\text{CO})<em>{2}(\mu-\text{dppm})]^{2}\text{ClO}</em>{4})</td>
<td>(^{31}P: 8.11\text{ (m, dppm, } 1\text{H}<em>{\text{Rh-P}} \cdot X\text{H}</em>{\text{Rh-P}} = 82.7\text{ Hz}))</td>
</tr>
<tr>
<td>([\text{Rh}<em>{2}(\mu-\text{O}CH</em>{3})\text{Cl}<em>{2}(\text{CO})</em>{2}(\mu-\text{dppm})]^{2}\text{ClO}_{4})</td>
<td>(^{31}P: 15.90\text{ (m, dppm, } 1\text{H}<em>{\text{Rh-P}} \cdot X\text{H}</em>{\text{Rh-P}} = 83.5\text{ Hz}))</td>
</tr>
</tbody>
</table>

\(1\text{H: 7.68 (m, 40H, Phenyl)); 6.36 (s, 1H, CH); 3.40 (t, 3H, CH_{3}); 1.15 (t, 3H, CH_{3})\) 

\(31\text{P: 15.90 (m, dppm, } 1\text{H}_{\text{Rh-P}} \cdot X\text{H}_{\text{Rh-P}} = 83.5\text{ Hz})\)

(continued)
Table 5.4. (continued)

<table>
<thead>
<tr>
<th>Compound</th>
<th>NMR a,b</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Rh₂(μ-OC₃H₅)Br₂(CO)₂(u-dppm)₂]ClO₄</td>
<td>31P : 13.68 (m, dppm, J_{Rh-P} + X_{Rh-P} = 82.0 Hz)</td>
</tr>
<tr>
<td></td>
<td>1H : 7.69 (m, 40H, Phenyl); 5.32 (s, CH₂Cl₂);</td>
</tr>
<tr>
<td></td>
<td>4.09 (m, 2H, CH₂-dppm); 3.40 (g, 2H, OCH₂₂, J_{H-H} = 7.0 Hz);</td>
</tr>
<tr>
<td></td>
<td>1.15 (t, 6H, CH₃, J_{H-H} = 7.0 Hz); 0.55 (s, 3H, CH₃)</td>
</tr>
<tr>
<td>[Rh₂(μ-OC₃H₅)I₂(CO)₂(u-dppm)₂]ClO₄</td>
<td>31P : 9.27 (m, dppm, J_{Rh-P} + X_{Rh-P} = 83.38 Hz)</td>
</tr>
<tr>
<td></td>
<td>1H : 7.50 (m, 40H, Phenyl); 4.98 (m, 2H, CH₂-dppm);</td>
</tr>
<tr>
<td></td>
<td>4.31 (m, 2H, CH₂-dppm); 0.60 (s, 3H, CH₃)</td>
</tr>
<tr>
<td>[Rh₂(μ-OCF₃)Br₂(CO)₂(u-dppm)₂]ClO₄</td>
<td>31P : 15.95 (m, dppm, J_{Rh-P} + X_{Rh-P} = 74.5 Hz)</td>
</tr>
<tr>
<td>[Rh₂(μ-OCF₃)I₂(CO)₂(u-dppm)₂]ClO₄</td>
<td>31P : 13.91 (m, dppm, J_{Rh-P} + X_{Rh-P} = 79.5 Hz)</td>
</tr>
<tr>
<td>[Rh₂(μ-OCF₃)I₂(CO)₂(u-dppm)₂]ClO₄</td>
<td>31P : 9.93 (m, dppm, J_{Rh-P} + X_{Rh-P} = 81.1 Hz)</td>
</tr>
</tbody>
</table>

(a) Chemical shifts (in ppm) relative to tetramethylsilane (1H) and 85% phosphoric acid (31P).
(b) 1H NMR spectra were recorded in dichloromethane-d₂.
(c) The degree of dichloromethane solvation was determined by recording 1H NMR spectrum in acetone-d₆ (5.60, s, 1H).
(d) These peaks could be resolved at 360 MHz (3.99 (m, 2H), 4.25 (m, 2H)).
CHAPTER 6
SYNTHESIS AND REACTIVITY OF
$\sigma$-$\pi$ BRIDGING ACETYLIDE COMPLEXES

6.1. Introduction

The carboxylate bridged complexes $[\text{Rh}_2(\mu-O\text{CR'})_2\text{(CO)}_2(\mu\text{-dppm})_2\text{ClO}_4](R' = \text{CH}_3$ and $\text{CP}_3$) react with terminal acetylenes $\text{RC}_2\text{H} (R = \text{H, Ph, } \text{Bu})$ to yield the $\sigma$-$\pi$ acetylide complexes $[\text{Rh}_2(\mu-\text{C}_2\text{R})(\text{CO})_2(\mu\text{-dppm})_2\text{ClO}_4]$, the synthesis and characterization of which form the subject of this chapter. In addition, preliminary studies concerning the reactivity of these acetylide complexes with carbon monoxide, sulphur dioxide, hydrides, tertiary phosphines, hydrogen and a mixture of dihydrogen/carbon monoxide (1:1) will be discussed. One member of this series, $[\text{Rh}_2(\mu-\text{C}_2\text{tBu})(\text{CO})_2(\mu\text{-dppm})_2\text{ClO}_4]$ has been structurally characterized by X-ray crystallography to confirm the $\sigma$-$\pi$ bridging mode.

Two structural types are known for acetylide groups when bridging two metal centres; the $\sigma$-$\pi$ bridging mode (104) and the symmetrical bridge (105). These can be conveniently distinguished by using the $\mu_2$-$\pi^n$ notation where $\mu_2$ specifies that two metal centres are involved and $\pi^n$ refers to the number of ligand atoms ($n$) formally bound to the second metal.
The acetylide function formally donates 3 electrons when bridging in the \( \sigma^* \) fashion. A similar mode of bonding has been previously described for carbon monoxide, isocyanides, cyanides, and cyamnides in \( \text{Mn}_2(\mu_2-\eta^2-\text{CO})(\text{CO})_4 \) (\( \mu \)-dppm)_2, \( 171^\text{a} \), \( \text{Mn}_2(\mu_2-\eta^2-\text{CN})_2(\text{CO})_4(\mu-\text{dppm})_2 \) (R = p-toly), \( 201^\text{a} \), \( [\text{Cp}_2\text{Mo}_2(\mu_2-\eta^2-\text{CN})(\text{CO})_4]^\text{170^a} \text{NET}_4 \), and \( (\eta^5-C_5\text{H}_5)_2\text{Mo}_2(\mu_2-\eta^2-\text{NCNMe}_2)^2(\text{CO})_4 \) \( 202^\text{a} \), respectively. In the case of symmetrical bridging, the acetylide function acts as a one electron donor, analogous to a bridging hydride ligand. There are numerous examples reported in the literature, especially associated with cluster complexes of group VIII metals, in which an acetylide bridges two metals in a \( \sigma^* \) fashion. The symmetrical \( \mu_2-\eta^1 \) bonding mode of acetylides is rare, however. The only known examples are the beryllium compound \( [[\text{MeBe}[\text{C}_2\text{Me}]\text{NMe}_3]_2] \), \( 203^\text{a} \), the copper cluster \( \text{Cu}_6\text{R}_4(\text{C}_2\text{R}')_2 \) \( (\text{R} = \text{O}-\text{NMe}_2\text{C}_6\text{H}_4, \text{R}' = \text{Ph}) \), \( 204^\text{b} \), and the trinuclear ruthenium cluster, \( \text{Ru}_6(\text{CO})_6(\mu_2-C_2\text{Bu})_2(\mu_2-\eta^2-\text{C}_2\text{Bu})_2(\text{PPh}_2)_2 \).
The latter complex contains both symmetrical and unsymmetrical bridging acetylide groups. A complex containing an asymmetric acetylide bridge has also been recently synthesized.

Acetyldes bridging in a σ-π fashion are known to exhibit unusual patterns of chemical reactivity, being susceptible to attack by neutral nucleophiles such as phosphines and amines to generate zwitterionic complexes. The most intensively studied σ-π acetylide complex is the structurally characterized binuclear complex, Fe₂[(μ₂-η²-η₂-C₂Ph):(μ-PPh₂)(CO)₆] (106), prepared by the reaction of Fe₂(CO)₉ with PPh₂C=O. This complex reacts with trialkyl and triaryl phosphites (P(OR)₃) (R = alkyl, aryl), with attack at

![Diagram of Fe₂[(μ₂-η²-η₂-C₂Ph):(μ-PPh₂)(CO)₆]](image)

the α carbon to give complexes that can best be described as phosphonium-betaine (107) or ylide carbene (108) complexes. In such compounds, the two carbon bridge functions as a three electron donor. An X-ray structure determination of the triethyl phosphite derivative reveals that
there are contributions from both forms to the structure.

In contrast to the reaction with tertiary phosphites, the reaction of \( \text{Fe}_2(\mu_2-\eta^2-C_2\text{Ph})(\mu-\text{PPh}_2)(\text{CO})_6 \) with secondary and tertiary amines takes place at the \( \beta \) carbon to give complexes of the type represented by 109 and 110 respectively, which contain bridging three electron donors. The former has been characterized by single crystal X-ray diffraction studies and found to be best described by the 1,3 dipolar structure 109. This
structure is implied by the planar geometry at both carbon and nitrogen as well as the approximately tetrahedral geometry at the carbon attached to the iron atoms. The formation of structure 109 can be considered as resulting from the addition of N-H across the triple bond followed by valence isomerization, or by the attack of diethylamine at the β carbon followed by hydrogen transfer to the carbon bridging the metal centers. The structure 110 is, however, indistinguishable from 111 in which the carbon bridge acts as a two electron donor.

Attempts to add P-H moieties across the carbon-carbon triple bond of Fe₂(μ₂-η²-C₄Ph)(μ-PPh₂)(CO)₆ using secondary phosphines (Cy₂PH, Cy = cyclohexyl) were unsuccessful. Instead, the attack was at the β carbon to yield Fe₂(μ-CCPh(Cy₂PH)(μ-PPh₂)(CO)₆ (112). The formation of this species is quite unusual when compared to the reaction with phosphites, whereas the attack was at the α position to give phosphonium-betaine (or ylide carbene) structures.
6.2. Results and Discussion

IR data for all complexes are tabulated in table 6.1 whereas the NMR (1H and 31P(1H)) data are presented in table 6.2. All other physical data for the complexes are given in the experimental section.

6.2.1 The Synthesis and Characterization of Bridging Acetylide Complexes

Mague et al. have reported the reaction of carboxylate bridged rhodium dppm and dpam complexes with activated acetylene to yield complexes containing the acetylene bound between the metal centres as a cis-dimetallated olefin, with the carboxylate remaining attached to only one metal centre in a bidentate fashion (scheme 6; section 1.2.3). 77

Contrary to Mague's results, the carboxylate complexes [Rh2(μ-O2CR')(CO)2(μ-dppm)2]ClO4 (R' = CH₃, CF₃)
reacted with terminal acetylenes $RHC$ ($R = H, Ph,$ and $^\text{t}Bu$ ($R' = C_2F_5$ only)) with the removal of the carboxylate group to yield the acetylide complexes, $[\text{Rh}_2(\mu_2-\eta^2-C_2R)(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4$ (113), in which the acetylide function bridges the metal centres in a $\sigma-\pi$ fashion (equation 49).

The treatment of $[\text{Rh}_2(\mu-\text{O}_2\text{CCF}_3)(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4$ with tert-butylacetylene in dichloromethane, followed by the addition of diethyl ether after a reaction time of 4.5 h, gave orange or red crystals (or sometimes both) identified as $[\text{Rh}_2(\mu_2-\eta^2-C_2^t\text{Bu})(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4$ from analytical, spectroscopic and X-ray crystallographic data. No such reaction was, however, observed between $[\text{Rh}_2(\mu-\text{O}_2\text{CH}_3)(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4$ and the acetylene, even after stirring for 15 h. An X-ray structure determination of $\text{Rh}_2(\mu_2-\eta^2-C_2^t\text{Bu})-(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4$ was performed by Prof. M. Cowie. This study revealed that the acetylide function bridged the metal centres in a $\sigma-\pi$ fashion.
The equatorial plane of the cation with some relevant bond distances and angles is given in figure 6.1. No appendix will be associated with this structure since the structural parameters were unavailable at the time of writing of this thesis. The centres appear to be approximately square planar with a rhodium-rhodium distance of 3.15 Å. This value indicates the absence of a rhodium-rhodium single bond and falls in the range (3.1520(8) - 3.386(1) Å) normally observed for such complexes. Considering the acetylide to be a 3 electron donor, the absence of a rhodium-rhodium bond is implied by conventional electron counting techniques. The most notable feature of this structure is the presence of an asymmetrically bridging acetylide group. The criterion put forward by Curtis et al. to distinguish between four electron and two electron bridging carbonyls has been successfully extended to bridging cyanides. Extending the same criterion to the acetylide function gives an asymmetry parameter of 0.08 with an M-C-C angle of 168.0°. This clearly places the acetylide function on the published curve for σ-π bridging carbonyls. The difference in distance between the acetylenic carbons, C(3) and C(4) and Rh(2) is 0.415 Å. This compares favourably to that observed for the difference in distance of the carbon and nitrogen atoms of the cyanide ligand with the second rhodium atom in [Rh₂(μ-CN)(μ-CO)-(CO)₂(μ-dppm)₂]ClO₄ (Chapter 3). The tert-butylacetylide
Figure 6.1. The Equatorial Plane of the Cation, $[\text{Rh}_2(\mu_2-\eta^2-C_2^t\text{Bu})(\text{CO})_2(\mu\text{-dppm})_2]^+$. 
function is significantly distorted from linearity with "bent back" angles of 12° at C(3) and 7.2° at C(4). This distortion is probably steric in origin arising to avoid interactions between the phenyl rings of the dppm ligands with the tert-butyl group. As observed in all structurally characterized A-frame complexes, the methylene groups of the dppm ligands appear to be cis folded and bent towards the bulky bridgehead ligand, C₂Bu (figure 6.2).

The IR spectrum of the orange crystals in the solid state showed two terminal carbonyl bands at 1993 (s) and 1962 (vs) and a medium to weak intensity band at 2026 cm⁻¹, which was attributed to the v(C≡C) of the acetylide function (vide infra). No bands indicative of the presence of either a bridging or terminal trifluoroacetate group were seen. The carbonyl region of the IR spectrum of the red crystals was very complex (five maxima) and a medium band corresponding to v(C≡C) appeared at 2023 (mw) cm⁻¹. In dichloromethane solution, however, the IR spectra of both the red and orange crystals were identical (v(CO), 1996 (sh), 1982 (vs); v(C≡C), 2022 (mw) cm⁻¹) which indicates that the above behaviour probably arises as a result of some as yet unidentified solid-state effect rather than from two different formulations. The assignment of v(C≡C) was confirmed unambiguously by labelling the complex with 13-carbon monoxide. Rapid exchange of the terminal carbonyls was found to take
Figure 6.2. Perspective View of the Cation, 
\([\text{Rh}_2(\mu_2-\eta^2-C_2tBu)(\text{CO})_2(\mu-\text{dppm})_2]^+\)
place when $[\text{Rh}_2(\mu_2-\eta^2-\text{C}_2\text{Bu})(\text{CO})_2(\mu\text{-dppm})_2]\text{ClO}_4$ reacted with labelled carbon monoxide ($^{13}\text{CO}$) in dichloromethane solution. New bands appeared at 1955(s) and 1936(vs) with the complete disappearance of the original bands at 1996(sh) and 1982(vs) cm$^{-1}$. The band at 2022(mw) cm$^{-1}$, however, remained virtually unchanged during the exchange process. The $^{31}\text{P}^1\text{H}$ NMR spectrum of $[\text{Rh}_2(\mu_2-\eta^2-C_2\text{Bu})(\text{CO})_2(\mu\text{-dppm})_2]\text{ClO}_4$ at room temperature showed a symmetrical second order pattern (20.47 ppm, $|J_{\text{Rh}-\text{P}+} + J_{\text{Rh}-\text{P}}| = 113.7$ Hz) indicating that all four phosphorus atoms are equivalent. This was somewhat surprising since a $\sigma-\pi$ bridging acetylide complex, in principle, should give rise to a pattern that would be characteristic of an AA'BB'XY spin system. The symmetric pattern observed, however, can be explained by invoking a fluxional process whereby the acetylene exhibits a "wind shield wiper" type motion (equation 50), as observed for the cyanide in $[\text{Rh}_2(\mu\text{-CN})(\mu\text{-CO})(\text{CO})_2(\mu\text{-dppm})_2]\text{ClO}_4 \cdot \text{CH}_2\text{Cl}_2$. Cooling the solution even down to -80 °C did not freeze out

\begin{equation}
\begin{align*}
\text{Rh} & \quad \text{Rh} \\
\text{C} & \quad \text{C} \\
\text{R} & \quad \text{R} \\
\text{OC} & \quad \text{OC} \\
\end{align*}
\end{equation}

$R = \text{t-Bu}$
this motion of the acetylide function, since the symmetrical pattern remained virtually unchanged down to that temperature. Another possible explanation for the observed $^{31}P\{^1H\}$ NMR spectrum would have the complex adopting a symmetrical bridging mode (114) different from that observed in the solid state structure. This has been rejected on the basis of the adduct with carbon monoxide (vide infra) and IR spectroscopy, since no significant change was observed for the acetylene stretch on going from the solid state to the solution phase.

The $^1H$ NMR of $[\text{Rh}_2(\mu_2-\eta^2-C_2^2\text{t-Bu})(\text{CO})_2(\mu-\text{dppm})_2]ClO_4$ in dichloromethane-$d_2$ showed a singlet for the tert-butyl group at 0.47 ppm, complex multiplets for the dppm methylene protons at 4.25 and 3.66 and a complex multiplet for phenyl protons at 7.53 ppm.

Unlike tert-butylacetylene, phenylacetylene and acetylene reacted with both $[\text{Rh}_2(\mu_2-\text{O}_2\text{CR})(\text{CO})_2(\mu-\text{dppm})_2]ClO_4$
(R = CH₃, CF₃) to give the corresponding acetylide complexes.

The reaction of \([\text{Rh}_2(\mu-O_2CCH_3)(CO)_2(\mu-dppm)_2]ClO_4\) with phenylacetylene in dichloromethane, followed by precipitation with diethyl ether after a reaction time of 3.5 h, gave \([\text{Rh}_2(\mu_2-\eta^2-C_2Ph)(CO)_2(\mu-dppm)_2]ClO_4\) as red crystals. The IR spectrum of this complex in dichloromethane (\(\nu(CO)\) 1998\,(sh), 1983\,(vs); \(\nu(C=C)\) 2021\,(mw) \,cm\(^{-1}\)) was very similar to that of \([\text{Rh}_2(\mu_2-\eta^2-C_2tBu)(CO)_2(\mu-dppm)_2]ClO_4\). This indicated that these complexes are in fact very similar.

In the solid state, \([\text{Rh}_2(\mu_2-\eta^2-C_2Ph)(CO)_2(\mu-dppm)_2]ClO_4\) showed terminal carbonyl bands at 1979\,(s), 1962\,(vs) and an acetylenic stretch at 2019\,(mw). The position of the latter was also confirmed by exchanging the terminal carbonyl ligands with 13-carbon monoxide.

The \(^{31}\text{P}\{^1\text{H}\}\) NMR spectrum of this complex behaved in an identical fashion to that of \([\text{Rh}_2(\mu_2-\eta^2-C_2tBu)(CO)_2(\mu-dppm)_2]ClO_4\). Both at room temperature (20.79 ppm, \(|J_{\text{Rh-P}} + X_{\text{Rh-P}}| = 113.0 \,\text{Hz}\)) and at -78 \,\text{°C}, the spectrum was a symmetrical second order multiplet characteristic of an A-frame complex. The \(^1\text{H}\) NMR spectrum of \([\text{Rh}_2(\mu_2-\eta^2-C_2Ph)(CO)_2(\mu-dppm)_2]ClO_4\) in dichloromethane-d\(_{1}\) showed two complex multiplets for the dppm methylene protons (4.26, 3.48 ppm) and a multiplet for the phenyl protons (6.68 ppm) attached to the acetylenic group slightly upfield from the phenyl protons (7.34 ppm). This upfield shift of the phenyl
protons may arise from ring current effects caused by a stacking up of the phenyl group between the phenyl groups of the trans dppm ligands. A similar upfield shift of the protons in the phenylene group in Pd$_2$(μ-C$_6$H$_4$)$_2$I$_2$(μ-dppm) and the phenyl group of the isocyanide ligand in Mn$_2$(μ$_2$-η$^2$-CNR)(CO)$_4$(μ-dppm)$_2$ (R = p-tolyl) has been observed. In the latter case, stacking of the two dppm phenyl rings about the isocyanide ligand has been confirmed by an X-ray structure determination.

The reaction between acetylene and [Rh$_2$(μ-O$_2$CR')$_2$(μ-dppm)$_2$]ClO$_4$ (R' = CH$_3$, CF$_3$) produced a red-orange crystalline complex, [Rh$_2$(μ$_2$-η$^2$-C$_2$H$_2$)(CO)$_2$(μ-dppm)$_2$]ClO$_4$. 0.5CH$_2$Cl$_2$. This formulation was verified by microanalytical data, IR, $^1$H and $^{31}$P($^1$H) NMR data. The IR spectrum in the solid state had the following characteristic bands: ν(CH), 3218 (mw); ν(CO), 2010 (s), 1986 (vs); ν(C≡C), 1886 (mw) cm$^{-1}$. Additionally, a weak band occurring at 1856 cm$^{-1}$ was found to be present in every sample that was prepared. The $^{31}$P($^1$H) NMR spectrum of this complex at room temperature gave two broad unresolved multiplets centred at 20.15 ppm (figure 6.3) which indicated that some dynamic process was occurring. On cooling to -40 °C, however, this broad multiplet sharpened to give a symmetric second order multiplet (19.24 ppm, $|{^1}J_{Rh-P} + {^X}J_{Rh-P}| = 113.4$ Hz) similar to that observed for the other two acetylide complexes.
Figure 6.3. $^{31}P{^1}H$ NMR Spectrum of $[\text{Rh}_2(\mu_2-\eta^2-\text{C}_2\text{H})-(\text{CO})_2(\mu\text{-dppm})_2]\text{ClO}_4\cdot 0.5\text{CH}_2\text{Cl}_2$, in Dichloromethane at 22 °C.
Furthermore, a weak, symmetric second order multiplet also emerged at 27.96 ppm with \( |\frac{1}{2}J_{\text{Rh-P}} + \frac{1}{2}J_{\text{Rh-P}}| = 99.5 \text{ Hz} \). The position and coupling constants of the weaker pattern compare favourably with those normally encountered for binuclear A-frame complexes with carbon monoxide in the endo pocket. A typical example would be \( \text{Rh}_2(\mu-\text{Cl})(\mu-\text{CO})-(\text{CO})_2(\mu-\text{dppm})_2\text{BPh}_4 \) (26.00 ppm, \( |\frac{1}{2}J_{\text{Rh-P}} + \frac{1}{2}J_{\text{Rh-P}}| = 94.2 \text{ Hz} \)). The most likely explanation for this behaviour would be that the parent complex, \( [\text{Rh}_2(\mu_2-\eta^2-\text{C}_2\text{H})(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4 \) is in equilibrium with a small amount of the carbon monoxide adduct, \( \text{Rh}_2(\mu-\text{CO})(\mu_2-\eta^2-\text{C}_2\text{H})(\text{CO})_2(\mu-\text{dppm})_2 \) \text{ClO}_4, with these complexes undergoing intramolecular carbonyl exchange (equation 51) at such a rate at room temperature that the \( \text{^31P} \) resonances appear broad and unresolved. The peaks associated with this minor component are barely visible at room temperature as a hump in the baseline because of the broadening. Similar behaviour has been observed by Cowie et al.\(^{41}\) for \( [\text{Rh}_2(\mu-\text{Cl})(\mu-\text{CO})(\text{CO})_2(\mu-\text{dppm})_2]\text{BPh}_4 \) and \( [\text{Rh}_2(\mu-\text{Cl})(\text{CO})_2(\mu-\text{dppm})_2]\text{BPh}_4 \) when mixed together. The presence of a small amount of \( [\text{Rh}_2(\mu-\text{CO})(\mu_2-\eta^2-\text{C}_2\text{H})(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4 \) in \( [\text{Rh}_2(\mu_2-\eta^2-\text{C}_2\text{H})(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4 \) was confirmed by recording the \( \text{^31P} \{(\text{H}) \} \) NMR spectrum of \( \text{Rh}_2(\mu_2-\eta^2-\text{C}_2\text{H})(\text{CO})_2(\mu-\text{dppm})_2\text{ClO}_4 \) at -40 °C under an atmosphere of carbon monoxide. This caused the symmetric multiplet at 19.24 ppm to disappear completely with the appearance of symmetric multiplet (27.97 ppm,\( \ldots \)
Figure 5.4. $^{31}$P$^1$H NMR Spectrum of $[\text{Rh}_2(\mu_2-\eta^2-C_2H)_2(CO)_2(\mu-dppm)_2]ClO_4 \cdot 0.5CH_2Cl_2$ in Dichloromethane at $-40 \degree C$.
Figure 6.5. $^{31}p^{1}{^1}H$ NMR Spectrum of $[Rh_2(\mu_2-\eta^2-C_2H)(CO)_2(u-dppm)]ClO_4\cdot0.5CH_2Cl_2$ after Reacting with Carbon Monoxide in Dichloromethane at $-40\, ^\circ C$. 
\[ |J_{\text{Rh-P}} + xJ_{\text{Rh-P}}| = 99.4 \text{ Hz} \] whose chemical shift and coupling constant were virtually identical to those observed for the minor component (figure 6.5). The IR spectrum of the solid isolated from the carbon monoxide reaction showed terminal carbonyl bands at 1987 (sh), 1973 (vs) and bridging carbonyl absorption at 1856 (m) cm\(^{-1}\), the latter being identical to the additional peak found in the IR spectrum of \( [\text{Rh}_2(\mu_2-\eta^2-C_2H)(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4 \) (vide supra). To date, it has not been possible to obtain pure samples of
The origin of the extra carbon monoxide adduct is not certain. A probable source is the presence of carbon monoxide as a contaminant in the acetylene gas used.

The \( ^1H \) NMR spectrum of \([\text{Rh}_2(\mu_2-\eta^2-C_2H)(CO)_2(\mu-\text{dpmm})_2] \) \( \text{ClO}_4 \cdot 0.5\text{CH}_2\text{Cl}_2 \) showed complex multiplets for phenyl (7.43 ppm) and methylene protons (4.28 and 3.46 ppm). No signal was observed for the acetylenic hydrogen which is presumably overlapped by other resonances.

An unusually low acetylenic stretch has been observed for the complex, \([\text{Rh}_2(\mu_2-\eta^2-C_2H)(CO)_2(\mu-\text{dpmm})_2] \) \( \text{ClO}_4 \cdot 0.5\text{CH}_2\text{Cl}_2 \) \( \nu(\text{C}=\text{C})\), 1886 (\( \text{mw} \)) cm\(^{-1}\)) by comparison to its congenors, \([\text{Rh}_2(\mu_2-\eta^2-C_2\text{R})(CO)_2(\mu-\text{dpmm})_2] \) \( \text{ClO}_4 \) \( \text{(R=Ph, } \nu(\text{C}=\text{C}), 2019 (\text{mw}) \text{ cm}^{-1}; \text{R=}^{t}\text{Bu, } \nu(\text{C}=\text{C}), 2023 (\text{mw}) \text{ cm}^{-1}) \). High values of \( \nu(\text{C}=\text{C})\) when \( \text{R=}^{t}\text{Bu} \) suggest that the acetylenic linkages are less involved in \( \pi \)-bonding to the second metal. By contrast, the acetylenic linkage in \([\text{Rh}_2(\mu_2-\eta^2-C_2H)(CO)_2(\mu-\text{dpmm})_2] \) \( \text{ClO}_4 \) is probably involved to a greater extent in \( \pi \)-bonding to the second metal since the acetylide function \( (C_2H) \) can achieve a closer approach to the second rhodium atom. These differences are probably associated with the size of the substituent on the acetylide function. The bulky groups such as \( ^{t}\text{Bu} \) and phenyl may orient themselves in such a way as to minimize interaction with the phenyl groups of the
bridging dppm ligand. This may be evident from Rh(1)-C(3)-C(4) angle of 168° which shows significant deviation from linearity for tert-butyl (figure 6.1). This value contrasts with the Rh(2)-C(6)-N angle of 177°(1)° found in [Rh₂(μ₂-η²-CN)(μ-CO)(CO)₂(μ-dppm)₂]ClO₄·CH₂Cl₂ where an unusually low ν(CN) frequency was observed (Chapter 3). A similar situation is expected for the acetylide function C₂H because of its small size.

As expected, all three acetylide complexes, [Rh₂(μ₂-η²-C₂)(μ-dppm)₂]ClO₄ (R = H, Ph, tBu) behaved as 1:1 electrolytes in acetone solution. Additionally, all these complexes showed good thermal and air stability both in the solid state and in dichloromethane solution.

6.2.2. Reactions with Carbon Monoxide and Sulphur Dioxide

All three acetylide complexes reacted with carbon monoxide and sulphur dioxide reversibly to yield complexes of the type [Rh₂(μ-L)(μ₂-η²-C₂R)(CO)₂(μ-dppm)₂]ClO₄ (115) (L = CO, SO₂) in which a formal rhodium-rhodium single bond is present (equation 52). The reactions were carried out in dichloromethane solution and the products isolated by the addition of diethyl ether in the presence of the appropriate gas.
All three acetylide complexes reacted smoothly with carbon monoxide in dichloromethane solution. Although no significant colour change was observed for these complexes with \( R = H, \text{Ph} \) the reaction of carbon monoxide with the tert-butylacetylide complex was accompanied by a rapid colour change from red to red-brown. All three carbonyl adducts, \( \{\text{Rh}_2(\mu-\text{CO})(\mu_2-\eta^2-\text{C}_2\text{R})(\text{CO})_2(\mu-\text{dppm})_2\}\text{ClO}_4 \) \( (R = H, \text{Ph} \text{ and } ^t\text{Bu}) \) displayed bridging carbonyl stretches in the IR spectrum at 1856(m), 1872(m) and 1860(w) cm\(^{-1}\) respectively in the solid state. The bridging carbonyl groups were extremely labile in all three complexes, and were readily lost in solution. Similar behaviour was observed in the solid state for the complexes, \( \{\text{Rh}_2(\mu-\text{CO})(\mu_2-\eta^2-\text{C}_2\text{R})(\text{CO})_2(\mu-\text{dppm})_2\}\text{ClO}_4 \) \( (R = \text{Ph}, ^t\text{Bu}) \), in which the bridging carbonyl was lost within a period of 24 h. By contrast, \( \{\text{Rh}_2(\mu-\text{CO})(\mu_2-\eta^2-\text{C}_2\text{R})(\text{CO})_2(\mu-\text{dppm})_2\}\text{ClO}_4 \) was relatively stable and did not show any signs of carbon monoxide loss.
even after a period of one week. The $^{31}\text{P}({}^1\text{H})$ NMR spectra of the carbon monoxide adducts at -40 °C in dichloromethane under an atmosphere of carbon monoxide showed symmetrical second order multiplets indicating that in all complexes, the four phosphorus atoms were equivalent. This type of symmetrical pattern is possible only if the $\sigma-\pi$ acetylide function remains fluxional. The chemical shifts and coupling constants obtained for the carbon monoxide adducts (table 6.2) compare favourably with those obtained for electronically similar $[\text{Rh}_2(\mu-\text{Cl})(\mu-\text{CO})(\text{CO})_2(\mu-\text{dppm})_2]\text{BF}_4$ in which a formal rhodium-rhodium single bond is present.

The bridging carbonyl frequencies of $[\text{Rh}_2(\mu-\text{CO})(\mu_2-\eta^2-\text{C}_2\text{R})(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4$ ($\text{R} = \text{H, Ph, and }^t\text{Bu}$) also indicate that they are normal bridging carbonyl groups accompanied by a metal-metal bond. If the acetylide bridge were symmetrical, no formal rhodium-rhodium bond should be present since the complex would have a 32 electron configuration. Under these circumstances, the bridging carbonyls should be of the ketonic type with frequencies in the 1750-1700 cm$^{-1}$ region.

The reaction of $[\text{Rh}_2(\mu_2-\eta^2-\text{C}_2\text{H})(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4$ with sulphur dioxide in dichloromethane solution produced no observable colour change. The addition of diethyl ether yielded a red complex, identified as $[\text{Rh}_2(\mu-\text{SO}_2)(\mu_2-\eta^2-\text{C}_2\text{H})(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4$. The IR spectrum of the solid showed
two terminal \( \nu(CO) \) bands at 2015(s) and 1977(vs), and a medium to weak intensity band at 1230 cm\(^{-1}\) that could be attributed to the asymmetric S-O stretch. Unfortunately, interference from the perchlorate absorption at 1100 cm\(^{-1}\) prevented identification of the \( \nu_s(SO) \) at ca. 1050 cm\(^{-1}\). The band at 1230 cm\(^{-1}\) agrees closely with values obtained for the sulphur dioxide ligand bridging two singly bonded rhodium centres. For example, \([\text{Rh}_2(\mu-\text{Cl})(\mu-\text{SO}_2)(\text{CO})_2(\mu-\text{dppm})_2]\text{BPh}_4\) showed \( \nu(SO) \) stretches at 1229(m) and 1070(m). Although the acetylide complexes, \([\text{Rh}_2(\mu_2-\eta^2-\text{C}_2\text{R})(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4\) (\( R = \text{Ph}, \text{tBu} \)) reacted rapidly with sulphur dioxide to produce significant colour changes, the solids isolated from these reactions upon the addition of diethyl ether did not show \( \nu(SO) \) bands in the IR spectrum and the terminal bands were in good agreement with those of the parent complexes. For \( R = \text{Ph} \), the absence of peaks corresponding to bridging sulphur dioxide resulted from the loss of sulphur dioxide upon grinding, which was evident from the characteristic smell of sulphur dioxide liberated while samples were being milled. Similar behaviour was observed for \( R = \text{tBu} \). Recording of the solution IR spectra of the acetylide complexes, \([\text{Rh}_2(\mu_2-\eta^2-\text{C}_2\text{R})(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4\) (\( R = \text{H}, \text{Ph} \)) in dichloromethane saturated with sulphur dioxide also supported the formation of genuine sulphur dioxide adducts. This was evident from the dramatic shift of the carbonyl absorptions to higher frequencies.
(table 6.1). [Rh$_2$(μ$_2$-η$^2$-C$_2$Bu)(CO)$_2$(μ-dppm)$_2$]ClO$_4$, however, exhibited unusual behaviour. Although the $^{31}$P{$_1$H} NMR spectrum of [Rh$_2$(μ$_2$-η$^2$-C$_2$Bu)(CO)$_2$(μ-dppm)$_2$]ClO$_4$ in the presence of sulphur dioxide indicated the formation of a genuine sulphur dioxide adduct, no dramatic shift of the carbonyl frequencies was observed in the IR spectrum under similar conditions. The new frequencies (2000(vs), 1983(s) cm$^{-1}$) observed were very close to those of the parent complex (1996(sh), 1982(s) cm$^{-1}$) and the only difference that was apparent was the resolution of the high energy shoulder. The reason for this behaviour remains unanswered. The formation of genuine sulphur dioxide adducts by all three acetylide complexes was apparent from their $^{31}$P{$_1$H} NMR spectra. Recording of the $^{31}$P{$_1$H} NMR spectra at -40 °C under an atmosphere of sulphur dioxide showed the typical AA'X'A'' pattern. The chemical shifts and coupling constants obtained (table 6.2) agree favourably with values obtained for complexes such as [Rh$_2$(μ-Cl)-(μ-ClO$_2$)(CO)$_2$(μ-dppm)$_2$]BPh$_4$ (24.5 ppm, $|^{1}$J$_{Rh-P} + ^{10}$J$_{Rh-P}$| = 91.3 Hz) where a formal metal-metal bond is present. The presence of a metal-metal bond indicates that the acetylide function of the sulphur dioxide adducts continues to bind in a σ-π fashion rather than adopting a symmetrical bridging mode.
6.2.3. Reactions with Hydrides

All three acetylide complexes, \([\text{Rh}_2(\eta^2-\text{C}_2\text{R})(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4\) (\(\text{R} = \text{H}, \text{Ph} \text{ and } \text{tBu}\)) reacted with lithium triethylborohydride (LiB(Et)_3H) to give highly coloured extremely air sensitive complexes. With the evidence so far available, these complexes have been tentatively identified as the bridging vinylidene complexes, \([\text{Rh}_2(\mu-\text{CC}[\text{H}]\text{R})(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4\) formed by the attack of hydride at the \(\beta\) carbon atom of the bridging acetylide. Further work in this area is required to confirm the formulation of these products. The characterization of these bridging vinylidene complexes has been mainly from solution IR and \(^{31}\text{P}\{^1\text{H}\}\) NMR spectroscopy because of their extreme air sensitivity.

The treatment of \([\text{Rh}_2(\eta^2-\text{C}_2\text{H})(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4\) (\(\text{R} = \text{H}, \text{tBu}\)) with lithium triethylborohydride in dichloromethane produced deep blue solutions whereas \([\text{Rh}_2(\eta^2-\text{C}_2\text{Ph})(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4\) gave an intense purple solution. The \(^{31}\text{P}\{^1\text{H}\}\) NMR spectra of the deep blue solution (\(-35^\circ\text{C}\)) obtained by the reaction of \([\text{Rh}_2(\eta^2-\text{C}_2\text{H})(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4\) with \([\text{BH}(\text{Et})_3]^\text{-}\) showed a symmetric second order pattern centred at 30.99 ppm (167 MHz) with two principal lines separated by 167 Hz. By contrast, \([\text{Rh}_2(\mu-\text{C}_2\text{Ph})(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4\) and \([\text{Rh}_2(\mu-\text{C}_2\text{tBu})(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4\) showed complicated asymmetric patterns (40.5 MHz) when reacted
with \([BH(Et)_3]^-\). The IR spectra of these highly coloured dichloromethane solutions showed terminal carbonyl bands at 1945(s), 1923(vs) cm\(^{-1}\) for \(R = H\), 1948(s), 1924(vs) cm\(^{-1}\) for \(R = Ph\) and 1943(s), 1918(vs) cm\(^{-1}\) for \(R = t^1Bu\), with no bands that could be attributed to bridging carbonyls being apparent. As anticipated, the formation of a neutral complex was evident by the significant shift of the terminal carbonyls to lower energies. The close similarity of the position and band profiles of the carbonyl absorption indicated that the products are in fact similar for all three acetylide complexes. The complete disappearance of the acetylenic stretch during the reaction implies that the attack of the hydride takes place at either the \(\alpha\) or \(\beta\) carbon of the \(\sigma-\pi\) acetylide function. Attack at the \(\alpha\) carbon will give the acetylene complexes, \([Rh_2(\mu-HCCR)-(CO)_2(\mu-dppm)_2]ClO_4\) (116) \((R = H, Ph, t^1Bu)\) whereas the attack at the \(\beta\) carbon will yield bridging vinylidene complexes (117) (equation 53). The formation of acetylene complexes has been ruled out on the basis of Eisenberg's work, wherein he reported the addition of terminal acetylenes, \(RC_2H\) \((R = H, Ph)\) across the rhodium-rhodium single bond in \(Rh_2(CO)_2(\mu-dppm)_2\) to give the acetylene complexes, \(Rh_2(\mu-HCCR)(CO)_2(\mu-dppm)_2\). These acetylene complexes have physical properties totally unlike those of the complexes prepared in this study. For example, benzene solutions of \(Rh_2(\mu-HCCH)(CO)_2(\mu-dppm)_2\) and \(Rh_2(\mu-HCCPh)\)
(CO)$_2$(μ-dppm)$_2$ are emerald green and blue green in colour respectively, whereas the reactions of [Rh$_2$(μ$_2$-η$_2$-C$_2$H)$_2$(μ-dppm)$_2$]ClO$_4$ and Rh$_2$(μ$_2$-η$_2$-C$_2$Ph)(CO)$_2$(μ-dppm)$_2$ClO$_4$ with lithium triethylborohydride in benzene solutions imparted intense blue and purple colour respectively. The $^{31}$P($^1$H) NMR spectrum of Rh$_2$(μ-HCCH)(CO)$_2$(μ-dppm)$_2$ consists of a symmetric multiplet with principal lines separated by 133 Hz whereas Rh$_2$(μ-HCCPh)(CO)$_2$(μ-dppm)$_2$ exhibits a complicated asymmetric pattern. All the chemical shifts of these complexes have been reported with respect to trimethylphosphite and hence could not be directly compared with the products obtained by the reaction of [BH(Et)$_3$]$^-$ with the acetylides. The bridging mode of the acetylene
molecule in these complexes has not been determined. Although the reaction of tert-butylacetylene with \( \text{Rh}_2(\text{CO})_2(\mu\text{-dppm})_2 \) has not been reported by Eisenberg, it is quite clear from physical data obtained for the reaction of \( [\text{Rh}_2(\mu_2-\eta^2-C_2t^*\text{Bu})(\text{CO})_2(\mu\text{-dppm})_2]\text{ClO}_4 \) with lithium triethyl borohydride that the product is similar to that obtained for its counterparts.

The most stable of these vinylidene complexes, \( [\text{Rh}_2(\mu-\text{CC}[\text{H}]t^*\text{Bu})(\text{CO})_2(\mu\text{-dppm})_2] \) can also be isolated as a dark blue solid by the reaction of sodium borohydride with \( [\text{Rh}_2(\mu_2-\eta^2-C_2t^*\text{Bu})(\text{CO})_2(\mu\text{-dppm})_2]\text{ClO}_4 \) in ethanol suspension. The IR spectrum of the solid showed terminal carbonyl bands at 1940 (s) and 1919 (vs) \( \text{cm}^{-1} \). In solution they appeared at 1943 (s) and 1918 (vs) \( \text{cm}^{-1} \), identical to those obtained by the reaction of \( [\text{Rh}_2(\mu_2-\eta^2-C_2t^*\text{Bu})(\text{CO})_2(\mu\text{-dppm})_2]\text{ClO}_4 \) with \( [\text{BH}($$\text{Et}$$)_3]^- \). The absence of perchlorate absorptions in the solid state IR spectrum indicated that the complex was neutral, which was further confirmed by measuring the electrical conductance in acetone (1 x 10^{-3} \( \text{M} \) solution, \( \Lambda_m = 0 \)). Solid \( \text{Rh}_2(\mu-\text{CC}[\text{H}]t^*\text{Bu})(\text{CO})_2(\mu\text{-dppm})_2 \) could be handled in air for a period of 1-2 h without extensive decomposition. When dissolved in dichloromethane, however, this complex was rapidly oxidized to \( [\text{Rh}_2(\mu_2-\eta^2-C_2t^*\text{Bu})(\text{CO})_2(\mu\text{-dppm})_2]^+ \), unless protected from the atmosphere. This could be monitored very effectively via solution.
IR spectroscopy. The terminal carbonyl absorptions of the deep blue solution gradually disappeared with the concomitant growth of bands at 2022 (m), 1996 (sh) and 1982 (vs) cm$^{-1}$, identical to those obtained for $[\text{Rh}_2(\mu_2-\eta^2-C_2\text{t}Bu)(\text{CO})_2- (\mu-\text{dppm})_2]^+$. During this process the colour changes from deep blue to red. The nature of the anion associated with the cation $\text{Rh}_2(\mu_2-\eta^2-C_2\text{t}Bu)(\text{CO})_2(\mu-\text{dppm})_2]^+$ is unknown but presumably could be hydroxide formed either by the reaction of oxygen or water with the vinylidene hydrogen. The $^1\text{H}$ NMR spectrum of the blue solid in dichloromethane-$d_2$ showed a broad multiplet at 4.60 ppm corresponding to one hydrogen in addition to phenyl, dppm methylenes and tert-butyl resonances. The complex multiplet at 4.60 ppm was assigned to the proton of the vinylidene group. This assignment was confirmed by preparing the deuterio analogue which exhibited the identical spectrum except that the resonance at 4.60 ppm was absent.

Although there are a number of structurally characterized examples of bridging vinylidene complexes\textsuperscript{211-213} it appears that the formation of bridging vinylidene ligands by the attack of anionic nucleophiles on cationic bridging acetylides has no precedents in the chemical literature. A comparison, however, of the hydride addition reaction with the reaction of $\text{Fe}_2(\mu_2-\eta^2-C_2\text{Ph})-(\mu-\text{PPh}_3)(\text{CO})_6$, with $\text{NET}_3$ and $\text{Cy}_2\text{PH}$ to give bridging
zwitterionic complexes (*vide supra*, section 6.1), and their structural similarity to vinylidene complexes, suggests that it is not unreasonable to assume the formation of bridging vinylidene complexes by the reaction of 

\[ \text{[BH(} \text{Et}_3 \text{]}^- \text{ on the cationic acetylide complexes, } \text{Rh}_2(\mu_2^-\eta^2-\text{C}_2\text{R})(\text{CO})_2(\mu\text{-dppm})_2\text{ClO}_4 \]. No general methods for the synthesis of bridging vinylidene complexes are known and very little is known about their subsequent chemistry. This is in contrast to the mononuclear system wherein vinylidene chemistry is well established. Two general routes are known for the synthesis of mononuclear vinylidene complexes. These invariably involve the protonation and alkylation of the $\beta$ carbon of a $\sigma$ acetylide ligand or by rearrangement of coordinated alkynes.

6.2.4. Reactions with Phosphines

\[ \text{[Rh}_2(\mu_2^-\eta^2-\text{C}_2\text{H})(\text{CO})_2(\mu\text{-dppm})_2\text{ClO}_4 \] reacted instantaneously with tertiary phosphines such as methyldiphenylphosphine and triphenylphosphine in dichloromethane to produce deep violet solutions from which violet crystalline solids, analyzing approximately for \[ \text{[Rh}_2(\text{C}_2\text{HL})(\text{CO})_2(\mu\text{-dppm})_2\text{ClO}_4 \) \( L = \text{PMePh}_2, \text{PPPh}_3 \), could be isolated by the addition of diethyl ether. This confirmed the stoichiometry of the reaction as 1:1. By contrast, no reactions were observed with \[ \text{[Rh}_2(\mu_2^-\eta^2-\text{C}_2\text{R})(\text{CO})_2(\mu\text{-dppm})_2\text{ClO}_4 \]
(R = Ph, t-Bu). These violet solids were found to slowly decompose in the solid state. Their decomposition was very rapid in dichloromethane, however, but could be somewhat minimized by the addition of excess phosphine. In spite of the presence of excess phosphine, however, these complexes did decompose or rearrange to produce red solutions over a period of 24-48 h, from which only amorphous solids could be obtained. To date, these solids have defied characterization. IR spectra of the violet solids obtained from the reaction of \([\text{Rh}_{2}(\mu_2-n^2-C_2H)(\text{CO})_2(\mu-dppm)]_2\text{ClO}_4\) with tertiary phosphines (PPh$_3$, PMePh$_2$) showed terminal carbonyl bands at 1959(s), 1937(vs) cm$^{-1}$ (PPh$_3$) and 1959(s), 1940(vs) (PMePh$_2$). In dichloromethane they appeared at 1973(s) and 1957(vs) cm$^{-1}$ (PPh$_3$) and 1974(s) and 1956(vs) cm$^{-1}$ (PMePh$_2$). The latter values were obtained in the presence of excess phosphine to minimize decomposition. The absence of bands in the solid state that could be attributed to $\nu$(C=C) and $\nu$(CH) indicated that the attack of the phosphine takes place at the acetylide function. The band profiles of the terminal carbonyl absorptions for these complexes were virtually identical to those obtained from the reaction of \([\text{Rh}_{2}(\mu_2-n^2-C_2R)(\text{CO})_2(\mu-dppm)]_2\text{ClO}_4\) with [BH(Et)$_3$]$^-$. This tends to suggest that the products formed in these reactions have similar structures. The $^{31}\text{P}^_{(1)}\text{H}$ NMR spectra (40.5 MHz) of a \([\text{Rh}_{2}(\mu_2-n^2-C_2H)(\text{CO})_2(\mu-dppm)]_2\text{ClO}_4\) solution in dichloromethane at room
temperature containing a five fold excess of phosphine (PPh$_3$ or PMePh$_2$) showed an asymmetric pattern for the dppm phosphorus resonances centred at 24.29 ppm and 27.66 ppm respectively. In addition, signals attributable to coordinated triphenylphosphine and methyldiphenylphosphine appeared as complex multiplets at -11.73 and -14.3 ppm respectively. The $^1$H NMR spectra of [Rh$_2$(μ$_2$-η$_2$-C$_2$H)(CO)$_2$(μ-dppm)$_2$]ClO$_4$ in dichloromethane-d$_2$ solution containing excess phosphine (PPh$_3$, PMePh$_2$), both at room temperature and -35 °C, did not show resonances that could be attributed to an alkene or acetylenic hydrogen, probably as a result of overlap with other resonances. As mentioned in the beginning of the chapter, bridging acetylides are susceptible to attack at either the α or β carbon atoms. Attack at the α carbon would lead to cis-dimetallated olefin type complexes (117) whereas attack at the β carbon would yield vinylidene type complexes (119) (equation 54). The physical data available to date do not permit one to distinguish between these structures 118 and 119. The deep purple colour of these complexes and the carbonyl band profile suggest that the attack is probably occurring at the β carbon to give bridging vinylidene complexes comparable to those produced by the reaction of [Rh$_2$(μ$_2$-η$_2$-C$_2$R)(CO)$_2$(μ-dppm)$_2$]ClO$_4$ (R = H, Ph
and \( ^{t}\text{Bu} \)) with lithium triethylborohydride. The inability of \([\text{Rh}_2(\mu_2-n^2-C_2R)(\text{CO})_2(\mu-\text{dppm})_2]\) to react with phosphines under similar conditions may indicate that there is significant steric interaction between the phosphines and the substituents attached to the \( \beta \) carbon (\( R = \text{Ph}, \ ^{t}\text{Bu} \)) with dppm phenyl rings.
6.2.5 Reactions with Dihydrogen/Carbon Monoxide

All three acetylide complexes, \[ \text{[Rh}_2(\mu_2-\eta^2-C_2R)(\text{CO})_2(\mu-\text{dppm})_2]ClO}_4 \] \( R = \text{H, Ph and } \text{tBu} \) reacted with dihydrogen at room temperature and one atmosphere. Time did not permit however, a detailed examination of these reactions to be performed in order to characterize the products formed, although preliminary studies using IR spectroscopy did indicate the involvement of the acetylide function in these reactions. All three acetylide complexes also reacted with a mixture of dihydrogen/carbon monoxide (1:1) to produce \[ \text{[Rh}_2(\mu-H)(\mu-\text{CO})(\text{CO})_2(\mu-\text{dppm})_2]ClO}_4 \] by comparison with authentic samples. The rates of these reactions were found to be a function of the type of substituent attached to the \( \beta \) carbon. Thus, the reaction times for \( R = \text{H, Ph and } \text{tBu} \) were 1.5 h, 7 hr and 18 h respectively. The first step of these reactions may involve the formation of the carbon monoxide adduct, \[ \text{[Rh}_2(\mu-\text{CO})(\mu_2-\eta^2-C_2R)(\text{CO})_2(\mu-\text{dppm})_2]ClO}_4 \] which may initiate heterolytic activation of hydrogen to give \[ \text{[Rh}_2(\mu-H)(\mu-\text{CO})(\text{CO})_2(\mu-\text{dppm})_2]ClO}_4 \] and the corresponding terminal alkane as postulated for the bridging carboxylate complexes.
6.3. Experimental

6.3.1. List of Complexes Synthesized

<table>
<thead>
<tr>
<th>Complex</th>
<th>Page</th>
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<tbody>
<tr>
<td>([\text{Rh}_2(\mu_2-\eta^2-C_2H)(\text{CO})_2(\mu\text{-dppm})_2]\text{ClO}_4 \cdot 0.5\text{CH}_2\text{Cl}_2)</td>
<td>313</td>
</tr>
<tr>
<td>([\text{Rh}_2(\mu_2-\eta^2-C_2\text{Ph})(\text{CO})_2(\mu\text{-dppm})_2]\text{ClO}_4)</td>
<td>313</td>
</tr>
<tr>
<td>([\text{Rh}_2(\mu_2-\eta^2-C_2\text{tBu})(\text{CO})_2(\mu\text{-dppm})_2]\text{ClO}_4)</td>
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</tr>
<tr>
<td>([\text{Rh}_2(\mu-\text{CO})(\mu_2-\eta^2-C_2\text{R})(\text{CO})_2(\mu\text{-dppm})_2]\text{ClO}_4) (\text{R} = \text{H, Ph and tBu})</td>
<td>314</td>
</tr>
<tr>
<td>([\text{Rh}_2(\mu-\text{SO}_2)(\mu_2-\eta^2-C_2\text{R})(\text{CO})_2(\mu\text{-dppm})_2]\text{ClO}_4) (\text{R} = \text{H, Ph and tBu})</td>
<td>315</td>
</tr>
<tr>
<td>Reaction of ([\text{Rh}_2(\mu_2-\eta^2-C_2\text{H})(\text{CO})_2(\mu\text{-dppm})_2]\text{ClO}_4 \cdot 0.5\text{CH}_2\text{Cl}_2) with phosphines</td>
<td>316</td>
</tr>
<tr>
<td>Reaction of ([\text{Rh}_2(\mu_2-\eta^2-C_2\text{tBu})(\text{CO})_2(\mu\text{-dppm})_2]\text{ClO}_4) with sodium borohydride</td>
<td>317</td>
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<tr>
<td>Reaction of ([\text{Rh}_2(\mu_2-\eta^2-C_2\text{R})(\text{CO})_2(\mu\text{-dppm})_2]\text{ClO}_4) with lithium triethylborohydride (\text{R} = \text{H, Ph and tBu})</td>
<td>317</td>
</tr>
<tr>
<td>Reaction of ([\text{Rh}_2(\mu_2-\eta^2-C_2\text{R})(\text{CO})_2(\mu\text{-dppm})_2]\text{ClO}_4) with dihydrogen/carbon monoxide (1:1) (\text{R} = \text{H, Ph and tBu})</td>
<td>318</td>
</tr>
<tr>
<td>Preparation of ([\text{Rh}_2(\mu-\text{H})(\mu-\text{CO})(\text{CO})_2(\mu\text{-dppm})_2]\text{ClO}_4)</td>
<td>318</td>
</tr>
</tbody>
</table>
6.3.2. Synthetic Procedures

Preparation of \( [\text{Rh}_2(\mu_2-n^2-C_2\text{H})(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4 \cdot 0.5\text{CH}_2\text{Cl}_2 \)

\( [\text{Rh}_2(\mu-\text{O}_2\text{CCH}_3)(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4 \) (0.10 g, 0.084 mmol) was dissolved in 10 mL of dichloromethane in a two necked flask and acetylene gas was bubbled through the solution for a period of 5 min. The flask was then sealed under an atmosphere of acetylene and stirred for 1 h during which time the solution became dark red in colour. The addition of diethyl ether to this solution precipitated a red-orange solid which was removed by filtration and recrystallized from dichloromethane-diethyl ether to give red-orange crystals (0.074 g, 74%).

Anal. Calcd for \( C_{54.5}H_{46}P_4O_6\text{Cl}_2\text{Rh}_2 \): C, 54.61; H, 3.79; P, 10.35%. Found: C, 54.28; H, 3.75; P, 10.02%.

\( \lambda_M = 127 \text{ cm}^2 \text{ mol}^{-1} \text{ mol}^{-1} \) (acetone).

Preparation of \( [\text{Rh}_2(\mu_2-n^2-C_2\text{Ph})(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4 \)

To a solution of \( [\text{Rh}_2(\mu-\text{O}_2\text{CCH}_3)(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4 \) (0.10 g, 0.084 mmol) in 5 mL of dichloromethane was added excess phenylacetylene (0.10 mL, 0.91 mmol). No colour change was observed. The solution was stirred for 3.5 h and the addition of diethyl ether precipitated the product which was removed by filtration and washed with diethyl ether. Recrystallization from dichloromethane-diethyl ether.
ether gave red crystals (0.089 g, 86%).

Anal. Calcd for C_{54}H_{45}P_{4}O_{6}ClRh_2: C, 58.53; H, 4.01; P, 10.06%. Found: C, 57.95; H, 4.06; P, 9.83%.

M = 122 cm² g⁻¹ mol⁻¹ (acetone).

Preparation of [Rh₂(μ₂-η²-C₂tBu)(CO)₂(μ-dppm)₂]ClO₄

[Rh₂(μ-O₂CCF₃)(CO)₂(μ-dppm)₂]ClO₄ (0.10 g, 0.080 mmol) was dissolved in 5 mL of dichloromethane and to it added excess tert-butyl acetylene (0.20 mL, 1.86 mmol). No colour change was observed. The solution was stirred for 4.5 h during which time no significant colour change occurred although the colour did seem to intensify. Diethyl ether was then added to precipitate the product either as red or orange crystals. Recrystallization from dichloromethane-diethyl ether gave either red or orange crystals or sometimes both (0.075 g, 77% (av.)).

Anal. Calcd for C_{58}H_{53}P_{4}O_{6}ClRh_2: C, 57.52%; H, 4.41%; P, 10.23%. Found: C, 57.22%; H, 4.43%; P, 11.05%.

M = 131 cm² g⁻¹ mol⁻¹ (acetone).

Preparation of [Rh₂(μ-CO)(μ₂-η²-C₂R)(CO)₂(μ-dppm)₂]ClO₄ (R = H, Ph and tBu)

In a typical experiment, [Rh₂(μ₂-η²-C₂R)(CO)₂(μ-dppm)₂]ClO₄ (0.10 g) was dissolved in 10 mL of dichloromethane and carbon monoxide was bubbled gently through the
solution for a period of 10 min. Colour changes were as follows: $R = H$, red to red-orange; $R = Ph$, no significant change; $R = tBu$, red to red-brown. The addition of diethyl ether while maintaining the carbon monoxide flow, precipitated the product which was recrystallized from dichloromethane-diethyl ether in an atmosphere of carbon monoxide.

<table>
<thead>
<tr>
<th>$R$</th>
<th>colour and appearance</th>
<th>$%$ yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>orange crystalline solid</td>
<td>(0.082 g, 80%)</td>
</tr>
<tr>
<td>Ph</td>
<td>orange solid</td>
<td>(0.080 g, 78%)</td>
</tr>
<tr>
<td>tBu</td>
<td>orange-brown solid</td>
<td>(0.072 g, 70%)</td>
</tr>
</tbody>
</table>

Preparation of $[\text{Rh}_2(\mu_2-\text{SO}_2)(\mu_2-\text{n}-\text{C}_2\text{R})_2(\text{CO})_2(\mu_\text{dppm})_2]\text{ClO}_4$

In a typical experiment, $[\text{Rh}_2(\mu_2-\text{n}-\text{C}_2\text{R})(\text{CO})_2(\mu_\text{dppm})_2]\text{ClO}_4$ was dissolved in 10 mL of dichloromethane and sulphur dioxide was bubbled through the solution for a period of 10 min. Colour changes were as follows: $R = H$, no change in colour; $R = Ph$, red to dark brown; $R = tBu$, red to magenta. The addition of diethyl ether while the sulphur dioxide flow was maintained precipitated the product ($R = H, tBu$) which was removed by filtration and washed with diethyl ether. In case of $R = Ph$, the product was isolated by slow diffusion of diethyl ether in an atmosphere of sulphur dioxide.
<table>
<thead>
<tr>
<th>R</th>
<th>colour and appearance</th>
<th>% yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>red solid</td>
<td>(0.072 g, 67%)</td>
</tr>
<tr>
<td>Ph</td>
<td>red-brown solid</td>
<td>(0.081 g, 75%)</td>
</tr>
<tr>
<td>t-Bu</td>
<td>orange crystals</td>
<td>(0.083 g, 77%)</td>
</tr>
</tbody>
</table>

Reaction of \([\text{Rh}_2(\mu_2-\eta^2-C_2H)(\text{CO})_2(\mu\text{-dppm})_2]\text{ClO}_4 \cdot 0.5\text{CH}_2\text{Cl}_2\) with Phosphines (PPh₃, PMePh₂)

\([\text{Rh}_2(\mu_2-\eta^2-C_2H)(\text{CO})_2(\mu\text{-dppm})_2]\text{ClO}_4 \cdot 0.5\text{CH}_2\text{Cl}_2\) (0.10 g, 0.084 mmol) was dissolved in 5 mL of dichloromethane and five fold excess of the appropriate phosphine (PPh₃: 0.01 g, 0.42 mmol; PMePh₂: 0.085 mL, 0.42 mmol) was added with stirring. The solution immediately turned bright purple. The addition of diethyl ether precipitated a purple solid which was removed by filtration and recrystallized from dichloromethane-diethyl ether in the presence of excess phosphine (PPh₃: 0.089 g, 75%; PMePh₂: 0.080 g, 71%).

The products have been tentatively identified as \([\text{Rh}_2(\mu-CCHL)(\text{CO})_2(\mu\text{-dppm})_2]\text{ClO}_4\) (L = PPh₃, PMePh₂).

L = PPh₃: Anal. Calcd for C₇₂H₆₀P₉O₅ClRh₂: C, 61.01; H, 4.27; P, 10.93%. Found: C, 59.15; H, 4.23; P, 11.20%.

L = PMePh₂: Anal. Calcd for C₆₇H₅₈P₅O₅ClRh₂: C, 59.38; H, 4.31; P, 11.43%. Found: C, 58.34; H, 4.38; P, 11.55%.
Reaction of $[\text{Rh}_2(\mu_2-\eta^2-\text{C}_2\text{tBu})\{\text{CO}\}_2(\mu\text{-dppm})_2]\text{ClO}_4$ with Sodium Borohydride

$[\text{Rh}_2(\mu_2-\eta^2-\text{C}_2\text{tBu})\{\text{CO}\}_2(\mu\text{-dppm})_2]\text{ClO}_4$ (0.10 g, 0.083 mmol) was suspended in 20 mL of degassed absolute ethanol and to it added sodium borohydride (0.10 g, 2.63 mmol) with stirring. The solution immediately turned dark blue and on stirring for 1 h, precipitated a dark blue solid. This was removed by filtration under dinitrogen and washed with ethanol followed by diethyl ether (0.089 g, 97%). This product has been tentatively identified as $\text{Rh}_2(\mu\text{-CCH}^+\text{Bu})(\text{CO})_2(\mu\text{-dppm})_2$. $\lambda_M = 0$ (acetone).

Reaction of $[\text{Rh}_2(\mu_2-\eta^2-\text{C}_2\text{R})\{\text{CO}\}_2(\mu\text{-dppm})_2]\text{ClO}_4$ (R = H, Ph and tBu) with Lithium Triethylborohydride

$[\text{Rh}_2(\mu_2-\eta^2-\text{C}_2\text{R})\{\text{CO}\}_2(\mu\text{-dppm})_2]\text{ClO}_4$ (0.05 g) was dissolved in 5 mL of dichloromethane and titrated with lithium triethylborohydride, monitoring the reaction by solution IR spectroscopy. As the reaction proceeded the intensity of the terminal carbonyl bands dropped with the appearance of new bands in the region 1950-1900 cm$^{-1}$. The end of the titration corresponded to the complete disappearance of carbonyl bands of the reactants at which point the solutions were deep blue (R = H, tBu) and deep purple (R = Ph).
Reaction of $[{\text{Rh}}_2(\mu_2-{n^2-C_2R})(\text{CO})_2(\mu\text{-dppm})_2]\text{ClO}_4$ ($R = \text{H}, \text{Ph}$ and $\text{tBu}$) with Dihydrogen/Carbon Monoxide (1:1)

Preparation of $[{\text{Rh}}_2(\mu-\text{H})(\mu\text{-CO})(\text{CO})_2(\mu\text{-dppm})_2]\text{ClO}_4$

In a typical experiment, $[{\text{Rh}}_2(\mu_2-{n^2-C_2R})(\text{CO})_2(\mu\text{-dppm})_2]\text{ClO}_4$ ($R = \text{H}, \text{Ph}$ and $\text{tBu}$) (0.05 g) was dissolved in 5 mL of dichloromethane in a two-necked flask. A mixture of dihydrogen/carbon monoxide was bubbled for 5 min. The flask was sealed at this stage under an atmosphere of dihydrogen/carbon monoxide mixture and stirred for 1.5 h, 7 h and 20 h for $R = \text{H}, \text{Ph}$ and $\text{tBu}$ respectively during which time the solutions had turned wine red. The addition of diethyl ether to the solutions, under a stream of dihydrogen/carbon monoxide precipitated a red-brown crystalline solid. These were removed by filtration and washed with diethyl ether ($R = \text{H}: 0.041 \text{ g, 85%; } R = \text{Ph}: 0.040 \text{ g, 84%; } R = \text{tBu}: 0.039 \text{ g, 83%}$). The IR spectra of these red-brown products were identical to those obtained by the reaction of $[{\text{Rh}}_2(\mu_2-\text{O}_2\text{CH})(\text{CO})_2(\mu\text{-dppm})_2]\text{ClO}_4$ with carbon monoxide (Chapter 5).
<table>
<thead>
<tr>
<th>Compound</th>
<th>( \nu(\text{CO})^a, \text{cm}^{-1} )</th>
<th>( \nu(\text{CO})^b, \text{cm}^{-1} )</th>
<th>Others$^c, \text{cm}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Rh}_2(u_2-\eta^2-\text{C}_2\text{H})(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4\cdot0.5\text{CH}_2\text{Cl}_2)</td>
<td>2010 (s), 1986 (vs)</td>
<td>1994 (s), 1960 (vs)</td>
<td>( \nu(\text{C=C}), 1886 \text{ (mw)} ); ( \nu(\text{CH}), 3216 \text{ (mw)} )</td>
</tr>
<tr>
<td>([\text{Rh}_2(u_2-\eta^2-\text{C}_2\text{Ph})(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4)</td>
<td>1998 (sh), 1983 (vs)</td>
<td>1979 (s), 1962 (vs)</td>
<td>( \nu(\text{C=C}), 2019 \text{ (mw)} )</td>
</tr>
<tr>
<td>([\text{Rh}_2(u_2-\eta^2-\text{C}_2\text{tBu})(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4) (Red)</td>
<td>1996 (sh), 1982 (vs)</td>
<td>1993 (s), 1962 (vs)</td>
<td>( \nu(\text{C=C}), 2026 \text{ (mw)} )</td>
</tr>
<tr>
<td>([\text{Rh}_2(u_2-\eta^2-\text{C}_2\text{tBu})(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4) (Orange)</td>
<td>1996 (sh), 1982 (vs)</td>
<td>1993 (s), 1962 (vs)</td>
<td>( \nu(\text{C=C}), 2026 \text{ (mw)} )</td>
</tr>
<tr>
<td>([\text{Rh}_2(u'-\text{SO})_2(u_2-\eta^2-\text{C}_2\text{H})(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4)</td>
<td>2008 (sh), 1992 (vs), 1873 (m)</td>
<td>1987 (sh), 1973 (vs), 1856 (m)</td>
<td>( \nu(\text{C=C}), 1886 \text{ (mw)} )</td>
</tr>
<tr>
<td>([\text{Rh}_2(u'-\text{SO})_2(u_2-\eta^2-\text{C}_2\text{Ph})(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4)</td>
<td>2009 (sh), 1986 (vs), 1874 (m)</td>
<td>1988 (sh), 1969 (vs), 1872 (m)</td>
<td>( \nu(\text{C=C}), 2018 \text{ (sh)} )</td>
</tr>
<tr>
<td>([\text{Rh}_2(u'-\text{SO})_2(u_2-\eta^2-\text{C}_2\text{tBu})(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4)</td>
<td>1998 (sh), 1983 (vs), 1883 (mw)</td>
<td>1998 (s), 1977 (vs), 1860 (w)</td>
<td>( \nu(\text{C=C}), 2023 \text{ (mw)} )</td>
</tr>
<tr>
<td>([\text{Rh}_2(u'-\text{SO})_2(u_2-\eta^2-\text{C}_2\text{H})(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4)</td>
<td>2043 (m), 2021 (s)</td>
<td>2015 (s), 1977 (vs)</td>
<td>( \nu_{\text{as}}(\text{SO}), 1236 \text{ (mw)} )</td>
</tr>
</tbody>
</table>
Table 6.1. (continued)

<table>
<thead>
<tr>
<th>Compound</th>
<th>(CO)&lt;sup&gt;a&lt;/sup&gt;, cm&lt;sup&gt;-1&lt;/sup&gt;</th>
<th>(CO)&lt;sup&gt;b&lt;/sup&gt;, cm&lt;sup&gt;-1&lt;/sup&gt;</th>
<th>Others&lt;sup&gt;c&lt;/sup&gt;, cm&lt;sup&gt;-1&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Rh&lt;sub&gt;2&lt;/sub&gt;(μ-&lt;sub&gt;S&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt;)(μ-&lt;sub&gt;2&lt;/sub&gt;-&lt;sub&gt;η&lt;/sub&gt;-&lt;sub&gt;2&lt;/sub&gt;-&lt;sub&gt;C&lt;/sub&gt;&lt;sub&gt;2&lt;/sub&gt;Ph)(CO)&lt;sub&gt;2&lt;/sub&gt;(μ-dppm)&lt;sub&gt;2&lt;/sub&gt;]ClO&lt;sub&gt;4&lt;/sub&gt;</td>
<td>2036 (m), 2014 (s)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Rh&lt;sub&gt;2&lt;/sub&gt;(μ-&lt;sub&gt;S&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt;)(μ-&lt;sub&gt;2&lt;/sub&gt;-&lt;sub&gt;η&lt;/sub&gt;-&lt;sub&gt;2&lt;/sub&gt;-&lt;sub&gt;C&lt;/sub&gt;&lt;sub&gt;2&lt;/sub&gt;t&lt;sub&gt;Bu&lt;/sub&gt;)(CO)&lt;sub&gt;2&lt;/sub&gt;(μ-dppm)&lt;sub&gt;2&lt;/sub&gt;]ClO&lt;sub&gt;4&lt;/sub&gt;</td>
<td>2000 (s), 1963 (vs)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Rh&lt;sub&gt;2&lt;/sub&gt;(μ-&lt;sub&gt;CC&lt;/sub&gt;[H]PPh&lt;sub&gt;3&lt;/sub&gt;)(CO)&lt;sub&gt;2&lt;/sub&gt;(μ-dppm)&lt;sub&gt;2&lt;/sub&gt;]ClO&lt;sub&gt;4&lt;/sub&gt;</td>
<td>1973 (s), 1957 (vs)</td>
<td>1959 (s), 1937 (vs)</td>
<td></td>
</tr>
<tr>
<td>[Rh&lt;sub&gt;2&lt;/sub&gt;(μ-&lt;sub&gt;CC&lt;/sub&gt;[H]PMePh&lt;sub&gt;2&lt;/sub&gt;)(CO)&lt;sub&gt;2&lt;/sub&gt;(μ-dppm)&lt;sub&gt;2&lt;/sub&gt;]ClO&lt;sub&gt;4&lt;/sub&gt;</td>
<td>1974 (s), 1956 (vs)</td>
<td>1959 (s), 1940 (vs)</td>
<td></td>
</tr>
<tr>
<td>Rh&lt;sub&gt;2&lt;/sub&gt;(μ-&lt;sub&gt;C&lt;/sub&gt;&lt;sub&gt;C&lt;/sub&gt;Ch&lt;sub&gt;2&lt;/sub&gt;)(CO)&lt;sub&gt;2&lt;/sub&gt;(μ-dppm)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>1945 (s), 1923 (vs)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rh&lt;sub&gt;2&lt;/sub&gt;(μ-&lt;sub&gt;CC&lt;/sub&gt;[H]t&lt;sub&gt;Bu&lt;/sub&gt;)(CO)&lt;sub&gt;2&lt;/sub&gt;(μ-dppm)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>1948 (s), 1924 (vs)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rh&lt;sub&gt;2&lt;/sub&gt;(μ-&lt;sub&gt;CC&lt;/sub&gt;[H]t&lt;sub&gt;Bu&lt;/sub&gt;)(CO)&lt;sub&gt;2&lt;/sub&gt;(μ-dppm)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>1943 (s), 1918 (vs)</td>
<td>1940 (s), 1919 (vs)</td>
<td>ν(C=O), 1666 (w)</td>
</tr>
</tbody>
</table>

(a) Recorded in dichloromethane solution.
(b) Recorded as nujol mulls on potassium bromide plates
(c) Very complex (five maxima).
Table 6.2. NMR (¹H and ³¹P(¹H)) Data of Bridging Acetylide and Vinlylidene Complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>NMR a, b</th>
</tr>
</thead>
</table>
| [Rh₂(µ₂-η²-C₂H) (CO)₂ (µ-dppm)]₂ ClO₄·0.5CH₂Cl₂ | ³¹P : 19.24 (m, dppm, 1J_Rh-P + 1J_Rh-P = 113.4 Hz)  
  ¹H : 7.43 (m, 40H, Phenyl); 5.60 (s, CH₂Cl₂); 4.28 (m, 2H, CH₂-dppm); 3.46 (m, 2H, CH₂-dppm) |
| [Rh₂(µ₂-η²-C₂Ph) (CO)₂ (µ-dppm)]₂ ClO₄       | ³¹P : 20.79 (m, dppm, 1J_Rh-P + 1J_Rh-P = 113.0 Hz)  
  ¹H : 7.34 (m, 40H, Phenyl-dppm); 6.68 (m, 5H, Phenyl); 4.26 (m, 2H, CH₂-dppm); 3.48 (m, 2H, CH₂-dppm) |
| [Rh₂(µ₂-η²-C₂tBu) (CO)₂ (µ-dppm)]₂ ClO₄      | ³¹P : 20.47 (m, dppm, 1J_Rh-P + 1J_Rh-P = 113.7 Hz)  
  ¹H : 7.53 (m, 40H, Phenyl); 4.25 (m, 2H, CH₂-dppm); 3.66 (m, 2H, CH₂-dppm); 0.47 (s, 9H, tBu) |
| [Rh₂(µ-CO) (µ₂-η²-C₂H) (CO)₂ (µ-dppm)]₂ ClO₄ | ³¹P : 27.96 (m, dppm, 1J_Rh-P + 1J_Rh-P = 99.4 Hz)  
  ³¹P : 28.10 (m, dppm, 1J_Rh-P + 1J_Rh-P = 100.2 Hz)  
  ³¹P : 31.41 (m, dppm, 1J_Rh-P + 1J_Rh-P = 103.7 Hz)  
  ³¹P : 22.52 (m, dppm, 1J_Rh-P + 1J_Rh-P = 98.5 Hz) |

(continued)
Table 6.2. (continued)

<table>
<thead>
<tr>
<th>Compound</th>
<th>NMR a, b</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Rh}_2(\mu-\text{SO}_2)\left(\mu_2-\eta^2-\text{C}<em>2\text{Bu}\right)</em>{\text{CO}}_2(\mu-\text{dppm})_2]\text{ClO}_4)</td>
<td>(31^P: 22.63) (m, dppm), (1^J_{\text{Rh-P}} + x^J_{\text{Rh-P}} = 98.9) Hz (^d)</td>
</tr>
<tr>
<td>([\text{Rh}_2(\mu-\text{SO}_2)\left(\mu_2-\eta^2-\text{C}<em>2\text{Bu}\right)</em>{\text{CO}}_2(\mu-\text{dppm})_2]\text{ClO}_4)</td>
<td>(31^P: 25.17) (m, dppm), (1^J_{\text{Rh-P}} + x^J_{\text{Rh-P}} = 99.9) Hz (^d)</td>
</tr>
<tr>
<td>([\text{Rh}_2(\mu-\text{CC}[\text{H}]\text{PMePh}<em>2)</em>{\text{CO}}_2(\mu-\text{dppm})_2]\text{ClO}_4)</td>
<td>(31^P: 24.29) (asymmetric multiplet, dppm); (-11.73) (m, PPh(_3))</td>
</tr>
<tr>
<td>([\text{Rh}_2(\mu-\text{CC}[\text{H}]\text{PMePh}<em>2)</em>{\text{CO}}_2(\mu-\text{dppm})_2]\text{ClO}_4)</td>
<td>(31^P: 27.66) (asymmetric multiplet, dppm); (-14.3) (m, PMePh(_2))</td>
</tr>
<tr>
<td>([\text{Rh}<em>2(\mu-\text{CC}[\text{H}])\text{Ph})</em>{\text{CO}}_2(\mu-\text{dppm})_2)</td>
<td>(31^P: 30.99) (m, (1^J_{\text{Rh-P}} + x^J_{\text{Rh-P}} = 167.9) Hz (^d)</td>
</tr>
<tr>
<td>([\text{Rh}<em>2(\mu-\text{CC}[\text{H}])\text{Ph})</em>{\text{CO}}_2(\mu-\text{dppm})_2)</td>
<td>(31^P: 29.53) (asymmetric multiplet, dppm)</td>
</tr>
<tr>
<td>([\text{Rh}<em>2(\mu-\text{CC}[\text{H}])\text{tBu})</em>{\text{CO}}_2(\mu-\text{dppm})_2)</td>
<td>(31^P: 30.13) (asymmetric multiplet, dppm)</td>
</tr>
<tr>
<td>([\text{Rh}<em>2(\mu-\text{CC}[\text{H}])\text{tBu})</em>{\text{CO}}_2(\mu-\text{dppm})_2)</td>
<td>(1^H: 7.31) (m, 40H, Phenyl); 4.60 (m, 1H, H); 2.95 (m, 2H, CH(_2)-dppm); 3.75 (m, 2H, CH(_2)-dppm); 0.41 (s, 9H, tBu)</td>
</tr>
</tbody>
</table>

(a) Chemical shifts (in ppm) relative to tetramethylsilane \((^1H)\) and 85% phosphoric acid \((^31P)\) in dichloromethane.
(b) \(^1H\) NMR spectra were recorded in dichloromethane-d\(_2\).
(c) The degree of dichloromethane solvate was determined by recording the spectrum in acetone-d\(_6\) (5.60, s, 1H).
(d) At \(-40^\circ\)C.
CHAPTER 7

SUMMARY AND CONCLUSIONS

The reaction of trans-Rh₂Cl₂(CO)₂(μ-dppm)₂ with sodium carbonate in aqueous ethanol gave the A-frame complex, Rh₂(μ-OH·Cl)(CO)₂(μ-dppm)₂·H₂O. This complex has been structurally characterized and shown to possess a chloride group hydrogen bound to the bridging hydroxide ligand, accounting for the low equivalent conductance observed in dichloromethane solution. Attempted exchange of the chloride in Rh₂(μ-OH·Cl)(CO)₂(μ-dppm)₂·H₂O with sodium perchlorate monohydrate in alcoholic solvents (ROH: R = CH₃, C₂H₅) yielded [Rh₁(μ-OR)(CO)₂(μ-dppm)₂]ClO₄ (R = CH₃, C₂H₅), which can also be conveniently prepared by the direct action of sodium alkoxide (NaOR) on trans-Rh₂Cl₂(CO)₂(μ-dppm)₂, followed by treatment with sodium perchlorate. [Rh₂(μ-OR)(CO)₂(μ-dppm)₂]ClO₄ (R = CH₃, C₂H₅), however, was readily converted to [Rh₂(μ-OH)(CO)₂(μ-dppm)₂]ClO₄ by recrystallizing in the presence of excess perchloric acid. ¹H NMR spectra of the alkoxy complexes, [Rh₂(μ-OR)(CO)₂(μ-dppm)₂]ClO₄ (R = CH₃, C₂H₅) indicated that these complexes are sensitive to hydrolysis. As anticipated, the bridging hydroxide and alkoxy ligands in these complexes were acid labile, enabling a range of substitution reactions to be performed.
Thus the oxygen bridged complexes represent a relatively simple route to a wide variety of other A-frame complexes. As a matter of convenience, [Rh₂(u-OC₂H₅)(CO)₂(u-dppm)₂]ClO₄ was selected to use in all substitution reactions. Thus, one equivalent of DMA.HX (X = Cl, Br and I) gave [Rh₂(u-X)(CO)₂(u-dppm)₂]ClO₄. For both X = Cl and Br dichloromethane solutions of the complexes were found to be very stable for long periods of time. In contrast, [Rh₂(u-I)(CO)₂(u-dppm)₂]ClO₄ was found to break down in a complex manner to give [Rh₂(u-I)(μ-CO)(CO)₂(u-dppm)₂]ClO₄ as one of the products. [Rh₂(u-Cl)(CO)₂(u-dppm)₂]ClO₄ was observed as the only product when Rh₂(u-OC₂H₅)(CO)₂(u-dppm)₂]ClO₄ was treated with excess DMA.HCl. A four fold excess of DMA.HBr, however, gave a mixture of [Rh₂(u-Br)(μ-CO)(CO)₂(u-dppm)₂]⁺ and [Rh₂(u-H)(μ-CO)Br₃(u-dppm)₂]₀.5CH₂Cl₂.₀.5C₄H₁₀O whereas with a ten fold excess the latter was formed exclusively. Conductivity data indicated that the latter complex exists as a strong ion pair in acetone solution. Treatment of [Rh₂(u-OC₂H₅)(CO)₂(u-dppm)₂]ClO₄ with a three fold excess of DMA.HI gave at least two products, identified as [Rh₂(u-I)(CO)₂(u-dppm)₂]ClO₄ and [Rh₂(u-I)(μ-CO)(CO)₂(u-dppm)₂]⁺ whereas with a twelve fold excess, additional [Rh₂(u-H)(μ-CO)I₃(u-dppm)₂] appeared to be formed as a minor product. This difference in behaviour has been attributed, at least in part, to the size of the halogen atom. The reaction of
[Rh$_2$(µ-OC$_2$H$_5$)(CO)$_2$(µ-dppm)$_2$]ClO$_4$ with carboxylic acid (RCOOH) gave [Rh$_2$(µ-O$_2$CR)(CO)$_2$(µ-dppm)$_2$]ClO$_4$ (R = H, CH$_3$, CH$_2$Cl, CHCl$_2$, CCl$_3$, CF$_3$) which so far represents the only general synthetic method for such compounds. One member of this series has been structurally characterized to confirm the bidentate bridging mode of the carboxylate function. The trifluoroacetate group was extremely labile, making this compound a useful synthon. With one equivalent of potassium cyanate, ammonium thiocyanate or sodium azide, [Rh$_2$(µ-O$_2$CCF$_3$)(CO)$_2$(µ-dppm)$_2$]ClO$_4$ gave [Rh$_2$(µ-X)(CO)$_2$(µ-dppm)$_2$]ClO$_4$ (X = NCO, NCS, N$_3$) in which the thiocyanate or cyanate group bridge via the nitrogen atom. With excess cyanate or thiocyanate, the face to face dimers, Rh$_2$X$_2$-(NCO)$_2$(µ-dppm)$_2$ (X = NCO, NCS) resulted. Rh$_2$(NCS)$_2$(CO)$_2$(µ-dppm)$_2$ was shown to be identical to a complex previously formulated as Rh$_2$(NCS)$_2$(CO)$_2$(µ-dppm)$_2$. Rh$_2$(NCS)$_2$(CO)$_2$(µ-dppm)$_2$ could also be prepared by the reaction of [Rh$_2$(µ-OC$_2$H$_5$)(CO)$_2$(µ-dppm)$_2$]ClO$_4$ with excess ammonium thiocyanate. [Rh$_2$(µ-X)(CO)$_2$(µ-dppm)$_2$]ClO$_4$ (X = NCO, NCS and N$_3$) were also prepared by treatment of [Rh$_2$(µ-OC$_2$H$_5$)-(CO)$_2$(µ-dppm)$_2$]ClO$_4$ with stoichiometric amounts of the appropriate salts in the presence of perchloric acid. When [Rh$_2$(µ-OC$_2$H$_5$)(CO)$_2$(µ-dppm)$_2$]ClO$_4$, however, was treated with stoichiometric amounts of ammonium thiocyanate in the absence of perchloric acid, Rh$_2$(NCS)$_2$(CO)$_2$(µ-dppm)$_2$ was formed as the minor product. The nature of the major
product, which contains a thiocyanate group, is somewhat uncertain. The data available to date suggest that this complex could be reformulated as \([\text{Rh}_2(\text{CO})_2(\text{SCN})(\mu\text{-dppm})_2]\)ClO_4, which is fluxional at room temperature. The fluxionality has been ascribed tentatively to a bridge-terminal exchange process. \(\text{Rh}_2(\mu\text{-O}_2\text{CCF}_3)(\text{CO})_2(\mu\text{-dppm})_2\)ClO_4 also reacted with diethylamine and the data favour the formation of \(\text{Rh}_2(\text{CO})_2(\mu\text{-OH.NHEt}_2)(\mu\text{-dppm})_2\)ClO_4 as opposed to \([\text{Rh}_2(\mu\text{-NEt}_2)(\text{CO})_2(\mu\text{-dppm})_2]\)ClO_4.

Reactions of the A-frame complexes, \(\text{Rh}_2(\mu\text{-OH.Cl})(\text{CO})_2(\mu\text{-dppm})_2\) and \([\text{Rh}_2(\mu\text{-X})(\text{CO})_2(\mu\text{-dppm})_2]\)ClO_4 (X = QH, OCH_3, OC_2H_5, Br, I, NCO, N_3 and NCS) with carbon monoxide and sulphur dioxide have been examined. The reactions were somewhat unusual, except in the case of X = Br, I since, where reactions occurred the bridging ligand X was involved. As could be expected, the complexes with X = Br, I were found to bind carbon monoxide and sulphur dioxide in the endo pocket of the A-frame to give \(\text{Rh}_2(\mu\text{-X})(\mu\text{-L})(\text{CO})_2(\mu\text{-dppm})_2\)ClO_4 (X = I, Br). In contrast, no reaction was observed for those complexes with X = OH, Cl, OCH_3; OC_2H_5, NCO with carbon monoxide at one atmosphere. The pseudo-halide complexes \([\text{Rh}_2(\mu\text{-N}_3)(\text{CO})_2(\mu\text{-dppm})_2]\)ClO_4 and \([\text{Rh}_2(\mu\text{-NCS})(\text{CO})_2(\mu\text{-dppm})_2]\)ClO_4, however, reacted with carbon monoxide at one atmosphere to give \([\text{Rh}_2(\mu\text{-NCO})(\text{CO})_2(\mu\text{-dppm})_2]\)ClO_4 and \([\text{Rh}_2(\mu\text{-CN})(\mu\text{-CO})(\text{CO})_2(\mu\text{-dppm})_2]\)ClO_4.
The latter molecule has been structurally characterized and found to possess an unusual asymmetric bridging cyanide ligand. Spectroscopic data indicated that the molecule is fluxional at room temperature with at least two and possibly three fluxional processes taking place. One of the fluxional processes was responsible for all four phosphorus atoms remaining chemically equivalent down to -80 °C, and a "wind shield wiper" type motion of the bridging cyanide group was invoked to explain this phenomenon. The other fluxional process (or processes) was responsible for the apparent chemical equivalence of the dppm methylene protons (A-frame inversion) and the carbonyl groups. Since intermolecular processes appeared unlikely, a walking motion of the cyanide and carbonyl groups around the equatorial plane of the complex was invoked to explain both the inversion process and the carbonyl exchange. This appears to be the first example of A-frame inversion occurring in a doubly bridged complex and the first evidence for a walking type mechanism in A-frame chemistry. The reaction of the face to face dimer Rh₂(NCS)₂(CO)₂(μ-dppm)₂ with carbon monoxide pressure (25 psi) was examined. The product obtained in this reaction has been tentatively identified as Rh₂(μ-S)(μ-CO)(CN)₂(CO)(μ-dppm)₂·CH₂Cl₂.

The reaction of [Rh₂(μ-OH·Cl)(CO)₂(μ-dppm)₂]H₂O with sulphur dioxide afforded [Rh₂(μ-Cl)(CO)₂(μ-dppm)₂]HSO₄.
eventually, whereas those complexes with X = N\textsubscript{3}, NCO, NCS gave weak Lewis acid-base adducts, involving an interaction between sulphur dioxide and the bridgehead ligand. The nature of the products obtained from the reaction of 
\[ \text{[Rh}_2(\mu-\text{OR})(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4 (R = \text{H, CH}_3 \text{ and C}_2\text{H}_5) \] with sulphur dioxide is not certain since IR data favoured the formation of a genuine bridging sulphur dioxide adduct whereas the \(^{31}\text{P} \{^1\text{H}\} \text{ NMR favoured the formation of weak Lewis acid-base adducts. The product tentatively identified as Rh}_2(\text{CO})_2(\text{SCN})(\mu-\text{dppm})_2 reacted with sulphur dioxide to form the A-frame complex, [Rh}_2(\mu-\text{NCS})(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4. \] It would thus appear that the formation of simple bridging carbon monoxide and sulphur dioxide adducts in A-frame complexes (with rhodium-rhodium bonds) with single donor atom bridges is, at this stage, limited to those A-frames with X = H, Cl, Br and I. All the other examples examined in this study, i.e. those with X = OH, Cl, OH, OCH\textsubscript{3}, OCH\textsubscript{2}H\textsubscript{5}, NCS, NCO, N\textsubscript{3} and in other studies, i.e. X = S (only with sulphur dioxide), SR, PHCy show no reactivity at all. Even with such a large number of examples to generalize from, it is not immediately obvious what factors are essential for carbon monoxide and sulphur dioxide coordination in the endo pocket.

Although no reactions were observed between \text{Rh}_2(\mu-\text{OH(Cl)})(\text{CO})_2(\mu-\text{dppm})_2\cdot\text{H}_2\text{O and [Rh}_2(\mu-\text{OR})(\text{CO})_2.}
(μ-dppm)₂ClO₄ (R = H, CH₃ and C₂H₅) and carbon monoxide at one atmosphere, they all reacted with carbon monoxide under 30 psi pressure. Under these conditions, Rh₂(μ-ΟΗ.Cl)(CO)₂(μ-dppm)₂H₂O gave trans-Rh₂Cl₂(CO)₂(μ-
 dppm)₂ as the only isolable product and the [Rh₂(μ-ΟR)(CO)₂-(μ-dppm)]₂ClO₄ (R = H, CH₃ and C₂H₅) gave the novel, 46, electron trinuclear cluster, [Rh₃(μ-CO)₃(CO)₃(μ-dppm)]₃ClO₄.

CH₂Cl₂. The structure of the latter complex has been determined and shown to possess three rhodium atoms joined by rhodium-rhodium single bonds to form an isosceles triangle. The unique terminal carbonyl group on the bridging rhodium atom underwent rapid exchange with 13-carbon monoxide and was readily substituted by tertiary phosphines to give complexes, [Rh₃(μ-CO)₃(CO)₂(3-L)(μ-1,2-dppm)]₂ClO₄ where L = PPh₃, PMePh₂, PET₃ and η¹-dppm. When L = η¹-dppm, the complex was found to be fluxional on the NMR time scale. This was attributed to rapid intramolecular exchange of the free and coordinated end of the η¹-dppm ligand on the bridging rhodium atom. Unlike the parent cluster, the phosphine-substituted complexes underwent relatively rapid 13-carbon monoxide of the two equivalent bridging carbonyl groups. Mechanisms have been postulated to account for the 13-carbon monoxide exchange in both the parent cluster and the phosphine substituted derivatives. The use of conventional electron counting techniques and isolobal analogies both suggest that the forty electron species [Rh₃(CO)₇-
would be favoured as a product over $[\text{Rh}_3(\mu-\text{CO})_3(\text{CO})_3(\mu-1,2\text{-dppm})_2]\text{ClO}_4$ in the carbonylation reaction. The relative merits of the two formulations are discussed and a rationale proposed to explain the observation of the 46 electron species as the product of the reaction.

The reactions of the carboxylate complexes $[\text{Rh}_2(\mu-\text{O}_2\text{CR})(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4$ ($R = \text{H, CH}_3$, $\text{CH}_2\text{Cl}$, $\text{CHCl}_2$, $\text{CCl}_3$ and $\text{CF}_3$) with carbon monoxide, dihydrogen/carbon monoxide (1:1), halogens and terminal acetylenes have been examined. When $R = \text{CH}_3$, no reaction was observed with carbon monoxide whereas the reaction of the formate derivative proceeded with decomposition of the formate group to give $[\text{Rh}_2(\mu-\text{H})(\mu-\text{CO})(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4$. In contrast, all the other carboxylate complexes reacted reversibly to form the bridging carbon monoxide adducts, $[\text{Rh}_2(\mu-\text{O}_2\text{CR})(\mu-\text{CO})(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4$. The trifluoroacetate derivative has been structurally characterized and shown to possess a bridging bidentate carboxylate function with the carbon monoxide symmetrically bridging between the metal centres. All the carboxylate complexes reacted with 1:1 dihydrogen/carbon monoxide mixtures to give $[\text{Rh}_2(\mu-\text{H})(\mu-\text{CO})(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4$ via their respective carbon monoxide adducts. No such heterolytic activation of hydrogen was observed in the absence of carbon monoxide and it appears possible that the
observed lengthening of the Rh-O bonds on formation of
\[ \text{[Rh}_2(\mu-\text{CO})(\mu-\text{O}_2\text{CCF}_3)(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4 \]
may have a role to play in this reaction, possibly by promoting dissociation of the carboxylate group. Several of the carboxylate complexes underwent 1,2 oxidative addition reactions with halogens \((X_2 = \text{Cl}_2, \text{Br}_2 \text{ and } \text{I}_2)\) to form \[ \text{Rh}_2(\mu-\text{O}_2\text{CR})(\text{CO})_2(\mu-\text{dppm})_2\text{ClO}_4 \]
\((R = \text{H, CH}_3 \text{ and CF}_3)\). For \(R = \text{H, CH}_3\) this product was obtained exclusively, whereas for \(R = \text{CF}_3\), the formation of other minor products was observed. Tentative structures have been assigned for those minor products and the nature of the product was found to depend upon the size of the halogen atom. This difference in behaviour for \(R = \text{H, CH}_3\) versus \(R = \text{CF}_3\) can probably be attributed to the increased lability of the trifluoroacetate group.

Reacting the carboxylate complexes, \[ \text{[Rh}_2(\mu-\text{O}_2\text{CR})(\text{CO})_2(\mu-\text{dppm})_2] \]
with the terminal acetylenes \(R'C_2\text{H} \ ((R' = \text{H, Ph, } ^7\text{Bu} \text{ (R' = CF}_3 \text{ only)})\) resulted in the formation of \(\sigma-\pi\) acetylide complexes, \[ \text{[Rh}_2(\mu-\text{O}_2\text{CR})^2(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4 \]. One member of the series \((R' = ^7\text{Bu})\) has been structurally characterized to confirm the \(\sigma-\pi\)
bridging mode. The acetylide stretching frequency for \(R = \text{H,} \) was unusually low by comparison to the other two complexes \((R = \text{Ph, } ^7\text{Bu})\). This was attributed to the bulky nature of the substituent on the acetylide function inhibiting a clear approach of the acetylene triple bond to the second metal atom. All three complexes were
fluxional at -80 °C and "wind shield wiper" motion, akin to that invoked in the case of \([\text{Rh}_2(\mu-CN)(\mu-CO)(CO)_2(\mu-dppm)_2]\text{ClO}_4\cdot\text{CH}_2\text{Cl}_2\) has been postulated to account for this observation. In addition, the unsubstituted derivative exhibited another fluxional process at room temperature. This has been attributed to the presence of a small amount of \([\text{Rh}_2(\mu-CO)(\mu_2-\eta^2-C_2^t\text{H})_2(\mu-dppm)_2]\text{ClO}_4\) present which undergoes intermolecular carbonyl exchange. \([\text{Rh}_2(\mu_2-\eta^2-C_2^t\text{R}')(\mu-dppm)_2]\text{ClO}_4\) \((\text{R}^t = \text{H, Ph and } \text{Bu})\) all reacted reversibly with carbon monoxide to form the bridging carbon monoxide adducts, \([\text{Rh}_2(\mu-CO)(\mu_2-\eta^2-C_2\text{R})_2(\mu-dppm)_2]\text{ClO}_4\) that with \(\text{R} = \text{H}\) being the most stable in the solid state. Similarly, the three acetylide complexes reacted with sulphur dioxide reversibly to form bridging sulphur dioxide adducts, although a stable adduct could only be isolated for the simple acetylide \((\text{R} = \text{H})\). Some ambiguity resulted regarding the reaction of \([\text{Rh}_2(\mu_2-\eta^2-C_2^t\text{Bu})_2(\mu-dppm)_2]\text{ClO}_4\) with sulphur dioxide. Although the \(^{31}\text{P}(^1\text{H})\) NMR data indicate the formation of a genuine bridging sulphur dioxide adduct, IR spectroscopy did not reflect the formation of such a product. The reason for this behaviour remains as yet unexplained. The cationic bridging acetylide complexes, \([\text{Rh}_2(\mu_2-\eta^2-C_2\text{R})(\mu-dppm)_2]\text{ClO}_4\) \((\text{R} = \text{H, CH}_3\text{ and } \text{CF}_3)\) were also found to react with hydride and phosphines \((\text{PPh}_3, \text{PMePh}_2\text{ for } \text{R} = \text{H only})\) to form highly coloured, air sensitive compounds.
which have been tentatively identified as bridging vinylidene complexes, \( \text{Rh}_2(\mu-\text{CC}[H]R')(\text{CO})_2(\mu-\text{dppm})_2 \) and 
\[ \text{Rh}_2(\mu-\text{CCLR'}) (\text{CO})_2(\mu-\text{dppm})_2 \] \( \text{ClO}_4 \) (\( \text{L}^\prime = \text{PPh}_3, \text{PMePh}_2 \)) respectively. The atmospheric oxidation of \( \text{Rh}_2(\mu-\text{CC}[H] t^\prime \text{Bu}) - \) 
\( (\text{CO})_2(\mu-\text{dppm})_2 \) gave the starting material, 
\[ \text{Rh}_2(\mu_2-\eta^2-\text{C}_2 t^\prime \text{Bu})(\text{CO})_2(\mu-\text{dppm})_2 \] \( ^+ \) presumably as the hydroxide salt. This represents a rare, if not unique, example of facile homogeneous oxidation of an organic ligand attached to a group VIII. With dihydrogen/carbon monoxide (1:1), all three acetylide complexes generated \( \text{Rh}_2(\mu-\text{H}) - \) 
\( (\mu-\text{CO})(\text{CO})_2(\mu-\text{dppm})_2 \) \( \text{ClO}_4 \) quantitatively and the rate of these reactions appeared to be dependent on the substituent on the acetylide function. The acetylide complexes also underwent reactions with dihydrogen although the exact nature of these reactions has not been ascertained. Prior to the acetylide complexes described here, all \( \sigma-\pi \) acetylide derivatives described involved saturated 18 electron metal centres. Consequently, all the chemistry exhibited by these acetylide group involved direct or exo attack upon the acetylide group. The complexes isolated in this study, however, have the \( \sigma-\pi \) acetylide group bridging two 16 electron centres allowing for the possibility of endo attack via the metal centres. Although the reactions with hydride and phosphines almost certainly occur via direct attack, it would seem likely that the reactions with hydrogen
occurring via the activation of hydrogen at the metal centres and a complete elucidation of these reactions would appear to be a most fruitful avenue for further research.
APPENDICES

Appendices I-V contain some crystallographic data of the complexes $\text{Rh}_2(\mu-\text{OH} \cdot \text{Cl})_2(\mu\text{-dppm})_2$, $[\text{Rh}_2(\mu-\text{CN})(\mu-\text{CO})-(\text{CO})_2(\mu\text{-dppm})_2]\text{ClO}_4 \cdot \text{CH}_2\text{Cl}_2$, $[\text{Rh}_3(\mu-\text{CO})_3(\text{CO})_3(\mu-1,2\text{-dppm})_2]-\text{ClO}_4 \cdot \text{CH}_2\text{Cl}_2$, $[\text{Rh}_2(\mu-\text{CO})(\mu-\text{O}_2\text{CCF}_3)(\text{CO})_2(\mu\text{-dppm})_2]\text{ClO}_4 \cdot \text{CH}_2\text{Cl}_2$, $[\text{Rh}_2(\mu-\text{O}_2\text{CCF}_3)(\text{CO})_2(\mu\text{-dppm})_2]\text{ClO}_4$. All other information of these complexes including atomic parameters, temperature factors and calculated and observed structure factors can be obtained by writing to:

Prof. T.S. Cameron  
Department of Chemistry  
Dalhousie University  
Halifax, N.S.  
Canada, B3H 4J3.
APPENDIX I

Some X-ray Crystallographic Data of the Complex

\[ \text{Rh}_2(\mu-\text{OH}.\text{Cl})(\text{CO})_2(\mu-\text{dppm})_2\cdot\text{H}_2\text{O} \]

Table I.1. Summary of Crystal Data and Intensity Collection
of \( \text{Rh}_2(\mu-\text{OH}.\text{Cl})(\text{CO})_2(\mu-\text{dppm})_2\cdot\text{H}_2\text{O} \)

Bright yellow crystals suitable for X-ray diffraction studies were grown by slow diffusion of diethyl ether to a dichloromethane solution of the title compound.

**formula** : \( \text{C}_5\text{H}_{47}\text{P}_4\text{O}_4\text{ClRh}_2 \)

**fw** : 1101.11

**cell parameters:**

\begin{align*}
\text{a} & : 13.860(3) \text{ Å} \\
\text{b} & : 14.680(5) \text{ Å} \\
\text{c} & : 25.48(1) \text{ Å} \\
\text{z} & : 4
\end{align*}

**space group** : \( \text{P}2_12_12_1 \) (orthorhombic)

**radiation** : \( \text{Mo-K}_\alpha \) (\( \lambda = 0.71069 \text{ Å} \))

**\( \mu \)** : 7.74 cm\(^{-1}\)

**total number of unique reflections** : 2690

**unique data used** : 2160

\( \text{(I > } \sigma(\text{I})) \)

**R** : 0.062
Table 1.2. Selected Interatomic Distances (Å) and Angles (Deg) in Rh₂(μ-OH.C1)(CO)₂(μ-dppm)₂.H₂O

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Other Angles

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Figure I.1. Perspective View of the Complex

\[ \text{Rh}_2(\mu-\text{OH.CI})(\text{CO})_2(\mu-\text{dpdm})_2 \cdot \text{H}_2\text{O} \]
APPENDIX II

Some X-ray Crystallographic Data of the Complex

\[ \text{[Rh}_2(\mu-\text{CN})(\mu-\text{CO})(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4\cdot\text{CH}_2\text{Cl}_2 \]

Table II.1. Summary of Crystal Data and Intensity Collection of \[ \text{[Rh}_2(\mu-\text{CN})(\mu-\text{CO})(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4\cdot\text{CH}_2\text{Cl}_2 \]

Reddish-orange crystals, suitable for X-ray diffraction studies were grown by slow diffusion of diethyl ether to a dichloromethane solution of the title compound.

formula : \( \text{C}_{55}\text{H}_{46}\text{P}_4\text{NO}_7\text{Cl}_3\text{Rh}_2 \)

\( \text{fw} \) : 1269.05

cell parameters:

\( a : 10.889(2) \text{ Å} \)
\( b : 20.040(4) \text{ Å} \)
\( c : 26.638(4) \text{ Å} \)
\( \gamma : 94.777(16) \text{ Å} \) (C axis unique)

\( z : 4 \)

space group : \( \text{P2}_1/\text{n} \) (monoclinic)

radiation : \( \text{Mo-K\( \alpha \)} \) (\( \lambda = 0.70926 \text{ Å} \))

\( \mu : 8.66 \text{ cm}^{-1} \)

total number of unique reflections : 5742

unique data used : 3440
(I > 3\( \sigma(I) \))

\( R \) : 0.066
Table II.2. Selected Bond Distances (Å) in [Rh$_2$(μ-CN)-
(μ-CO)(CO)$_2$(μ-dppm)$_2$ClO$_4$.CH$_2$Cl$_2$

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<th>Distance (Å)</th>
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<tr>
<td>P(4)-C(2)</td>
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Table II.3. Selected Bond Angles (deg) in 
\[ \text{[Rh}_2(\mu-\text{CN})(\mu-\text{CO})(\text{CO})_2(\mu-\text{dppm})_2\text{ClO}_4\cdot\text{CH}_2\text{Cl}_2} \]

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<tbody>
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</tr>
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<tr>
<td>P(1)-Rh(1)-C(5)</td>
<td>92.1(4)</td>
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<tr>
<td>P(4)-Rh(1)-C(3)</td>
<td>86.7(5)</td>
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<tr>
<td>P(4)-Rh(1)-C(5)</td>
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<td>96.3(5)</td>
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<tr>
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<tr>
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<td>101.2(6)</td>
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<td>C(5)-Rh(2)-C(6)</td>
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<td>C(5)-Rh(2)-P(2)</td>
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<td>Rh(1)-C(3)-O(1)</td>
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<td>Rh(2)-C(4)-O(2)</td>
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<td>Rh(2)-P(2)-C(1)</td>
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</table>
Figure II.1. Perspective View of the Cation

\[ \text{[Rh}_2(\mu-\text{CN})(\mu-\text{CO})(\text{CO})_2(\mu-\text{dppm})_2]^+ \]
APPENDIX III

Some X-ray Crystallographic Data of the Complex
\[ \text{[Rh}_3(\mu-\text{CO})_3(\text{CO})_3(\mu-1,2\text{-dppm})_2]ClO}_4\cdot\text{CH}_2\text{Cl}_2 \]

Table III.1. Summary of Crystal Data and Intensity Collection
of \[ \text{[Rh}_3(\mu-\text{CO})_3(\text{CO})_3(\mu-1,2\text{-dppm})_2]ClO}_4\cdot\text{CH}_2\text{Cl}_2 \]

Orange needles used in the X-ray diffraction studies were grown by slow diffusion of diethyl ether to a dichloromethane solution of the title compound.

Formula       : \( \text{C}_{57}\text{H}_{46}\text{P}_4\text{O}_{10}\text{Cl}_3\text{Rh}_3 \)
fw            : 1429.95

Cell parameters:
\[ a : 19.413(16) \, \text{Å} \]
\[ b : 15.050(7) \, \text{Å} \]
\[ c : 20.501(16) \, \text{Å} \]
\[ \beta : 100.90(6)^\circ \]
\[ z : 4 \]

Space group  : C2/c (monoclinic)
radiation     : Mo-\( \text{K}\alpha \) (\( \lambda = 0.70926 \, \text{Å} \))
\[ \mu : 10.21 \, \text{cm}^{-1} \]

Total number of reflections : 2754
Unique data used (I > 3\sigma(I)) : 1191
R               : 0.086
### Table III.2. Selected Bond Distances (Å) in \([\text{Rh}_3(\mu-CO)_3(CO)_3(\mu-1,2-dppm)_2] ClO_4 \cdot CH_2Cl_2\)

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<td>Rh(1)-C(8)</td>
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<td>Rh(2)-P(2)</td>
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<tr>
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<tr>
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<tr>
<td>P(4)-C(2)</td>
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Table III.3. Selected Bond Angles (deg) in

\[ \text{[Rh}_3(\mu-\text{CO})_3(\text{CO})_3(\mu-1,2-\text{dppm})_2\text{ClO}_4\cdot \text{CH}_2\text{Cl}_2] \]

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<tr>
<td>Rh(3)-Rh(1)-C(8)</td>
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<tr>
<td>P(1)-Rh(1)-P(4)</td>
<td>173.4(7)</td>
</tr>
<tr>
<td>P(1)-Rh(1)-C(3)</td>
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<tr>
<td>P(1)-Rh(1)-C(6)</td>
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<tr>
<td>P(1)-Rh(1)-C(8)</td>
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<td>Rh(2)-Rh(1)-Rh(3)</td>
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Table III.3. (continued).

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<td>P(1)-C(1)-P(2)</td>
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Figure III.1. Stereoview of the Cation

\[ \text{[Rh}_3(\mu-\text{CO})_3(\text{CO})_3(\mu-1,2,-\text{dppm})_2]^+ \]
APPENDIX IV

Some X-ray Crystallographic Data of the Complex

\[ \text{[Rh}_2(\mu-\text{CO})(\mu-\text{O}_2\text{CCF}_3)(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4\cdot\text{CH}_2\text{Cl}_2 \]

Table IV.1. Summary of Crystal Data and Intensity Collection of \[ \text{[Rh}_2(\mu-\text{CO})(\mu-\text{O}_2\text{CCF}_3)(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4\cdot\text{CH}_2\text{Cl}_2 \]

Yellow crystals used in the X-ray diffraction studies were grown by slow diffusion of diethyl ether to a dichloromethane solution of the title compound in an atmosphere of carbon monoxide.

<table>
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<th>formula</th>
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<td>19.197(7) Å</td>
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<tr>
<td>( c )</td>
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</tr>
<tr>
<td>( \gamma )</td>
<td>100.996(28)° (C axis unique)</td>
</tr>
<tr>
<td>( z )</td>
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<td>space group</td>
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<td>radiation</td>
<td>( \text{Mo-k\alpha (}\lambda = 0.70926 \text{ Å)} )</td>
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<td>( \mu )</td>
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<tr>
<td>( R )</td>
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Table IV.2. Selected Bond Distances (Å) in 

$[\text{Rh}_2(\mu-\text{CO})(\mu-\text{O}_2\text{CCF}_3)(\text{CO})_2(\mu-\text{dppm})_2] \text{ClO}_4 \cdot \text{CH}_2\text{Cl}_2$

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<td>Rh(1)–P(2)</td>
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</table>
Table IV.3. Selected Bond Angles (deg) in 
$[\text{Rh}_2(\mu-\text{CO})(\mu-\text{O}_2\text{CCF}_3)(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4\cdot\text{CH}_2\text{Cl}_2$

<table>
<thead>
<tr>
<th>Bond Angle</th>
<th>Value (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(1)-Rh(1)-P(2)</td>
<td>169.8(1)</td>
</tr>
<tr>
<td>C(5)-Rh(1)-C(7)</td>
<td>110.7(6)</td>
</tr>
<tr>
<td>O(2)-Rh(1)-C(5)</td>
<td>118.4(5)</td>
</tr>
<tr>
<td>O(2)-Rh(1)-C(7)</td>
<td>130.9(5)</td>
</tr>
<tr>
<td>C(2)-Rh(1)-Rh(2)</td>
<td>45.9(4)</td>
</tr>
<tr>
<td>O(2)-Rh(1)-Rh(2)</td>
<td>85.1(2)</td>
</tr>
<tr>
<td>P(2)-Rh(1)-O(2)</td>
<td>85.0(3)</td>
</tr>
<tr>
<td>P(2)-Rh(1)-C(5)</td>
<td>90.1(5)</td>
</tr>
<tr>
<td>P(2)-Rh(1)-C(7)</td>
<td>92.4(4)</td>
</tr>
<tr>
<td>P(1)-Rh(1)-O(2)</td>
<td>86.3(3)</td>
</tr>
<tr>
<td>P(1)-Rh(1)-C(5)</td>
<td>89.4(5)</td>
</tr>
<tr>
<td>P(1)-Rh(1)-C(7)</td>
<td>97.3(4)</td>
</tr>
<tr>
<td>P(3)-Rh(2)-P(4)</td>
<td>169.5(2)</td>
</tr>
<tr>
<td>O(1)-Rh(2)-C(7)</td>
<td>127.3(4)</td>
</tr>
<tr>
<td>O(1)-Rh(2)-C(6)</td>
<td>120.7(5)</td>
</tr>
<tr>
<td>C(6)-Rh(2)-C(7)</td>
<td>112.0(6)</td>
</tr>
<tr>
<td>P(4)-Rh(2)-O(1)</td>
<td>85.0(3)</td>
</tr>
<tr>
<td>P(4)-Rh(2)-C(7)</td>
<td>96.9(4)</td>
</tr>
<tr>
<td>P(4)-Rh(2)-C(6)</td>
<td>89.8(5)</td>
</tr>
<tr>
<td>P(3)-Rh(2)-O(1)</td>
<td>87.2(3)</td>
</tr>
<tr>
<td>P(3)-Rh(2)-C(7)</td>
<td>93.4(4)</td>
</tr>
<tr>
<td>P(3)-Rh(2)-C(6)</td>
<td>89.8(5)</td>
</tr>
</tbody>
</table>

(continued)
Table IV.3. (continued)

<table>
<thead>
<tr>
<th>Bond</th>
<th>Angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(7)-Rh(2)-Rh(1)</td>
<td>45.0(4)</td>
</tr>
<tr>
<td>O(1)-Rh(2)-Rh(1)</td>
<td>82.4(3)</td>
</tr>
<tr>
<td>P(2)-C(1)-P(4)</td>
<td>110.1(8)</td>
</tr>
<tr>
<td>P(1)-C(2)-P(3)</td>
<td>108.9(8)</td>
</tr>
<tr>
<td>O(2)-C(3)-C(4)</td>
<td>114(2)</td>
</tr>
<tr>
<td>O(1)-C(3)-C(4)</td>
<td>116(1)</td>
</tr>
<tr>
<td>C(3)-C(4)-F(1)</td>
<td>115(1)</td>
</tr>
<tr>
<td>C(3)-C(4)-F(2)</td>
<td>118(1)</td>
</tr>
<tr>
<td>C(3)-C(4)-F(3)</td>
<td>112(1)</td>
</tr>
<tr>
<td>F(1)-C(4)-F(2)</td>
<td>107(1)</td>
</tr>
<tr>
<td>F(1)-C(4)-F(3)</td>
<td>102(1)</td>
</tr>
<tr>
<td>F(2)-C(4)-F(3)</td>
<td>102(1)</td>
</tr>
<tr>
<td>Rh(1)-C(5)-O(3)</td>
<td>173(1)</td>
</tr>
<tr>
<td>Rh(2)-C(6)-O(4)</td>
<td>172(1)</td>
</tr>
<tr>
<td>Rh(2)-C(7)-O(5)</td>
<td>134(1)</td>
</tr>
<tr>
<td>Rh(1)-C(7)-Rh(2)</td>
<td>89.1(5)</td>
</tr>
<tr>
<td>Rh(1)-C(7)-O(5)</td>
<td>137(1)</td>
</tr>
<tr>
<td>O(2)-C(3)-O(1)</td>
<td>129(1)</td>
</tr>
</tbody>
</table>
Figure IV.1. Perspective View of the Cation

\[ \text{[Rh}_2(\mu-\text{CO})(\mu-\text{O}_2\text{CCF}_3)(\text{CO})_2(\mu-\text{dppm})_2]^+ \]
Figure IV.2. Inner Coordination Geometry of the Cation
\[ \text{[Rh}_2(\mu-\text{CO})(\mu-O_2\text{CCF}_3)(\text{CO})_2(\mu-\text{dppm})_2]^+ \]
Showing the Numbering of the Atoms.
APPENDIX V

Some X-ray Crystallographic Data of the Complex
[Rh₂(μ-O₂CCF₃)(CO)₂(μ-dppm)₂]ClO₄

Table V.1. Summary of Crystal Data and Intensity Collection
of [Rh₂(μ-O₂CCF₃)(CO)₂(μ-dppm)₂]ClO₄

Red crystals suitable for X-ray diffraction studies were
obtained by slow diffusion of cyclohexane to a dichloro-
methane solution of the title compound.

formula : C₅₄H₄₄P₄O₈F₃ClRh₂
fw : 1243.10

<table>
<thead>
<tr>
<th>cell parameters:</th>
</tr>
</thead>
<tbody>
<tr>
<td>a : 11.665(5) Å</td>
</tr>
<tr>
<td>b : 22.142(10) Å</td>
</tr>
<tr>
<td>c : 22.921(10) Å</td>
</tr>
<tr>
<td>α : 100.669(36) Å (c axis unique)</td>
</tr>
<tr>
<td>γ : 4</td>
</tr>
</tbody>
</table>

space group : P2₁/b (monoclinic)
radiation : monochromatic Mo-κα (λ = 0.70926 Å)

μ : 6.96 cm⁻¹
total number of reflections : 5716
total number of unique reflections : 3605
unique data used (I > 3σ(I)) : 2759

R : 0.079
Table V.2. Selected Bond Distances (Å) in
\([\text{Rh}_2(\mu-\text{O}_2\text{CCF}_3)(\text{CO})_2(\mu-\text{dppm})_2]\text{ClO}_4\)

<table>
<thead>
<tr>
<th>Bond</th>
<th>Distance (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rh(1)-Rh(2)</td>
<td>2.982(2)</td>
</tr>
<tr>
<td>Rh(1)-P(1)</td>
<td>2.340(6)</td>
</tr>
<tr>
<td>Rh(1)-P(2)</td>
<td>2.323(6)</td>
</tr>
<tr>
<td>Rh(2)-P(3)</td>
<td>2.309(6)</td>
</tr>
<tr>
<td>Rh(2)-P(4)</td>
<td>2.301(6)</td>
</tr>
<tr>
<td>Rh(1)-C(51)</td>
<td>1.68(2)</td>
</tr>
<tr>
<td>Rh(1)-O(4')</td>
<td>2.09(1)</td>
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<tr>
<td>Rh(2)-C(52)</td>
<td>1.74(2)</td>
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<tr>
<td>Rh(2)-O(3)</td>
<td>2.15(1)</td>
</tr>
<tr>
<td>C(51)-O(1)</td>
<td>1.21(3)</td>
</tr>
<tr>
<td>C(52)-O(2)</td>
<td>1.18(3)</td>
</tr>
<tr>
<td>C(53)-O(3)</td>
<td>1.27(3)</td>
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<tr>
<td>C(53)-C(54)</td>
<td>1.52(3)</td>
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<tr>
<td>C(54)-F(1)</td>
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<tr>
<td>C(54)-F(2)</td>
<td>1.30(2)</td>
</tr>
<tr>
<td>C(54)-F(3)</td>
<td>1.28(3)</td>
</tr>
<tr>
<td>P(1)-C(49)</td>
<td>1.84(2)</td>
</tr>
<tr>
<td>P(2)-C(50)</td>
<td>1.87(2)</td>
</tr>
<tr>
<td>P(3)-C(49)</td>
<td>1.86(2)</td>
</tr>
<tr>
<td>P(4)-C(50)</td>
<td>1.83(2)</td>
</tr>
</tbody>
</table>
Table V.3. Selected Bond Angles (deg) in [Rh₂(μ-O₂CCF₃)(CO)₂(μ-dppm)₂]ClO₄

<table>
<thead>
<tr>
<th>Bond Angle</th>
<th>Value (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(1)-Rh(1)-P(2)</td>
<td>174.1(2)</td>
</tr>
<tr>
<td>O(4)-Rh(1)-C(51)</td>
<td>169.4(9)</td>
</tr>
<tr>
<td>P(1)-Rh(1)-C(51)</td>
<td>92.7(8)</td>
</tr>
<tr>
<td>P(1)-Rh(1)-O(4)</td>
<td>88.5(4)</td>
</tr>
<tr>
<td>P(2)-Rh(1)-C(51)</td>
<td>92.6(8)</td>
</tr>
<tr>
<td>P(2)-Rh(1)-O(4)</td>
<td>87.0(4)</td>
</tr>
<tr>
<td>Rh(2)-Rh(1)-C(51)</td>
<td>82.4(8)</td>
</tr>
<tr>
<td>P(3)-Rh(2)-P(4)</td>
<td>175.9(2)</td>
</tr>
<tr>
<td>O(3)-Rh(2)-C(52)</td>
<td>161.8(9)</td>
</tr>
<tr>
<td>P(3)-Rh(2)-O(3)</td>
<td>88.8(4)</td>
</tr>
<tr>
<td>P(3)-Rh(2)-C(52)</td>
<td>91.7(8)</td>
</tr>
<tr>
<td>P(4)-Rh(2)-C(52)</td>
<td>90.4(8)</td>
</tr>
<tr>
<td>P(4)-Rh(2)-O(3)</td>
<td>88.1(4)</td>
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<tr>
<td>Rh(1)-Rh(2)-C(52)</td>
<td>124.9(8)</td>
</tr>
<tr>
<td>P(1)-C(49)-P(3)</td>
<td>113.6(1)</td>
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<tr>
<td>P(2)-C(50)-P(4)</td>
<td>117.7(9)</td>
</tr>
<tr>
<td>O(3)-C(53)-C(54)</td>
<td>118(2)</td>
</tr>
<tr>
<td>O(4)-C(53)-C(54)</td>
<td>117(2)</td>
</tr>
<tr>
<td>F(1)-C(54)-F(2)</td>
<td>108(2)</td>
</tr>
<tr>
<td>F(2)-C(54)-C(52)</td>
<td>112(2)</td>
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<tr>
<td>F(1)-C(54)-F(3)</td>
<td>108(2)</td>
</tr>
<tr>
<td>C(53)-C(54)-F(3)</td>
<td>117(2)</td>
</tr>
</tbody>
</table>
Figure V.'l. Perspective View of the Cation

$$[\text{Rh}_2(\mu-O_2\text{CCF}_3)(\text{CO})_2(\mu-\text{dppm})_2]^+$$
Figure V.2. Inner Coordination Geometry of the Cation \([\text{Rh}_2(\mu-O_2\text{CCF}_3)(\text{CQ})_2(\mu-dpm)_2]^+\) Showing the Numbering of the Atoms
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