Synthetic, Structural, and Reactivity Investigations of Neutral, Cationic, and Zwitterionic Rh(I), Ir(I), and Mn(I) Derivatives of P,N-Substituted Indenes

by

Judy Cipot

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at

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Table of Contents

List of Figures .................................................................................................................. vii
List of Tables ...................................................................................................................... ix
List of Schemes .................................................................................................................. x
Abstract ............................................................................................................................... xi
List of Abbreviations and Symbols Used ........................................................................... xii
Acknowledgements ............................................................................................................ xiv

Chapter 1: Introduction .................................................................................................... 1
1.1 Platinum Group Metals in Catalysis ........................................................................... 1
1.2 General Ligation Strategies ....................................................................................... 2
1.3 Neutral Group 9 Catalysts ......................................................................................... 5
1.4 Cationic Group 9 Catalysts ....................................................................................... 9
    1.4.1 History of Cationic Complexes ........................................................................ 9
    1.4.2 Ligand Design in Group 9 Cationic Catalysts .................................................. 12
1.5 Group 9 Formal Zwitterions ..................................................................................... 15
    1.5.1 Definition ........................................................................................................ 15
    1.5.2 Development of Formal Zwitterions ............................................................... 16
1.6 Conclusions and Chapter Outlines .......................................................................... 25
1.7 References and Endnotes ......................................................................................... 27

Chapter 2: Preparation, Rh(I) Coordination Chemistry, and Isomerization Behavior of Group 15 Donor-Functionalized Indene, Indenyl, and Indenide Ligands ......................................................................................... 30
2.1 Indene Nomenclature ............................................................................................... 30
2.2 Introduction ................................................................................................................ 31
2.3 Results and Discussion ............................................................................................ 33
    2.3.1 Preparation of Substituted Indenes and their Isomerization Behavior .......... 33
    2.3.2 Rh(I) Coordination Chemistry of Group 15 Substituted Indene Ligands..... 40
Chapter 3: Cationic and Formally Zwitterionic Rh(I) and Ir(I) Derivatives of a P,N-Substituted Indene Ligand: A Comparative Synthetic, Structural and Catalytic Investigation ........................................ 70

3.1 Introduction ........................................................................................................ 70

3.2 Results and Discussion ..................................................................................... 74
    3.2.1 Synthesis and Characterization of Neutral and Cationic Rh(I) and Ir(I) Complexes of 2-2a ................................................................. 74
    3.2.2 Synthesis and Characterization of the Formally Zwitterionic Complexes 2-7 and 3-3 ........................................................................ 79
    3.2.3 Solubility and Substrate Reactivity of the Cationic and Formally Zwitterionic Complexes ................................................................. 81
    3.2.4 Thermal Stability of the Cationic and Formally Zwitterionic Complexes ...... 82
    3.2.5 Assessing the Binding Affinity of Neutral and Anionic κ²-P,N-2-2b and κ²-P,N-2-2e ........................................................................... 84
    3.2.6 Pursuit of Rh Carbonyl Complexes .......................................................... 88
    3.2.7 Alkene Hydrogenation Studies .................................................................. 92
    3.2.8 Styrene Hydrosilylation Studies ................................................................. 96

3.3 Summary and Conclusions .............................................................................. 100

3.4 Experimental Section ...................................................................................... 104

3.5 References and Endnotes ................................................................................. 122

Chapter 4: Synthesis and Crystallographic Characterization of New Mn(I) Complexes of Donor-Functionalized Indenes ........................................... 127

4.1 Introduction ...................................................................................................... 127

4.2 Results and Discussion ................................................................................... 128
    4.2.1 The Synthesis of κ²-P,N-Mn Complexes ................................................... 128
    4.2.2 Reactivity of κ²-P,N-Mn Complexes Towards Neutral Donors .................. 133
    4.2.3 Developing Synthetic Routes to η⁵-(2-2e)Mn(CO)₃ ...................................... 133

4.3 Summary and Conclusions ............................................................................. 141

4.4 Experimental Section ..................................................................................... 142

4.5 References and Endnotes ................................................................................. 153
List of Figures

Figure 1-1. Industrially Used Group 9 Homogeneous Catalysts ........................................... 1

Figure 1-2. Examples of Common Monodentate, Bidentate, and Chiral Ligands ................. 4

Figure 1-3. Knowles’ Chiral Rh(I) Catalyst System Featuring Monodentate Chiral Phosphine Ligands ............................................................................................................. 14

Figure 1-4. Ir(I) P,N-Bound Chiral Catalyst for Asymmetric Hydrogenation ....................... 15

Figure 1-5. Schrock and Osborn’s Tetraphenylborate Rh(I) Catalyst System ...................... 17

Figure 1-6. Rh(I) B(cat)₂ Zwitterions .................................................................................. 20

Figure 1-7. Recent Anionic Ancillary Ligands for Late-Metal Zwitterionic Complexes .......... 21

Figure 1-8. Peters’ Bis(pnictogen)borate and Bis(pnictogen)silane Ligands and Corresponding Rh(I) Complexes ......................................................................................... 22

Figure 2-1. Nomenclature of Indene and Derivatives ............................................................. 30

Figure 2-2. Proposed Ligand Architecture Based on P,N-Substituted Indenes ...................... 32

Figure 2-3. The crystallographically determined structure of 2-3a·C₆H₆, shown with 40% displacement ellipsoids ........................................................................................................... 36

Figure 2-4. The crystallographically determined structure of 2-2d, shown with 40% displacement ellipsoids ........................................................................................................... 38

Figure 2-5. The crystallographically determined structure of 2-5, shown with 40% displacement ellipsoids ........................................................................................................... 39

Figure 2-6. The crystallographically determined structures of [2-6a]⁺BF₄ and [2-6b]⁺BF₄·C₄H₈O, shown with 50% displacement ellipsoids ................................................. 42

Figure 2-7. The crystallographically determined structure of 2-7, shown with 40% displacement ellipsoids ........................................................................................................... 43

Figure 2-8. The crystallographically determined structure of 2-10·C₇H₈, shown with 40% displacement ellipsoids ................................................................................................. 48

Figure 3-1. The crystallographically determined structures of [3-2b]⁺SO₃CF₃⁻, [3-2b]⁺PF₆⁻, 3-3 and 3-4 shown with 50% displacement ellipsoids ......................................... 78
Figure 3-2. Variable Temperature $^1$H NMR Plot of 3-5 in Toluene-$d^8$ .................................. 87

Figure 3-3. The crystallographically determined structures of 3-6 and 3-9 shown with 50% displacement ellipsoids .......................................................... 90

Figure 4-1. The crystallographically determined structure of 4-2•0.5C$_7$H$_8$, shown with 50% displacement ellipsoids .................................................. 129

Figure 4-2. The crystallographically determined structure of 4-3a•0.5C$_7$H$_8$, shown with 50% displacement ellipsoids ........................................ 131

Figure 4-3. The crystallographically determined structure of 4-3b, shown with 50% displacement ellipsoids .................................................. 132

Figure 4-4. The crystallographically determined structure of 4-4, shown with 50% displacement ellipsoids ........................................ 132

Figure 4-5. The crystallographically determined structure of the cation (left) and the anion (right) in 4-5•0.5C$_7$H$_8$, shown with 50% displacement ellipsoids .... 135

Figure 4-6. The crystallographically determined structure of 4-8, shown with 50% displacement ellipsoids ........................................ 137

Figure 4-7. The crystallographically determined structure of 4-9, shown with 50% displacement ellipsoids ........................................ 139

Figure 4-8. The crystallographically determined structure of rac-4-10, shown with 50% displacement ellipsoids ........................................ 140

Figure 5-1. The crystallographically determined structure of 5-1•0.25CH$_2$Cl$_2$ and 5-2, shown with 50% displacement ellipsoids ........................................ 160
List of Tables

Table 2-1. Crystallographic Data for 2-2d, 2-3•C₆H₆, 2-5, and [2-6a]⁺BF₄⁻ and [2-6b]⁺BF₄⁻, 2-7, and 2-10•C₇H₈ .......................................................... 66

Table 3-1. Bond Lengths (Å) and Angles (°) for [3-2b]⁺OTf⁻, [3-2b]⁺PF₆⁻, and 3-3 ........ 79

Table 3-2. Crystallographic Data for [3-2b]⁺OTf⁻, [3-2b]⁺PF₆⁻, 3-3, 3-4, 3-6, and 3-9.. 121

Table 3-3. Hydrogenation of Styrene .......................................................... 93

Table 3-4. Hydrogenation of Substituted Alkenes at 0.5 mol% Catalyst Loading .......... 96

Table 3-5. Addition of Triethylsilane to Styrene ........................................... 98

Table 4-1. Crystallographic Data for 4-2, 4-3a, 4-3b, 4-4, 4-5, 4-8, 4-9, and 4-10 ...... 151

Table 5-1. Interatomic Distances (Å) and Angles (°) for 5-1·0.25CH₂Cl₂ and 5-2 .... 160

Table 5-2. Crystallographic Data for 5-1·0.25CH₂Cl₂ and 5-2 .......................... 176

Table 5-3. Alkene Hydrogenation Mediated by κ²-(P,O)M(COD) Complexes .......... 163

Table 5-4. Addition of Triethylsilane to Styrene, Employing 5 mol% Catalyst ....... 166
List of Schemes

Scheme 1-1. Wilkinson’s Catalyst System................................................................. 5

Scheme 1-2. Schrock and Osborn’s Dihydrde Cationic Catalyst System............... 9

Scheme 2-1. Stepwise Transformation of (C₉H₇)Ir(COD)........................................... 31

Scheme 2-2. Attempted Isomerization of 2-2a and Synthesis of 2-3......................... 34

Scheme 2-3. Synthesis and Attempted Isomerization of Compounds 2-2c and 2-2d.... 37

Scheme 2-4. Isomerization of 2-4a to 2-4b, Followed by Complexation with Rhodium to Produce 2-5................................................................. 39

Scheme 2-5. Synthetic Routes to the [κ²-P,N-Rh(diene)]⁺X⁻ Cations and the κ²-P,N-RhCOD Zwitterion ......................................................... 41

Scheme 2-6. Possible Resonance Contributors of 2-2e........................................... 43

Scheme 2-7. Generation of the Mononuclear η⁵-Complex, 2-9, and the Rh₂Li₂ Species, 2-10................................................................. 45

Scheme 2-8. Two Possible Mechanistic Routes to 2-10.............................................. 47

Scheme 3-1. Synthesis of Rh(I) and Ir(I) Complexes Derived from 2-2a..................... 75

Scheme 3-2. Depiction of Possible Geometries that would Give Rise to Metal-Carbonyl Complexes Displaying (a) One, (b) Two, or (c) Three IR Active Stretches.. 91

Scheme 3-3. Attempted Synthesis of 3-8..................................................................... 92

Scheme 4-1. Reagents: (i) BrMn(CO)₃; (ii) AgBF₄; (iii) AgSO₂CF₃; (iv)BrMn(CO)₃/AgBF₄ .................................................................................. 129

Scheme 4-2. Formation of 4-5..................................................................................... 135

Scheme 4-3. Reagents: (i) ClSiMe₃; (ii) nBuLi, (b) ClP̵Pr₂; (iii) BrMn(CO)₃ ............. 136

Scheme 4-4. Reagents: (i) BrMn(CO)₃; (ii) nBuLi, (b) ClP̵Pr₂; (iii) (a) nBuLi, (b) BrMn(CO)₃, (c) ClP̵Pr₂ ......................................................... 138

Scheme 5-1. Synthesis of the Neutral Phosphinoenolate Rh(I) and Ir(I) Complexes..... 159

Scheme 5-2. Attempted Synthetic Routes to 1-P̵Pr₂-2-Indanone ............................. 162
Abstract

Cationic rhodium and iridium complexes incorporating mixed donor bidentate P,N ancillary ligands are effective in mediating certain homogeneous catalytic reactions. However, two disadvantages of cationic catalysts that potentially limit their synthetic utility include: (1) their poor solubility properties; and (2) the somewhat unpredictable nature of the outershell counteranion on the catalytic performance of the complex. The development of alternative charge-neutral formally zwitterionic catalysts to overcome these challenges has received some attention, although the range of suitable anionic ligands to support Rh and Ir zwitterionic complexes remains limited. In the research presented in this thesis, a fundamentally new heterobidentate P,N ligand (1-PPr₂-2-NMe₂-indene, 2-2) has been prepared from readily available starting materials.

The ability of 2-2 to support Mn(I), Rh(I) and Ir(I) neutral and cationic metal fragments has been demonstrated. Interestingly, 2-2 can be deprotonated to form a 10π-indenide unit (2-2e) which can coordinate a cationic Rh or Ir fragment in the κ²-P,N chelate site to generate entirely new heterobidentate formally zwitterionic complexes. A comparison of the catalytic properties of these zwitterions with their isostructural and isosteric cationic relatives has provided the opportunity to assess the impact of altering only the electronic characteristics of a formally cationic metal fragment. These Rh and Ir zwitterions are effective catalysts for the hydrogenation and hydrosilylation of alkenes; their solubility and reactivity properties are in some instances divergent from and superior to those of more traditional Rh and Ir salts. In addition, these cationic [(κ²-P,N-2-2)M(COD)]⁺X⁻ and zwitterionic (κ²-P,N-2-2e)M(COD) complexes represent a complementary family of catalysts for the addition of E-H bonds to alkenes, when issues of catalytic activity/selectivity and solvent compatibility are considered.

Under appropriate reaction conditions, the (κ²-P,N)M(COD) catalysts (M = Rh, Ir) can be transformed into the corresponding (κ²-P,O)M(COD) complexes featuring 1-PPr₂-2-O-indene. This neutral κ²-P,O-Ir(I) complex 5-2 is able to reduce alkenes under very mild reaction conditions (~1 atm H₂, 22 °C) in a range of solvents including hexanes, benzene, THF, CH₂Cl₂, and CH₃CN. Notably, 5-2 represents the most active neutral Ir(I) alkene hydrogenation catalyst known.
List of Abbreviations and Symbols Used

9-BBN  9-borabicyclo[3.3.1]nonane
Å    angstrom
atm  atmospheres
binap  2,2’-(diphenylphosphino)-1,1’-binaphthyl
bipy  bipyridine
br   broad
BuLi  butyl lithium
COD  η⁴-1,5-cyclooctadiene
COE  η²-cyclooctene
Cp*  pentamethylcyclopentadienyl
Cy   cyclohexyl
d    day
diop  2,3-o-isopropylidene-2,3- dihydroxy-1,4-bis(diphenylphosphino)butane
DMSO dimethylsulfoxide
dppb  bis(diphenylphosphino)butane
dppe  bis(diphenylphosphino)ethane
dppp  bis(diphenylphosphino)propane
DS   dehydrogenative silylation
e-   electron
E    main group element
ee   enantiomeric excess
eq   equation
equiv equivalents
FID  free induction decay
GC   gas chromatography
HBe ca t catecholborane
HS   hydrosilylation
Hz   hertz
IR   infrared
\( nJ_{xy} \) n bond coupling constant between atoms x and y
\( \kappa \) kappa
L ligand
m multiplet
M concentration in mol/L (in experimental sections)
min minute
mmol millimole
mol mole
MS mass spectrometry
\( \eta \) eta
NBD \( \eta^4 \)-2,5-norbornadiene
NMR nuclear magnetic resonance
OTf \( \text{SO}_2\text{CF}_3 \) (triflate)
ppm parts per million
psi pounds per square inch
PTFE poly(tetrafluoroethene)
Py pyridine
Pz pyrazolyl
q quartet
RT room temperature
TOF turn over frequency
TMS trimethylsilyl group
Tpms tris(pyrazolyl)methanesulfonate
X non-coordinating counteranion
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Chapter 1: Introduction

1.1 Platinum Group Metals in Catalysis

Homogeneous transition metal catalysts have been developed into useful and versatile tools for the synthesis of fine and bulk chemicals over the last 40 years.\textsuperscript{1} Based on the ability of metals to effectively catalyze specific reactions, the periodic table can be classified into blocks, each describing the catalytic transformations best performed by that group. One group of metals that facilitate reduction chemistry such as hydrogenations, hydroformylations, and hydrosilylations are the "platinum-group metals," which consist of the late second- and third- row transition metals ruthenium, osmium, rhodium, iridium, palladium, and platinum, all of which are electron rich metals that are particularly reactive in low oxidation states.\textsuperscript{1,2a}

Platinum group metals and their salts are available in commercial quantities, and although they can be more costly than traditional catalytic metals such as zinc and copper, they have the potential to be much more catalytically active in the same types of organic transformations.\textsuperscript{1} While these platinum group metals are all especially active and efficient at E-H and E-C (E = H, B, C, Si, N, P, \textit{etc.}) bond activations and formations, some organic transformations are better facilitated by particular metals. For instance, the group 9 metals rhodium, and later iridium, are examples of transition metals used successfully as homogeneous catalysts in industrial processes to generate acetic acid (Figure 1-1).\textsuperscript{1}

\[
\begin{array}{l}
\text{[\text{Rh}(\text{CO})_2]}^+ \\
\text{[\text{Ir}(\text{CO})_2]}^+
\end{array}
\]

\textbf{Figure 1-1.} Industrially Used Group 9 Homogeneous Catalysts
While neutral complexes of the platinum group metals have figured prominently in homogeneous catalysis over the years, cationic systems are also widely used since they often provide increased activity and/or selectivity over neutral catalyst systems. Indeed, the ability of what can be viewed as more electrophilic cationic late metal complexes to effectively add main group E-H bonds to unsaturated substrates is widely exploited in synthetic chemistry.\(^2a\) As the field of ligand and catalyst design develops, not only are the efficiency and selectivity in known metal mediated reactions constantly improving, but new reactions are being developed, the applications of which are yet to be uncovered. For instance, the ability of cationic transition metal species to facilitate the dehydrogenative cross-coupling of C-H and E-H fragments has been exploited in the functionalization of alkanes.\(^3\)

1.2 General Ligation Strategies

While the catalytic activity of a platinum group metal complex can be ascribed to the innate properties of the metal itself, there is much to be said for the judicious use of well-chosen ligands to fill the coordination sphere of the metal. The electronic and steric contributions of the ligands can have a significant impact upon the reactivity and selectivity of the system in various catalytic reactions; as such, the development and incorporation of carefully chosen ligand components continues to be an active area of research.

Ligands can be classified into two main groups: reactive and ancillary. Reactive ligands are those that may be consumed or ultimately utilized in a reaction facilitated by the catalyst. For instance, in crude salts like RhCl\(_3\)·xH\(_2\)O, neither the chloride ligands nor
the water molecules are thought to offer any real influence on the progress of a reaction in which the complex may be used. Instead, these salts have been converted into refined complexes featuring rationally chosen (ancillary) ligands bound to the metal.

Ancillary is the term used to classify a second group of ligands of which the electronic and/or steric components prove to be important in altering the selectivity or reactivity of a metal complex for a given reaction. One class of ancillary ligands is multidentate ligands (ligands containing two or more donor atoms), which often include a mixed donor set where one donor atom is less tightly bound to the metal than the other. This design technique is built upon the hard-soft acid-base concept\textsuperscript{2b}: if the ligand is to be used with a soft late metal such as Ir, a hard oxygen donor, for instance, may be used as one donor site of the bidentate ligand, since it would be more easily displaced from the metal center by an incoming substrate molecule compared to a softer, more tightly bound donor such as phosphorus.\textsuperscript{2b} In this manner, incorporation of a mixed hard-soft donor set can help direct reactivity to a particular site on the metal. An advantage of bidentate ligands which include a mixed donor set is that the more readily displaced ligand ‘arm’ is then still available to re-coordinate and stabilize the metal via the Chelate Effect\textsuperscript{2} after the substrate has been transformed and released. In general, ancillary ligands are intended to remain bound in some predictable way to the metal during a reaction and their electronic and/or steric properties assists the metal in more efficiently catalyzing a given reaction. In the pursuit of new metal-mediated transformations, the development of ancillary ligands to support metal fragments is an active area of research.

Traditional ancillary ligands for late transition metals often involve neutral, two-electron group 15 donors such as nitrogen or phosphorus, which are manifested as
trialkyl- or triaryl-phosphines (Fig 1-2, A) or amines (Fig 1-2, B). However, chelating bis(phosphines) and bis(amines) tethered by various linker units have been used extensively in metal coordination chemistry in more recent years and are now common ligands. Examples of such compounds are dppe and bipy (Fig 1-2, C and D). These and other multidentate ligands offer a means of enhancing the reactivity properties of the metal center, while at the same time providing stability to the complex (vide supra). Multidentate ligands are also widely used as sources of chirality transfer for metal-mediated asymmetric catalysis when, for instance, chiral components are installed into the linker unit joining the donor atoms. One common example of a chiral bidentate ligand is binap (Fig 1-2, E), which incorporates axial chirality into the carbocyclic framework linking the phosphine donors.

![Chemical structures](image)

**Figure 1-2.** Examples of Common Monodentate, Bidentate, and Chiral Ligands

Homogeneous catalyst technology has evolved over the last 40 years and remains an active area of chemical research in many laboratories around the globe. In this chapter, a progression of group 9 catalyst design will be presented starting from one of the first neutral active hydrogenation catalysts developed by Wilkinson, to a series of cationic group 9 catalysts, and finally into current work in the pursuit of charge-neutral
zwitterionic catalyst systems. Collectively, this discussion will provide the general background to the remaining chapters in this thesis.

1.3 Neutral Group 9 Catalysts

In the 1960s, Wilkinson introduced one of the first examples of a homogeneous transition-metal catalyst, chlorotris(triphenylphosphine)rhodium(I) (Scheme 1-1, 1-1),\textsuperscript{5a} which proved to be the most effective hydrogenation and hydroformylation catalyst at the time.\textsuperscript{5b,c} While an effective catalyst, the limited solubility of 1-1 is a challenge; whereas a slurry in benzene yields only moderate catalytic hydrogenation activity, addition of a donor co-solvent such as acetonitrile or pyridine to the reaction mixture results in a marked increase in the rate of hydrogenation. This increased activity is ascribed to the in-situ formation of a proposed solvent-supported Rh(I) active catalyst species RhCl(PPh\textsubscript{3})\textsubscript{2}(solvent) (1-2), in which one triphenylphosphine group is displaced by a donor solvent molecule.\textsuperscript{5c,d}

\[
\begin{align*}
1-2: & \quad M = \text{Rh} \\
1-2': & \quad M = \text{Ir}
\end{align*}
\]

\[
\begin{align*}
1-1: & \quad M = \text{Rh} \\
1-1': & \quad M = \text{Ir}
\end{align*}
\]

\[
\begin{align*}
1-3: & \quad M = \text{Rh} \\
1-4: & \quad M = \text{Rh} \\
1-4': & \quad M = \text{Ir}
\end{align*}
\]

\[
\begin{align*}
1-5: & \quad M = \text{Rh}
\end{align*}
\]

\[\text{Scheme 1-1. Wilkinson's Catalyst System}\]
Upon establishing the utility of 1-1 for catalytic hydrogenation and hydroformylation, Wilkinson and co-workers then investigated the nature of the active catalyst species. In a series of detailed articles, they report numerous experiments that led to solid and solution state structural information on such species. These studies provide insight on how and if the ligands in 1-1 participate in a given metal-mediated catalytic cycle. Similar methodology is still used by many research groups to ascertain structural information regarding active catalysts in their systems. Generally, these investigations involve stoichiometric reactions between the pre-catalyst and the substrate or related small molecules, and subsequently attempting to observe complexes that are potential participants in the catalytic cycle in the solution phase (by NMR spectroscopy, for instance) and/or in the solid state (by X-ray crystallography, IR spectroscopy, or various other methods). The elegant studies undertaken by Wilkinson reveal the utility of this methodology: while the proposed structure of the active hydrogenation catalyst 1-2 could not be confirmed directly, support for this formulation was obtained upon studying the reactivity of 1-1 in the presence of various small molecules. For example, the reactivity of 1-1 with ethylene (along with other neutral, two-electron donors that were surveyed) rapidly produced the crystalline complex (C\textsubscript{2}H\textsubscript{4})Rh(PPh\textsubscript{3})\textsubscript{2}Cl, 1-3, at room temperature in either benzene or chloroform. The crystallographically characterized complex 1-3 supports the proposed trans-disposed phosphine groups in 1-2; in addition, dissolution of 1-3 and sparging with dinitrogen in the presence of PPh\textsubscript{3} facilitates rapid displacement of the ethene ligand, as observed by \textsuperscript{1}H NMR spectroscopy. Coupled together, the solid and solution state data provide strong evidence for the proposed
structure of 1-2 and suggests that species of this type represent the active catalyst configuration in reaction mixtures starting from 1-1.

Among the other neutral donors investigated by Wilkinson was carbon monoxide.\textsuperscript{5c,d} The resulting complex 1-4 formed from the substitution of a triphenylphosphine ligand is structurally similar to 1-3, however the CO ligand is not displaced by the introduction of other neutral donors, such as PPh\(_3\), as ethene was, which indicates that the CO ligand in 1-4 is more tightly bound to Rh than was the alkene in 1-3.\textsuperscript{5c} This is a significant observation since complex 1-4 is a far superior hydroformylation catalyst for the conversion of alkenes to aldehyde products relative to 1-1 when it is prepared and independently used as a catalyst; these data suggest that the active catalyst in hydroformylation catalysis is of a different nature than that proposed for the hydrogenations.\textsuperscript{5d,e} Wilkinson also showed that 1-1 is able to oxidatively add dihydrogen to yield the dihydride 1-5;\textsuperscript{5a,e} aside from Vaska's iridium system (1-4'), 1-1 was the only other group 9 catalyst reported at the time to demonstrate activation of molecular hydrogen.\textsuperscript{6a}

In the early 1960s, Vaska and co-workers described the coordination chemistry and small molecule reactivity of IrCl(CO)(PPh\(_3\))\(_2\) (1-4'), including its behaviour towards dihydrogen, various solvents, organic acids and carbon monoxide, in all cases finding structurally similar complexes to the Rh compounds examined by Wilkinson. However, in sharp contrast to the Rh complexes, the neutral Ir analogues 1-1' to 1-4' exhibit essentially no catalytic activity.\textsuperscript{5d-f} The observed inactivity of the Ir series is likely a result of the formation of stable Ir(III) intermediates that prevent the generation of coordinatively unsaturated species in solution, which are required to facilitate
coordination and subsequent transformation of incoming substrates. Despite decades of homogeneous catalyst development since this early work by Vaska and Wilkinson, and the generally quite reactive behaviour of neutral Ir(I) precatalysts in stoichiometric reactions, effective ligation methods to activate neutral Ir(I) complexes towards catalysis remain rare. As a result, neutral Ir(I) complexes have, until recently, received limited attention as catalysts compared to their Rh counterparts.

To effectively facilitate reactivity, either stoichiometric or catalytic, a group 9 metal center typically undergoes a series of oxidation and reduction sequences. This process can be augmented by the incorporation of well-chosen ligands; an example of this was discussed earlier, where the hydrogenation activity of Wilkinson’s Rh system is significantly greater when one of the triphenylphosphine ligands in 1-1 is replaced by a weaker bound solvent or ethene ligand as in 1-2 or 1-3. As will be discussed in more detail in the ensuing sections, use of mixed donor multidentate ligands is also an effective way to support a late metal center, since such ligands provide a labile donor that is easily displaced when needed, thus allowing for the redox sequence that is part of a catalytic cycle to occur.

An alternative conceptual method to improve the activity of a late transition metal complex is to reduce the electron density at the metal center by making it formally cationic. To accomplish this, the metal center is oxidized by one electron, generally through the abstraction of an anionic reactive ligand (e.g. Cl⁻). This process yields an electropositive metal center which is naturally more electrophilic, and tends to coordinate an alkene and oxidatively add (e.g. H₂) incoming substrate molecules faster than do the neutral analogues. Although some neutral heavier group 9 catalysts are still used in
industry today and continue to figure importantly in modern synthetic chemistry, there are many examples where cationic catalyst systems can offer enhanced reactivity, as discussed in the following section.

1.4 Cationic Group 9 Catalysts

1.4.1 History of Cationic Complexes

In the late 1960s and early 1970s, Schrock and Osborn developed a class of homogeneous cationic group 9 hydrogenation catalysts of the form \([M(\text{diene})(\text{PPh}_3)_2]^+X^-\) (\(M = \text{Rh or Ir}; \text{diene} = \text{COD or NBD}\)) which featured a variety of weakly or non-coordinating counteranions (\(X^-\)) such as perchlorate or hexafluorophosphate (1-7, Scheme 1-2). Not only did Schrock and Osborn extensively demonstrate the utility and diversity of their catalyst system in various reactions, but they also explored the mechanism, active species, and undesirable catalyst-deactivating side reactions that have provided useful information regarding optimal reaction conditions to other researchers in the field.\(^{7a-c}\)

![Scheme 1-2. Schrock and Osborn's Dihydride Cationic Catalyst System](image-url)
The metal-diene cation complexes 1-6 and 1-7, as well as several closely related species prepared by treating [M(diene)$_2$]$^+$X$^-$ with a variety of substrates including arenes, dienes, carbon monoxide, and alkyl phosphines, were readily synthesized, and characterized by use of infrared (IR) and 1D-NMR spectroscopic techniques.$^{7d,e}$ The active catalysts, identified in later work$^{7a-c}$ as either monohydride or dihydride species such as 1-8, were prepared by treating the cationic complexes 1-7 with an atmosphere of dihydrogen.$^{7f}$ The coordination array in 1-8 was confirmed on the basis of IR and NMR spectroscopic data, and on the crystallographically identified structure of the Ir congener, 1-8$^+$. $^{7f}$ Under mild reaction conditions, the dihydride iridium and rhodium cations 1-8 function as homogeneous hydrogenation catalysts for a variety of unsaturated substrates. In addition to their studies on the hydrogenation of olefins and alkynes, Schrock and Osborn found that 1-8 is useful in the reduction of ketones to alcohols, also under mild conditions (25 °C, 1 atm).$^{7g}$

One common trait among cationic group 9 catalyst systems is their inherently reduced solubility in low-polarity media; the salt nature of these complexes requires the use of donor solvents such as acetone or THF to facilitate complete dissolution of the catalyst. As shown in Scheme 1-2, these coordinated solvent molecules are easily displaced in 1-6 by stronger donor ligands. However, strongly coordinating solvents such as acetonitrile (in place of acetone or THF) are not readily displaced from the metal center by typically weaker donor substrate molecules. In effect, the catalytic hydrogenation abilities of 1-7 or 1-8 is significantly repressed in the presence of excess acetonitrile or other strong donors such as triphenylphosphine.$^{7f}$ This type of catalyst deactivation is observed for many cationic group 9 catalyst systems developed to date.
and continues to be a challenge for many researchers to find ways to utilize these typically active catalysts in less polar and less coordinating reaction conditions; if one could find a way to solubilize the cationic catalyst in a weakly coordinating solvent, such as benzene or hexane, increased catalytic reactivity might be observed. One method to investigate the utility of cationic catalyst systems in alternative reaction conditions is to develop more soluble zwitterionic analogues which incorporate the anionic charge into the backbone of the ancillary ligand, such that the molecule is formally charge neutral, yet still features a cationic metal fragment (*vide infra*).

While the Ir(III) complex 1-8' exhibited catalytic hydrogenation activity competitive with 1-8, the precursor Ir(I) complex 1-7' exhibited little hydrogenation activity towards various unsaturated substrates under the same reaction conditions used for 1-7. Upon investigation of this, Schrock and Osborn identified that the resistance of the NBD group (or COD group in related complexes) to undergo solvent substitution chemistry in the Ir congener 1-7' was the limiting step; unfortunately, this substitution had been identified as a key stage in rhodium catalysis. This apparent lack of reactivity of the diene fragment in 1-7' motivated Crabtree's research into the investigation of an Ir(I) hydrogenation catalyst system that would prove be more effective than analogous Rh(I) complexes.8

While the general formula of Crabtree's iridium system, [Ir(COD)L$_2$]$^+${PF$_6$} (L = tertiary phosphine), is not unlike that developed by Schrock and Osborn, his seminal investigation revealed that chlorinated solvents are not only viable reaction media but the *preferred* solvents for this typically non-catalytically active third-row metal. This was an initially surprising discovery since chlorinated solvents, especially CHCl$_3$ (and
sometimes CH₂Cl₂) normally deactivate electronically and coordinatively unsaturated hydrogenation catalysts, such as those Rh complexes introduced by Osborn.⁵c Yet in the case of these Ir(I) cations, and most cationic Ir(I) hydrogenation catalysts reported to date, chlorinated solvents remain the choice since they dissolve the catalyst, yet they do not compete with substrate molecules for coordination sites at the metal center.⁸a Interestingly, this iridium system [Ir(COD)L₂]⁺PF₆⁻ is also tolerant towards oxidants such as oxygen or ethyl iodide, which normally instantly deactivate other classes of hydrogenation catalysts. In addition, the system is highly active even at 0 °C and is tolerant towards several types of functionalized olefins, including those with polar substituents.

1.4.2 Ligand Design in Group 9 Cationic Catalysts

A second important contribution in the development of catalytically useful Ir(I) cationic complexes from Crabtree was the incorporation of an ancillary ligand set featuring mixed donor atoms. While his catalyst system initially integrated two phosphine ligands, Crabtree also prepared complexes featuring one amine and one phosphine ligand (eq 1-1), as in [Ir(COD)(ER₃)(E'R₃)]⁺ (1-9; E, E' = N or P).⁸b Alkene hydrogenation experiments revealed that while bisamine complexes of 1-9a were entirely inactive for catalytic hydrogenation, the mixed-ligand complexes (1-9c) containing one phosphine and one amine donor proved to be the most active hydrogenation catalysts yet observed (up to 80 times more efficient than bisphosphine (1-9b) complexes), particularly for hindered substrates such as 2,3-dimethyl-2-butene.⁸c This seminal result established that the use of a 'hard-soft' mixed donor ligand system can be an efficient way to enhance the reactivity of a metal due to the differing trans-labilizing effects between the two donors.
Optimization of the ancillary ligand set in 1-9 led to the development of "Crabtree's catalyst", where the mixed donor set incorporates a tricyclohexylphosphine and a pyridine group \([\text{Ir(COD)(PCy}_3\text{(Py))}]^{+}\text{PF}_6^-, 1-10\). This complex is commercially available and remains widely used as an alkene hydrogenation catalyst. A phosphorus-nitrogen mixed donor ligation strategy similar to that featured in 1-10 remains popular in the development of modern group 9 catalysts in various research groups.\(^9\)

Since this important contribution from Crabtree to the field of iridium catalysis, the pursuit of a highly active asymmetric version of Crabtree’s catalyst continues to be the goal of many research groups. Predisposing a metal to affect asymmetric transformations is a challenging task. A high degree of stereoselectivity in asymmetric catalysis requires catalysts which exhibit the following properties in order to avoid loss of chirality during catalytic transformations: (1) the chiral ligand must maintain a highly rigid conformation; and (2) the ligand(s) must stay firmly bound to the metal to effectively transfer chirality to the substrate. In this vein, two methods in group 9 chemistry that have been employed to incorporate chirality into a ligand are to either build chirality into the carbocyclic backbone of the ligand, or to use a phosphine with three inequivalent substituents on the phosphorus center. The latter technique was featured in early asymmetric catalyst design by Knowles (Fig 1-3).\(^{10a}\) While there are some other instances of using chiral phosphines with Rh to build Wilkinson-like
complexes (Fig 1-3), more typically the chirality comes from a carbocyclic framework bound to the phosphine or which acts as a bridge between two donor atoms to form a chiral mixed donor heterobidentate ligand.

\[
\begin{array}{c}
\text{R}^1 \quad \text{P} \quad \text{R}^3 \\
\text{R}^2 \\
\text{R}^1 = \text{Me, cy, o-anisyl} \\
\text{R}^2 = \text{Me, Ph, cy} \\
\text{R}^3 = \text{Ph, i-Pr, n-Pr, Me} \\
\text{where R}^1 \neq \text{R}^2 \neq \text{R}^3
\end{array}
\]

\[0.5 \text{[Rh(diene)Cl]}_2 \rightarrow 3 \text{equiv P}^* \rightarrow \text{Cl-Rh-P}^* \quad \text{P}^* = \text{chiral phosphine}
\]

**Figure 1-3.** Knowles’ Chiral Rh(I) Catalyst System Featuring Monodentate Chiral Phosphine Ligands

There are several advantages of using P,N-bidentate ancillary ligands with late transition metals; as discussed in Section 1.2, one benefit of a hard-soft bidentate design is that not only is one of the two donors (in this case, N) easily displaced by an incoming substrate molecule, but this donor arm remains ready to re-coordinate to the reactive metal fragment upon release of the transformed molecule. A second advantage is the rigidity inherent to a bidentate ligand architecture, which is useful in maintaining the desired catalyst structure, especially when chirality transfer in asymmetric catalysis is sought. The combination of these two effects obtained when mixed-donor bidentate ancillary ligands are used can often enhance the selectivity and activity of the catalyst. An important recent contribution to this type of ligand development is by Pfaltz, where he prepares mixed-donor bidentate ligated Ir(I) complexes structurally reminiscent of Crabtree’s catalyst that incorporate a phosphine donor bridging to a pyridyl group through a rigid chiral bicyclic backbone (Fig 1-4, 1-11). This catalyst and related derivatives effectively hydrogenate a variety of trisubstituted aryl alkenes at low catalyst
loadings within 2 h in CH$_2$Cl$_2$. As well, the hydrogenations are highly enantioselective, giving chiral substituted alkanes in over 90% ee in most cases.$^{9a,b}$

![Chemical structure](image)

**Figure 1-4.** Ir(I) P,N-Bound Chiral Catalyst for Asymmetric Hydrogenation

The generally enhanced electrophilicity of a cationic metal center facilitates increased catalytic reactivity over neutral systems in most instances. In the continuing evolution of ligand design, cationic Rh(I) and Ir(I) homogeneous catalyst systems have allowed admission to a wealth of previously inaccessible reactions, or have improved the efficiency of established processes, such as in the hydrogenation of alkenes. However, inherent disadvantages of cationic systems that include their limited solubility in less-polar solvents and the unpredictable nature of a counteranion,$^{11}$ motivate the continuing effort to find methods to overcome these challenges; as alluded to in Section 1.4.1, one method that is experiencing increasing attention is the development of charge-neutral formally zwitterionic metal complexes.

### 1.5 Group 9 Formal Zwitterions

#### 1.5.1 Definition

For the purposes of the discussion in this thesis, formally zwitterionic complexes are defined as those species lacking conventional resonance structures that place an
anionic charge onto one of the donor atoms of the ancillary ligand.\textsuperscript{12} These complexes can be considered as an “internal salt”, where the negative charge is sequestered into the backbone of the ligand framework, away from the positively charged metal center.

\textbf{1.5.2 Development of Formal Zwitterions}

As discussed in previous sections, cationic, coordinatively unsaturated metal complexes have played a critical role in enhancing the utility of organometallic catalysts in the preparation of functionalized organic molecules. Homogeneous cationic complexes are amongst the most widely studied systems in organometallic research; however, the range of reaction conditions under which these cationic complexes may be used is limited in part by their poor solubility properties. In addition, the systematic design of cationic complexes is complicated by the somewhat unpredictable influence of the outersphere counteranion on catalytic performance.

More recently, various research groups have focused on the development of charge-neutral formally zwitterionic alternatives to traditional cationic systems since zwitterionic catalysts can possess certain reactivity advantages over their cationic counterparts. One such advantage is the increased solubility of formal zwitterions in less-polar media that occurs upon incorporating the anionic charge into the backbone of the ancillary ligand. A second advantage is the that there is no longer a need for an outersphere counteranion in zwitterionic complexes, and this eliminates the problems associated with potential hindrance of the coordination and transformation of an incoming substrate molecule due to a counteranion. This section provides an overview of examples of formally zwitterionic Rh and Ir complexes that have been reported to date, with particular attention given to the importance of anionic ancillary ligand design.
The first identified formally zwitterionic homogeneous catalysts, developed by Schrock and Osborn in 1970, are the zwitterionic, \( \eta^6 \)-arene bound rhodium complexes shown in Figure 1-5 (1-12). The rhodium metal center bears a formal positive charge with the corresponding anionic charge sequestered in the borato fragment of the ligand backbone. These zwitterions were prepared by exchange of the outersphere PF\(_6^-\) counteranion (used in traditional Schrock and Osborn Rh(I) salts, see Scheme 1-2) for BPh\(_4^-\).\(^{7d,f,13}\) While determining the nature of the boratoarene-metal interaction was initially challenging, IR and NMR spectroscopic data provided strong evidence for \( \pi \)-bonding of one of the phenyl rings of the tetraphenylborate unit to the metal center, which was confirmed later when Nolte published a short communication reporting the crystal structure of a very similar \( \eta^6 \)-bound tetraphenylborate ligand to a rhodium metal center.\(^{14}\)

![Diagram of zwitterionic and cationic structures](image)

**Figure 1-5.** Schrock and Osborn's Tetraphenylborate Rh(I) Catalyst System

Investigation of the catalytic abilities of the zwitterions 1-12a, b compared to the related cation 1-13 were undertaken by Alper. In general, 1-12 required milder reaction conditions or exhibited greater selectivity than other known rhodium catalysts.\(^{15}\) One of the earliest reactions examined with 1-12 was the homogeneous hydroformylation of
olefins. While some neutral and cationic rhodium catalysts had been shown previously to be very effective at hydroformylation, high regioselectivity to form either branched or linear aldehyde products had not been observed. In the case of 1-12, hydroformylation of \( p \)-isobutylstyrene to yield the branched aldehyde product in 85% yield under 200 psi of syn gas (CO/H\(_2\)) was achieved, while the hydroformylation of the same substrate by the neutral catalyst [(CO)\(_2\)RhCl]\(_2\) required a remarkable 1400 psi of syn gas to achieve the same level of conversion. In addition, 1-12 proved to be relatively insensitive to electronic effects in the substrates; it effectively mediated the hydroformylation of a wide range of both electron rich and poor olefins with regioselectivities in most cases greater than 95%.

Despite the encouraging catalytic results obtained through the use of this zwitterionic catalyst in particular reactions, the limited strength of the boratoarene-metal interaction seems inherently problematic in this particular catalyst architecture. As demonstrated through introduction of a chelating bisphosphine ligand such as dpbb to a solution of 1-12, the \( \eta^6 \)-bound BPh\(_4^-\) anionic ancillary ligand is rapidly displaced to yield the cationic complex [(dpbb)\(_2\)Rh]\(^+\) BPh\(_4^-\) (eq 1-2).

\[\text{(1-2)}\]

\[
\begin{array}{c}
\text{1-12b} \quad \text{n equiv dpbb} \quad \text{1-12} \\
\begin{array}{c}
\text{I} \quad \text{II} \\
\text{\( \eta^6 \)-bound BPh\(_4^-\)} \\
\text{\text{cationic complex [(dpbb)\(_2\)Rh]\(^+\) BPh\(_4^-\)}} \\
\text{(eq 1-2)}
\end{array}
\end{array}
\]

<table>
<thead>
<tr>
<th>( n )</th>
<th>Ratio</th>
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<tbody>
<tr>
<td>1</td>
<td>90:10</td>
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<tr>
<td>2</td>
<td>57:43</td>
</tr>
<tr>
<td>4</td>
<td>0:100</td>
</tr>
</tbody>
</table>
This particular example highlights that rational design and construction of formally zwitterionic catalysts featuring non-labile anionic ligands is imperative to effectively implement such a ligation strategy. Two points that should be considered in the preparation of zwitterionic metal catalysts include: (1) anionic ligand architecture must effectively sequester the charge; and (2) a donor set must remain firmly bound to the cationic metal fragment under various reaction conditions in order to maintain a zwitterionic framework. In this vein, while 1-12 embodies an anionic ligand effective at localizing the negative charge in the backbone of the ligand, a stronger binding site is required to achieve success.

The popularity of a borate unit as the anionic charge carrier in ancillary ligand design for zwitterionic complexes is demonstrated in several of the other ligands that will be discussed in this section. In particular, the anionic ancillary ligand that was introduced in the early 1990s by Westcott, Marder and Baker\textsuperscript{16} features a borate unit that links two catechol units (Fig 1-6). This design is similar to that of 1-12, since the metal-ligand interaction is based on \( \eta^6 \)-bonding of one of the arene units to the cationic Rh(I) fragment. With derivatives of this zwitterionic design (1-14), the catalytic hydroboration\textsuperscript{16a,b} and diboration\textsuperscript{16c} of unsaturated substrates was targeted, achieving regio- and diastereoselectivity complementary to conventional non-metal catalyzed hydroboration agents such as 9-BBN.

The reactivity of 1-14 is markedly better than that of the zwitterionic system studied by Alper\textsuperscript{15} in the hydroboration of styrene derivatives such as 4-vinylanisole. In some instances, the formal zwitterion 1-14 can yield a selectivity of >99% for Markovnikov addition of a borane to an alkene. In a similar reaction, 1-12a generated a
non-selective mixture of Markovnikov and anti-Markovnikov addition products, as well as hydrogenated alkene.\textsuperscript{16b} The nature of the metal-anion interaction in 1-14 is clearly different than in the similar zwitterions 1-12, as is reflected in the differing catalytic reactivity of the two classes. The efficacy of 1-14 is attributed to the ability of the π-bound [B(cat)\textsubscript{2}]\textsuperscript{-} anion to ring slip from η\textsuperscript{6} to η\textsuperscript{4} or even to an η\textsuperscript{2} coordination mode, which allows access to a coordinatively and electronically unsaturated species poised for coordination and transformation of incoming substrates, without loss of the [B(cat)\textsubscript{2}]\textsuperscript{-} fragment.

![Chemical structure](image)

**Figure 1-6.** Rh(I) B(cat)\textsubscript{2} Zwitterions

Since the boratoarene-based anionic ligands featured in 1-12 and 1-14 were introduced, the development of anionic ancillary ligands that resemble the ubiquitous multidentate ligands discussed earlier have been sought by several researchers. This research goal has led to the introduction of ligands featuring group 15 and 16 donor atoms linked through an anionic charge carrier in the form of a substituted carborane,\textsuperscript{17} sulfate,\textsuperscript{18} or borate\textsuperscript{19,20} fragment (Fig 1-7). The carboranes (A) feature a chelating ligand architecture in which the charge is held in the anionic cluster of the backbone. Compared to the boratoarene ligation described previously, the CODRh(I) complexes of A are significantly more substitutionally-inert to a wide array of mono and chelating
phosphines, as well as carbon monoxide gas; in these substitution reactions, only the COD reactive ligand undergoes displacement.\textsuperscript{17} The greater stability of these formally zwitterionic Rh(I) complexes is attributed to the chelating capacity of the ancillary bisphosphine ligand relative to the boratoarene ligation strategy of previous generations.

\begin{figure}
\centering
\includegraphics[width=\linewidth]{fig1.png}
\caption{Recent Anionic Ancillary Ligands for Late-Metal Zwitterionic Complexes}
\end{figure}

Building on the development of chelating anionic ligands, a new class of poly(pyrazolyl) ligands has been introduced by Kläui.\textsuperscript{21} Here the pyrazolyl donor units are linked by a methanesulfonate group to generate the Tpms ligand (Fig 1-7, B). An interesting structural feature of this design is that the anionic charge is sequestered in a sulfonate group as opposed to a borate unit. While the sulfonate group does effect charge separation, it does not help facilitate solubility of the resulting transition metal complexes in low-polarity solvents. Reactivity studies involving metal complexes of B are few;\textsuperscript{18b-d} however, one theme that emerges from these reports is that the binding mode of this ligand is highly variable and can adopt a variety of conformations including $\kappa^2$-N,N; $\kappa^3$-N,N,N; and $\kappa^3$-N,N,O. In the case of $\kappa^3$-N,N,O coordination, the formally zwitterionic nature of the metal complex is lost due to direct neutralization between the anionic
oxygen of the sulfonate group and cationic metal. In some cases, the $\kappa^3$-N,N,N and $\kappa^3$-N,N,O are observed simultaneously in solution.$^{18c}$

More recently, new classes of tridentate ligands have been introduced by Tilley, and later developed by Peters, which transform simple chelating pnictogen donor ligands into anionic analogues (Figure 1-7, C).$^{19}$ The tripodal phosphine ligand $\text{C}$ has been shown to bind a variety of transition metal fragments including Co, Ru, Fe, Ni, Rh and Ir.$^{19}$ However, while no extensive catalytic reactivity studies have been communicated for these metal complexes, this general class of zwitterions are susceptible to decomposition by way of $B$-$\text{CH}_2\text{PR}_2$ bond cleavage to yield non-zwitterionic bis(phosphino)borane Rh(I) derivatives.$^{19a}$

A related class of anionic bidentate ligands that are closely related to the tridentate ligand $\text{C}$ were introduced by Peters.$^{20}$ Specifically, this bidentate system contains either a bisamine or an analogous bisphosphine donor set (Fig 1-8). The bisaminoborate ligand $[\text{Ph}_2\text{B}(\text{CH}_2\text{NR}_2)_2]^-$ reacts in a facile manner with the rhodium dimer $[\text{Rh}(\text{NBD})\text{Cl}]_2$ to generate a rhodium(I) neutral zwitterionic complex (1-15a) in high yield.

![Figure 1-8. Peters' Bis(pnictogen)borate and Bis(pnictogen)silane Ligands and Corresponding Rh(I) Complexes](image)

In addition to the preparation of the bisaminoborate ligands shown in 1-15a,$^{20a}$ Peters has prepared the analogous bisphosphinoborate ligands $[\text{Ph}_2\text{B}(\text{CH}_2\text{PR}_2)_2]^-$, which
feature a variety of alkyl and aryl substituents at both the phosphine and borate sites capable of binding Rh(I) cationic fragments (1-15b, Fig 1-8). To effectively assess the potential benefits of the formally zwitterionic Rh(I) complexes 1-15a or 1-15b, Peters has also prepared isoelectronic cationic complexes (1-16) supported by silane-bridged neutral ligands. Where the preparation of the anionic borate ligands is facile and the rhodium complexes 1-15a,b thereof are easily accessed and stable in solution, the cationic Rh(I) derivatives 1-16a,b are difficult to isolate, and in some cases are generated in-situ only. The relative electrophilicity of the metal center in the zwitterions 1-15 compared to the cationic complexes 1-16 was assessed through an IR study of the CO stretching frequencies in these compounds where L = CO. In all cases, results of the studies indicate that the zwitterionic complexes 1-15 have CO stretching frequencies lower than in the cationic systems; this suggests that there is more π-backboning between the metal and the ligand, and is indicative of a more electron-rich metal center, which implies that the ligand is more electron-donating in the zwitterionic complexes, as compared to the cationic analogues.

The catalytic reactivity of Rh(I) complexes 1-15 compared to those of 1-16 has been assessed in four separate reactions involving E-H bond activation: hydrogenation, hydroboration, hydrosilylation, and hydroacylation. In addition, traditional Rh(I) cations supported by chelating phosphine ligands dppe and dppp were investigated under the same reaction conditions. The hydrogenation of styrene revealed that the Rh(I) zwitterion 1-15a was over ten times more active than the phosphine congener 1-15b. In addition, zwitterionic 1-15a was twice as efficient as the cationic analogue 1-16a, and over 15 times more active than the known Rh(I) dppe and dppp cations. 1-15a also
proved to be very robust and tolerant to repeated additions of fresh styrene to the catalytic reaction mixture.\textsuperscript{20d}

The catalytic hydroacylation of 4-methyl-4-pentenal (eq 1-3) highlights the catalytic potential of the acetonitrile adducts of zwitterions 1-15. In particular, zwitterion 1-15b was extremely reactive, exhibiting turn-over frequencies (TOFs) over 40 times greater than any of the cationic catalysts studied and with product yield in excess of 95%. In addition, the zwitterions 1-15 maintain their high catalytic activity in solvents of varying polarity including benzene, THF, and acetonitrile, whereas the cationic analogues 1-16b are deactivated entirely.

\[
\begin{align*}
\text{1,3-diene} & \quad \text{0.5 mol\% catalyst} \\
& \quad \text{acetone} \\
& \quad \text{RT} \\
\rightarrow & \quad \text{cyclopropane} \\
\end{align*}
\]

\textbf{Catalyst* = 1-15a, 1-15b, or 1-16b}

\textsuperscript{*} L = \text{CH}_3\text{CN}; R = \text{Ph} \text{ for 1-15b and 1-16b; R = Me for 1-15a}

Results from an investigation of the catalytic hydroboration and hydrosilylation ability of 1-15 and 1-16 (L = CH\textsubscript{3}CN) (eq 1-4) indicate a weaker performance of the formal zwitterions relative to the cations; however, addition of a strongly coordinating solvent, such as acetonitrile, completely shuts down the catalytic activity of cation 1-16b and the Rh(I) dppe and dppp cations. In contrast, the activity of the zwitterions was attenuated only slightly.\textsuperscript{20d}
The skillful design of this class of zwitterionic late transition metal catalysts has demonstrated the potential utility and versatility of a zwitterionic design over more traditional cationic catalysts. However, the design of this bidentate anionic ligand class has associated drawbacks, such as the lack of synthetic modularity which prevents the preparation of a series of non-symmetric analogues (i.e. if phosphine arms containing different substituents are desired). In addition, preparation of a mixed-donor heterobidentate alternative is not synthetically viable.

1.6 Conclusions and Chapter Outlines

In summary, significant developments have been made towards finding new avenues of activating late transition metal fragments for use as catalysts in main-group bond making and breaking processes over the last 40 years. Understanding the effect of ancillary ligands, be they monodentate, multidentate and/or mixed donor, on the ability of a metal to interact and transform a substrate has led to the introduction of a wide range of homogeneous catalyst complexes, all designed to achieve better selectivity or more efficient reactivity over previous generations. From the wealth of information that has been obtained on the types of ancillary ligands that are best suited to enhance the reactivity of cationic group 9 metals in particular, two themes have emerged. The first of these is that mixed donor ligand sets incorporating one hard donor (such as N) and one soft donor (such as P) can increase the activity of the metal dramatically, as in the $\kappa^2$-
$P,N$-Ir(COD) complexes prepared by Pfaltz.$^{9a,b}$ A second theme is that while group 9 cationic complexes remain popular, the general utility of these systems in solvents of lower polarity presents a barrier due to their inherently reduced solubility in arene and aliphatic solvents, in addition to the somewhat unpredictable behavior of the counteranions in these complexes; one method that has received attention to overcome the somewhat limiting properties associated with cationic systems is to develop formally zwitterionic versions in which the anionic charge is held not by an outersphere counteranion, but rather is sequestered into the backbone of an ancillary ligand.

To date, while the preparation of formally zwitterionic Rh and Ir complexes has been reported, the anionic charge carrier has been almost exclusively a borate unit, and only recently have P or N bidentate and tridentate ligand architectures been developed.$^{19,20}$ While the properties of the formally zwitterionic Rh and Ir complexes reported suggest that such a design strategy can provide catalysts that may be used in less polar solvents and that they potentially have greater stability towards typically deactivating reaction conditions (such as the presence of a strong donor molecule like CH$_3$CN), there exists no mixed-donor anionic ligand variants. In addition, zwitterionic complexes featuring Ir(I) cationic centers are much less common than their Rh congeners, and while the synthetic utility of Ir cationic catalysts is well established, there are few reports describing the reactivity properties of Ir zwitterions.$^{19}$ In light of the superior catalytic properties exhibited by late transition metal complexes containing heterobidentate $\kappa^2$-$P,N$ ancillary ligands compared to homobidentate group 15 analogues, the preparation of a heterobidentate $P,N$ ligand capable of serving as an anionic charge reservoir without the use of a borate unit was identified as a particularly important target.
The design of a new class of isostructural and isoelectronic cationic and zwitterionic complexes that will be discussed in the body of this thesis feature new P,N-indene and P,N-indenide ligands. In particular, Chapter two presents a modular, two-step synthetic route to these functionalized indene ligands in addition to evaluation of the binding properties and preparative methods for the formation of neutral, cationic, and zwitterionic Rh(I) complexes. Chapter three expands on the utility of these P,N-indene and P,N-indenide ligands to support Ir(I) cationic fragments in addition to surveying the reactivity properties of the group 9 complexes in stoichiometric and catalytic applications. Upon establishing the efficacy of this new ligand set to support group 9 metals, a synthetic survey to include other transition metal fragments was undertaken; in this vein, the manganese coordination chemistry of the newly developed P,N-indene ligand is presented in Chapter four. Finally, while neutral Ir complexes have very little precedent as main group bond activation catalysts, the development of a highly active neutral Ir(I) alkene hydrogenation catalyst featuring a mixed donor P,O-indene ligand is described in Chapter five. The overall conclusions and significance of the work presented in this thesis, along with suggestions for future work are the subject of Chapter six.

1.7 References and Endnotes


2. Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals, Third Edition*; Wiley: Toronto, 2001; (a) chapter 9; (b) chapter 1.


Chapter 2: Preparation, Rh(I) Coordination Chemistry, and Isomerization Behavior of Group 15 Donor-Functionalized Indene, Indenyl, and Indenide Ligands

2.1 Indene Nomenclature

The bicyclic organic molecule $C_9H_8$ featuring a benzo unit fused to a cyclopentadiene ring is referred to as ‘indene’ (Fig 2-1). Substitution of indene with various groups leads to functionalized indenes. However, in the situation where there is at least one M-C linkage between a metal fragment and a $C_9H_7$ unit or functionalized relative, the term used to describe the bound ligand is ‘indenyl’. An uncoordinated $C_9H_7$ anion yields an anionic version that is termed ‘indenide’. The numbering used in conventional indene chemistry is also shown in Figure 2-1. In the case of functionalized indenes, the C1 position is always assigned to the $sp^3$ hybridized carbon of the C5-ring.

![Indene, $C_9H_8$](image)

![Indenyl, $C_9H_7^+$](image)

![Indenide, $C_9H_7^-$](image)

![C1-substituted indene](image)

![C3-substituted indene](image)

**Figure 2-1. Nomenclature of Indene and Derivatives**
2.2 Introduction

Transition metal complexes supported by π-coordinated, η⁵-indenyl ligands have a longstanding history in the field of organometallic chemistry and continue to figure importantly in current research.¹ For instance, the first Rh(I) complex featuring an η⁵-bound indenyl ligand was reported in 1977 by Green and co-workers.² Transition metal chemistry featuring indene or functionalized derivatives continues to emerge.¹ In part, the continuing interest in indenyl-metal chemistry is associated with the wealth of binding modes that indene can adopt to provide varying degrees of electronic support to a metal center. For example, the indenyl ligand can adopt not only an η⁵ coordination mode, but also an η⁹, η³, an η¹, and an η⁶ motif, depending on the system. In some cases, the stepwise transformation from η⁵ to η³ to η¹ can be observed by the sequential addition of another donor to the metal complex, as in the chemistry observed for (C₉H₇)Ir(COD) and PMe₃ (Scheme 2-1).³ While ligands such as Cp can undergo similar haptotropic shifts, the rate is greatly accelerated in the case of indenyl ligands.¹

Scheme 2-1. Stepwise Transformations of (C₉H₇)Ir(COD)

In particular, main group functionalized indenyl ligands have attracted considerable attention,⁴ since they have been shown to impart interesting reactivity properties to both early and late transition metal fragments.⁵ For instance, the efficiency
of (η^5^-Cp')Ru(PPh_3)Cl₂ (Cp' = Cp, indenyl, or dimethylaminoidenyl) to catalyze the metal-mediated living radical polymerization of styrene is significantly enhanced when the bound arene unit is the substituted indene.⁵d

Given the lack of P,N-functionalized indene ligands and the interesting reactivity properties that have been documented for mixed-donor ligand systems,⁶ compounds such as A (Figure 2-2) were targeted for investigation as potential bidentate ligands. This ligand architecture is attractive since it features a modular synthetic approach in terms of installing varying alkyl or aryl phosphine groups and/or varying amine fragments to ultimately tune the steric and electronic properties of the potential bidentate binding site. In addition, the proposed structure contains a relatively acidic proton in the indene carbocyclic backbone of the ligand, which could be exploited to generate a deprotonated version B featuring an extended Hückel aromatic carbanion within the periphery of an ancillary ligand.

![Diagram](image)

**Figure 2-2. Proposed Ligand Architecture Based on P,N-Substituted Indenes**

This ligand design should provide an efficient means of inducing formal charge separation in the resulting metal complexes, and was anticipated to provide access to fundamentally new late metal zwitterionic complexes. Although main group functionalized indene and indenyl compounds have been widely used as carbocyclic \(\pi\)-ligands, the sequestering of an anionic charge in the form of a 10-\(\pi\) indenide unit built
into the backbone of a bidentate ligand has thus far been overlooked. In this chapter, the synthesis of indene derivatives of the general formulation A are discussed. Following, an investigation of the experimental and ligand features that favor the selective binding of Rh(I) metal fragments to the periphery of the indenide carbanion generated upon deprotonation of A rather than coordinating in the usual $\eta^5$-indenyl manner to the face of the carbocyclic framework will be presented. The crystallographic identification of a new "non-pentahapto" structural motif for rhodium-indenide complexes is also presented.

2.3 Results and Discussion

2.3.1 Preparation of Substituted Indenes and their Isomerization Behavior

2-Dimethylaminoinedene, 2-1, is prepared from the condensation of 2-indanone and dimethylamine, via a published literature procedure. The indene-supported P$_2$N ligand, 2-2a, was prepared in 93% yield via low-temperature lithiation of 2-1 by employing $n$BuLi, followed by the addition of $^3$Pr$_2$PCl (eq 2-1). The NMR spectroscopic data on the resulting P$_2$N-functionalized indene is consistent with a $C_1$ symmetric structure; this is formulated as the C1 isomeric form of the ligand, where the phosphorus group is situated on the $sp^3$ carbon of the indene framework. In contrast, when phosphorus is placed at the vinylic position (C3 isomer, 2-2b), the symmetry of the ligand changes from $C_1$ to $C_5$, and a mirror plane containing the indene, P, and N donor atoms exists. The isopropyl groups bound to phosphorus and the methyl groups of nitrogen lie symmetrically on either side of the plane.
The conversion of 2-2a into 2-2b (Scheme 2-2) was attempted using the method of Anderson and co-workers, who reported that while the isomerization of 1-diphenylphosphinoindene into 3-diphenylphosphinoindene occurs slowly on standing in solution, this transformation proceeds rapidly and quantitatively upon exposure to alumina. After stirring a C₆D₆ solution of pure 2-2a over alumina for several hours, NMR signals attributable to 2-2a (19.6 ppm) and what is presumed to be the vinylic isomer (vide infra) 2-2b (-2.9 ppm) were observed. Although this transformation appeared to proceed without the formation of by-products, complete conversion could not be achieved; even after several days the ratio of 2-2a to 2-2b was found to be only $\approx 3:1$. Efforts to promote this isomerization process by heating a toluene solution of 2-2a at 80 °C were also unsuccessful, generating a mixture of 2-2a, 2-2b and other phosphorus-containing products.

Scheme 2-2. Attempted Isomerization of 2-2a and Synthesis of 2-3
Anderson and co-workers also observed that the C1 to C3 isomerization of diphenylphosphinoindene occurs when the phosphorus center is coordinated to platinum. In an effort to assess the effect of metal coordination to the ligand as a means to facilitate the isomerization process, 2-2a was reacted with a half equivalent of [(L2)RhCl]2 (L2 = (a) COD or (b) NBD) to generate [(κ1-P,N-2-2a)Rh(L2)Cl] (2-3). The crystallographically determined structure of [(κ1-P,N-2-2a)Rh(COD)Cl]+C6H6 (2-3a•C6H6, Figure 2-3) confirms that the coordinated indene ligand 2-2a is bound exclusively through the phosphorus donor and shows that the ligand does not undergo a structural rearrangement upon coordination to rhodium in 2-3a; this is supported by the solution NMR spectroscopic data for 2-3. Selected data for all of the crystallographically characterized compounds reported in this chapter are collected in Table 2-1 following a description of the crystallographic solution and refinement details in the experimental section. The rhodium center in 2-3a•C6H6 possesses a square-planar geometry commonly observed for Rh(I) (d8) complexes. As expected, the metrical parameters indicate that the alkene donor (C11, C12) trans to chloride binds more tightly to the metal center than the corresponding alkene (C15, C16) trans to phosphine; this is due to the increased π-backbonding between the phosphine and Rh which exerts a stronger trans influence compared to the chloride and is reflected in the elongated bond trans to the stronger donor. Attempts to promote the C1 to C3 isomerization of the indenyl fragment in 2-3, either by stirring over alumina or by heating, resulted in decomposition.
**Figure 2-3.** The crystallographically determined structure of 2-3a•C₆H₆, shown with 40% displacement ellipsoids. Selected hydrogen atoms and the benzene solvate have been omitted for clarity. Selected interatomic distances (Å): Rh-Cl 2.3774(5); Rh-P 2.3427(5); Rh-C11 2.137(2); Rh-C12 2.115(2); Rh-C15 2.232(2); Rh-C16 2.190(2); P-C1 1.882(2); N-C2 1.390(3); C1-C2 1.530(3); C2-C3 1.351(3). Selected interatomic angles (deg): C2-N-C27 118.0(2); C2-N-C28 116.2(2); C27-N-C28 112.3(2).

In an effort to determine the possible role of the isopropyl substituents on phosphorus in blocking the isomerization of 2-2a to 2-2b, the related 1-diphenylphosphino-substituted aminoindene (2-2c) was prepared and its isomerization behavior subsequently examined (Scheme 2-3). Similar to what was observed for 2-2a, a C₆D₆ solution of pure 2-2c was transformed into a mixture of 2-2c and 2-2d (≈ 1:3) after exposure to alumina for several hours. Also similar to the 2-2a/2-2b system, attempts to drive this rearrangement process by heating a 2-2c/2-2d mixture at 80 °C in toluene were unsuccessful, leading to the formation of numerous phosphorus-containing products.
Scheme 2-3. Synthesis and Attempted Isomerization of Compounds 2-2c and 2-2d

The efficient separation of 2-2c from 2-2d was not achieved, although the predominant formation of the latter species in the aforementioned isomerization experiment allowed for $^1$H and $^{31}$P NMR resonances attributable to 2-2d to be assigned. Moreover, in one instance a minute quantity of crystalline 2-2d suitable for single-crystal X-ray diffraction analysis was obtained, and the crystallographically determined structure of 2-2d is presented in Figure 2-4. By analogy, this provides indirect evidence for the structural formulation of 2-2b. The overall geometric features in 2-2d are comparable to those of 3-diphenylphosphinoindene. In addition, the co-planarity of the non-hydrogen atoms (excluding the phenyl substituents on phosphorus), and the short N-C2 distance (1.352(3) Å) indicate that the lone pair of electrons on nitrogen in 2-2d is in conjugation with the indene $\pi$-system. This bonding scenario provides a possible rationale as to why the isomerization of 2-2a/2-2b or 2-2c/2-2d over alumina is sluggish, whereas the transformation of 1-diphenylphosphinoindene or 1-diisopropylphosphinoindene (2-4a, *vide infra*) into the corresponding C3 isomer is rapid. In consideration of steric factors alone, it may be that the large R$_2$P fragment is best accommodated at the allylic (C1) position in either 2-2a or 2-2c, when the dimethylamino group adopts a co-planar geometry with the indene ring. Furthermore, conjugation of the lone pair on nitrogen with
the indene system should greatly increase the electron density of the indene group in either 2-2a or 2-2c, and in doing so should reduce the acidity of the benzylic hydrogen atom at the C1 position.\textsuperscript{12} Since the C1 to C3 isomerization of phosphinoindenes over alumina can be viewed as a deprotonation/reprotonation sequence,\textsuperscript{9,13} the increased pK\textsubscript{a} of the benzylic proton on going from 1-diphenylphosphinoindene to either 2-2a or 2-2c should be manifested in an increased barrier to isomerization.

![Diagram of molecular structure](image)

**Figure 2-4.** The crystallographically determined structure of 2-2d, shown with 40% displacement ellipsoids. Selected interatomic distances (Å): P-C3 1.807(2); N-C2 1.352(3); C1-C2 1.518(3); C2-C3 1.380(3). Selected interatomic and torsion angles (deg): C2-N-C8 121.6(2); C2-N-C9 122.8(2); C8-N-C9 115.5(2); C1-C2-N-C8 5.2(3); C3-C2-N-C9 -0.1(4).

In keeping with the aforementioned arguments, substitution of the 2-dimethylamino fragment in 2-2a for a hydrogen atom facilitates the C1 to C3 isomerization process. 1-Diisopropylphosphinoindene (2-4a) was prepared in 92% yield and in turn was cleanly converted to 3-diisopropylphosphinoindene (2-4b) upon exposure to alumina (Scheme 2-4). Treatment of 2-4b with 0.5 equiv of [CODRhCl]\textsubscript{2} generated the
expected coordination complex \([(\kappa^1-P\text{-}2\text{-}4b)\text{Rh} (\text{COD})\text{Cl}]\) (2-5) in 79% yield. The crystallographically determined structure of 2-5 is presented as Figure 2-5 and confirms the presence of the coordinated ligand, 2-4b. From the perspective of the rhodium coordination sphere, the structural attributes of 2-5 mirror those of 2-3a•C₆H₆.

**Scheme 2-4.** Isomerization of 2-4a to 2-4b, Followed by Complexation with Rhodium to Produce 2-5.

**Figure 2-5.** The crystallographically determined structure of 2-5, shown with 40% displacement ellipsoids. Selected hydrogen atoms have been omitted for clarity. Selected interatomic distances (Å): Rh-Cl 2.3589(6); Rh-P 2.3366(5); Rh-C11 2.136(2); Rh-C12 2.124(2); Rh-C15 2.211(2); Rh-C16 2.199(2); P-C3 1.821(2); C1-C2 1.500(3); C2-C3 1.344(3).
2.3.2 Rh(I) Coordination Chemistry of Group 15 Substituted Indene Ligands

The Rh(I) coordination chemistry of the P,N-indene and P,N-indenide (2-2e) ligands is presented here in the context of exploring the range of binding possibilities available to 2-2; in Chapter 3, an examination of the ability of these P,N-ligands to effectively support catalytically active Rh(I) and Ir(I) reactive metal fragments is discussed. As a result, the three Rh(I) derivatives of 2-2 that are presented in this chapter serve to highlight the range of binding possibilities accessible through 2-2 and related derivatives, and to identify the ligand attributes that promote peripheral over facial binding of a metal fragment.

As mentioned in Section 2.1, treatment of 2-2 with 0.5 equiv of either [CODRhCl]₂ or [NBDRhCl]₂ produces the corresponding mononuclear phosphine complexes, 2-3a and 2-3b, respectively. These and the other Rh(I) species depicted in Scheme 2-5 are formed quantitatively (on the basis of ³¹P NMR spectroscopic data obtained from the crude reaction mixtures), and in all cases the desired complexes can be isolated as analytically pure solids in high yield. Chloride abstraction (AgBF₄) from rhodium in either 2-3a or 2-3b generates the cationic chelate complexes, [2-6a]⁺BF₄⁻ and [2-6b]⁺BF₄⁻, respectively, in which the ligand framework has undergone a structural rearrangement that places the ⁴Pr₂P fragment at the C3 position. The crystallographically determined structures of [2-6a]⁺BF₄⁻ and [2-6b]⁺BF₄⁻ are shown in Figure 2-6, and are comparable to those of other [(κ²-P,N)Rh(olefin)₂]⁺X⁻ salts reported in the literature.¹⁴ In addition, the bond lengths within the indene portion of [2-6a]⁺BF₄⁻ and [2-6b]⁺BF₄⁻ are consistent with each other; the slightly shorter Rh-alkene interactions in [2-6b]⁺BF₄⁻ relative to [2-6a]⁺BF₄⁻ are attributed to the different electronic and steric profiles of the
Scheme 2-5. Synthetic Routes to the \([\kappa^2-P,N-Rh(\text{diene})]^+X^-\) Cations and the \(\kappa^2-P,N-Rh\text{COD} \) Zwitterion

COD and NBD units. As discussed in Section 2.2, the increased pKa of the benzylic proton may have relevance to the rapid C1 to C3 isomerization of the coordinated indene ligand on going from 2-3 to \([2-6]^+\text{BF}_4^-\) (Scheme 2-5). As in 2-2d, the short N-C2 distance in 2-3a•\text{C}_6\text{H}_6 (1.390(3) Å) suggests that the lone pair of electrons on the uncoordinated dimethylamino group is in conjugation with the indene ring, possibly inhibiting the C1 to C3 rearrangement of the bound ligand (2-2a) in 2-3a. Coordination of the nitrogen donor to rhodium following abstraction of the chloride ligand in 2-3 would disrupt this conjugation, enabling the isomerization of 2-2a to 2-2b to proceed within the metal coordination sphere, and leading to the exclusive formation of \([(\kappa^2-P,N-2b)\text{Rh}(L_2)]^+\text{BF}_4^- ([2-6]^+\text{BF}_4^-).^{15}
The crystallographically determined structures of $[2$-$6a]^+\text{BF}_4^-$ and $[2$-$6b]^+\text{BF}_4^-\cdot\text{C}_4\text{H}_8\text{O}$, shown with 50% displacement ellipsoids. Selected hydrogen atoms, as well as the THF solvate in $[2$-$6b]^+$ and the BF$_4^-$ counterions have been omitted for clarity. Selected bond lengths (Å) for $[2$-$6a]^+\text{BF}_4^-$: Rh-P 2.305(1); Rh-N 2.211(4); P-C3 1.809(4); N-C2 1.459(6); C1-C2 1.508(6); C2-C3 1.340(7); C3-C3a 1.486(6); C3a-C7a 1.411(6); C1-C7a 1.502(7). Selected bond lengths (Å) for $[2$-$6b]^+\text{BF}_4^-\cdot\text{C}_4\text{H}_8\text{O}$: Rh-P 2.2798(7); Rh-N 2.179(2); P-C3 1.806(3); N-C2 1.455(3); C1-C2 1.509(4); C2-C3 1.346(4); C3-C3a 1.477(4); C3a-C7a 1.404(4); C1-C7a 1.499(4).

The alkane-soluble zwitterionic Rh(I) species, 2-7, is without precedent. This novel complex can be cleanly generated either by deprotonation of $[2$-$6a]^+\text{BF}_4^-$, or via lithiation of 2-2 followed by treatment with 0.5 equiv of [CODRhCl]$_2$. The preference of the (COD)Rh$^+$ fragment in 2-7 to coordinate at the P,N site rather than binding in an η$^5$-fashion to the indenyl ring is highly unusual, especially in light of the numerous (η$^5$-indenyl)Rh(olefin)$_2$ complexes that are known.\(^{16}\) The crystallographically determined structure of 2-7 is shown in Figure 2-7. Particularly striking are the differences between the interatomic distances within the C$_5$ ring of $[2$-$6a]^+\text{BF}_4^-$ (e.g. C1-C2 = 1.508(6) Å; C2-C3 = 1.340(7) Å) and those found in 2-7 (e.g. C1-C2 = 1.386(3) Å; C2-C3 = 1.419(3) Å). Whereas the cation exhibits bond length alternation consistent with an indene framework, the indenide unit in 2-7 possesses a highly delocalized structure and is appropriately described as a “naked” indenide anion.\(^{17}\)
Interestingly, despite the clear structural differences in the C₅ portion of the ligand in these Rh complexes, the metal-ligand contacts within 2-7 do not differ significantly from those found in the corresponding cation [2-6a]⁺BF₄⁻, confirming the isosteric relationship of the metal coordination sphere between the κ²-P,N-2-2b- and κ²-P,N-2-2e-bound Rh(I) fragments. One other point that merits acknowledgement is that while 2-7 formally lacks a conventional resonance contributor that places the anionic charge onto either of the pnictogen donor groups, the short P-C3 and C1-C2 distances in 2-7, when compared with those found in the analogous cations [2-6a]⁺BF₄⁻ and [2-6b]⁺BF₄⁻, suggest that a methylene phosphide-type resonance structure featuring a ¹Pr₂P=C3 linkage and an anionic charge on phosphorus may also figure prominently in 2-7 (Scheme 2-6).

![Two possible resonance contributors of 2-2e](image)

**Scheme 2-6.** Possible Resonance Contributors of 2-2e

![Crystallographically determined structure of 2-7](image)

**Figure 2-7.** The crystallographically determined structure of 2-7, shown with 40% displacement ellipsoids. Non-indenide hydrogen atoms have been omitted for clarity. Selected interatomic distances (Å): Rh-P 2.3173(6); Rh-N 2.242(2); P-C3 1.758(2); N-C2 1.479(3); C1-C2 1.386(3); C2-C3 1.419(3); C3-C3a 1.446(3); C3a-C7a 1.442(4); C1-C7a 1.430(4).
On the basis of the interesting and exclusive formation of donor atom-bound metal complexes 2-3, [2-6]BF₄ and 2-7, studies were conducted in an effort to identify the substitution pattern on indene required to promote the peripheral (rather than facial) binding of indenide ligands to rhodium(I) fragments (Scheme 2-5). The initial approach to gain an understanding of the subtleties of metal binding to the indenide ligand involved systematically examining the impact of removing either the diisopropylphosphino or dimethylamino substituents from the precursor, 2-2a. Lithiation of 2-1 followed by treatment with 0.5 equiv of [CODRhCl]₂ produced the anticipated \( \eta^5 \)-indenyl complex, 2-8, in 53% yield (eq 2-2). Similarly, treatment of 2-4b with one equiv of \( n \text{BuLi} \) proceeded cleanly in diethyl ether; \textit{in situ} monitoring of the reaction (\(^{31}\)P NMR) confirmed the consumption of 2-4b, accompanied by the appearance of one new phosphorus-containing product (2-4c-Li) at -8.9 ppm. Addition of 0.5 equiv of [CODRhCl]₂ to the reaction mixture produced the pentahapto species, 2-9, as the only phosphorus-containing product (\( \delta^{31}\)P = -11.9), which in turn was isolated in 88% yield (Scheme 2-7). The lack of rhodium coupling to phosphorus is in keeping with the structural formulation proposed for 2-9. These preliminary experiments confirm that the ability of the adjacent phosphorus and nitrogen donors to chelate the Rh(I) center in 2-7 is critical in order to circumvent \( \eta^5 \)-coordination to the face of the indenide fragment.
Scheme 2-7. Generation of the Mononuclear \( \eta^5 \)-Complex, 2-9, and the Rh$_2$Li$_2$ Species, 2-10.

In the pursuit of 2-9, a reaction was inadvertently carried out in which 2-4b was initially treated with excess (2.5 equiv) rather than a stoichiometric quantity of nBuLi. Despite the excess base employed, the clean formation of 2-4c-Li was noted (\( ^{31} \)P NMR) and subsequently [CODRhCl]$_2$ (0.5 equiv) was added to the reaction mixture. After approximately 2 h, the consumption of 2-4c-Li along with the formation of 2-9 as the major product was observed (\( ^{31} \)P NMR); the mixture was then filtered and set to crystallize at -30 °C. Although no crystalline material was obtained from this reaction mixture initially, storage for an extended period of time at reduced temperatures ultimately produced a few X-ray quality crystals. Surprisingly, single-crystal X-ray diffraction analysis revealed that this material was not the anticipated \( \eta^5 \)-indenyl complex, 2-9, but rather the unusual dimeric Rh$_2$Li$_2$ species, 2-10 (Scheme 2-7).
Re-examination of the resulting supernatant solution by using $^{31}$P NMR techniques revealed the previously observed singlet at -11.9 ppm attributable to 2-9, along with a number of other rhodium-coupled signals between 49 and 75 ppm. Efforts to isolate more of 2-10 from this reaction mixture were in vain. Moreover, all attempts to rationally prepare 2-10, either by using the synthetic methodology presented above or via the addition of 1.0 equiv of 2-4c-Li to a pre-formed mixture of 0.5 equiv of [CODRhCl]$_2$ and 1.0 equiv of nBuLi (see Scheme 2-8, Path A) were unsuccessful, and thus no spectroscopic characterization data for this highly unusual rhodium-indenyl complex is presented.

The structure of 2-10•C$_7$H$_8$ is presented as Figure 2-8, and is comprised of a dimeric pair of rhodium-substituted lithium indenide fragments that are related by a crystallographically imposed center of inversion. Each of the [CODRh] fragments in 2-10 is coordinated both to a pendant phosphine donor and to the C7 position within a single indenide ring. In turn, the lithium atoms serve to bridge the two halves of 2-10, bonding to the C5 unit of one indenide fragment and to the C7 carbon of the adjacent indenide unit. The Rh-P distance in 2-10 (2.3536(6) Å) is comparable to those found in the related phosphinoindene complexes 2-3, 2-5 and 2-6. In contrast, the P-C1 bond in 2-10 (1.765(3) Å) is contracted significantly relative to the related distances in 2-3, 2-5 and [2-6]$^+$BF$_4^-$, and is best compared to the P-C$_{indenide}$ bond in the zwitterionic complex, 2-7 (1.758(2) Å).
Scheme 2-8. Two Possible Mechanistic Routes to 2-10
**Figure 2-8.** The crystallographically determined structure of 2-10$\cdot$C$_7$H$_8$, shown with 40% displacement ellipsoids. Selected hydrogen atoms and the toluene solvate have been omitted for clarity. Selected interatomic distances (Å): Rh-P 2.3536(6); Rh-C7 2.093(3); Rh-C11 2.161(3); Rh-C12 2.198(3); Rh-C15 2.198(3); Rh-C16 2.233(3); P-C1 1.765(3); Li-C1 2.264(5); Li-C2 2.257(5); Li-C3 2.267(5); Li-C3a 2.306(5); Li-C7a 2.293(5); Li-C7B* 2.193(5); C1-C2 1.422(4); C2-C3 1.388(4); C3-C3a 1.420(4); C3a-C4 1.420(4); C4-C5 1.364(5); C5-C6 1.414(4); C6-C7 1.400(4); C7-C7a 1.424(4); C7a-C1 1.428(4) (*C7B is the position related to C7 via the crystallographic inversion center).

In an attempt to rationalize the formation of 2-10, two simplified mechanistic pathways (A and B) are tentatively proposed, which are outlined in Scheme 2-7; other equally viable routes to 2-10 could also be envisioned. One of the proposed mechanistic pathways (A) begins with the reaction of [CODRhCl]$_2$ with the excess nBuLi remaining after the formation of 2-4c-Li, presumably leading to (COD)Rh(nBu) upon loss of LiCl. A sequence of β-hydride elimination, C-H oxidative addition and H$_2$ reductive elimination steps could then produce 2-11.$^{19}$ Coordination of rhodium to the phosphine unit of 2-4c-Li, as in 2-12, followed by insertion into the C7-H bond would generate the Rh(III) intermediate, 2-13. Reductive elimination of 2-butene, followed by dimerization, then generates 2-10. An alternative mechanistic pathway (B) has [CODRhCl]$_2$ reacting
directly with 2-4c-Li at the C7 position, producing 2-14. Subsequent rearrangement to 2-15 re-establishes the aromaticity of the C6 ring, and reaction with the excess nBuLi present, followed by dimerization, produces 2-10.

2.4 Conclusions

Variants of the P,N-indene ligand can be prepared using facile synthetic procedures, as has been demonstrated from the experimental data presented in this chapter. Interestingly, the isomerization behavior of indenes bearing only one group 15 donor can differ significantly from indenes containing two adjacent group 15 substituents; whereas 1-diisopropylphosphinoindene is easily transformed into 3-diisopropylphosphinoindene, the introduction of a 2-dimethylamino substituent greatly inhibits this rearrangement process.

A modular and high-yielding strategy for the construction of new classes of cationic and zwitterionic Rh(I) complexes has been introduced; this methodology provides access to the first \([\kappa^2-P,N]Rh(I)\) zwitterion, 2-7, a unique complex that in later chapters will be presented as a viable catalyst for processes involving the breaking of Si-H or H-H fragments. The synthetic work reported in this chapter demonstrates that while a lithiated indene bearing adjacent diisopropylphosphino and dimethylamino substituents has been shown to form the unusual zwitterionic \(\kappa^2-(P,N\text{-indenide})\) complex of rhodium(I), removal of either of these group 15 fragments results in the formation of the corresponding pnictogen-substituted \(\eta^5\text{-indenyl}Rh(I)\) species, in which the pendant group 15 donor is apparently not involved in bonding to rhodium.
The confluence of hemilabile and zwitterionic characteristics brought about by this new ligand are anticipated to engender useful reactivity in a variety of late transition metal fragments, as will be discussed in Chapter 3 in the context of Ir(I) metal fragments. Other transition metal coordination chemistry of this ligand set is under exploration by other researchers in the group and falls outside the scope of this thesis.

2.5 Experimental Section

General Considerations. These descriptions are applicable to the following chapters as well. Any additions or changes will be noted in the General Considerations of the experimental section in those chapters. All manipulations were conducted in the absence of oxygen and water under an atmosphere of dinitrogen, either by using standard Schlenk methods, or within an mBraun or an Innovative Technologies glove-box apparatus,\textsuperscript{20} utilizing glassware that was oven-dried (130 °C) and evacuated while hot prior to use. Celite\textsuperscript{®} (Aldrich) was oven dried (130 °C) for 5 d and then evacuated for 24 h prior to use. Diethyl ether, pentane, and toluene were dried and deoxygenated by refluxing for a minimum of 24 h under a flow of dinitrogen, in the presence of sodium wire. THF and benzene were dried and deoxygenated by refluxing for a minimum of 24 h under a flow of dinitrogen, in the presence of potassium metal. Dichloromethane was dried by three cycles of 24 h each of stirring over CaH\textsubscript{2}, followed by P\textsubscript{2}O\textsubscript{5}, followed by CaH\textsubscript{2} again. Benzophenone was added to the solvent/drying agent mixture in order to provide visual confirmation (i.e. the observed persistence of the benzophenone ketyl) that an appropriate level of purification had been achieved. The solvents used within the glove box were stored over activated 3-Å molecular sieves. C\textsubscript{6}D\textsubscript{6} (Aldrich) was degassed by using three
repeated freeze-pump-thaw cycles and then dried over 3-Å molecular sieves for 24 h prior to use. CDCl₃ (Aldrich) was degassed by using three repeated freeze-pump-thaw cycles, dried over CaH₂ for 7 d, and distilled in vacuo. iPr₂PCl, Ph₂PCl, and nBuLi (1.6 M in hexanes) were obtained from Aldrich and were used as received, while [CODRhCl]₂ and [NBDRhCl]₂ were obtained from Strem and dried in vacuo for 24 h prior to use. Indene was obtained from Aldrich, degassed by using three repeated freeze-pump-thaw cycles and distilled under static vacuum prior to use. Alumina (Aldrich, neutral, 150 mesh, activity Brockmann II) was degassed and dehydrated in vacuo for 48 h at temperatures between 200-300 °C, and subsequently deactivated using 2% deionized water under argon prior to use. 2-Dimethylaminoindene (2-1) was prepared by using literature procedures,⁸ and was dried in vacuo for 24 h prior to use. All NMR data were collected at ambient temperature on a Bruker AC-250 spectrometer at 250.1 MHz, 62.9 MHz and 101.3 MHz, for ¹H, ¹³C and ³¹P, respectively, with chemical shifts reported in parts per million downfield of tetramethylsilane (for ¹H and ¹³C) or 85% H₃PO₄ in water (for ³¹P). In some cases, slightly fewer than expected independent ¹³C NMR resonances were observed, despite prolonged data acquisition times. Elemental analyses were performed by Desert Analytics, Tucson AZ.

**Synthesis of 1-diisopropylphosphino-2-dimethylaminoindene (2-2a).** To a Schlenk flask containing a magnetic stir bar was added 2-dimethylaminoindene (4.85 g, 30.5 mmol) and tetrahydrofuran (60 mL), producing a tan solution. The reaction flask was then sealed with a septum, cooled to –80 °C and magnetic stirring was initiated to facilitate the complete dissolution of the indene starting material. A hexanes solution of nBuLi (19.2 mL of a 1.6 M solution, 30.7 mmol) was then introduced to the cooled reaction flask via
syringe over 30 min; a chalky brown precipitate formed following the addition. The reaction mixture was allowed to warm to room temperature over the course of 1 h, yielding a clear dark orange solution. After stirring at room temperature for an additional 2 h, the reaction flask was again cooled to −80 °C and chlorodiisopropylphosphine (4.65 g, 30.5 mmol) was added to the reaction mixture over 5 min via syringe. The reaction mixture was allowed to warm to room temperature with continued stirring over a period of 15 h; the THF solvent and other volatile materials were then removed in vacuo, yielding a beige solid. Diethyl ether (80 mL) was then introduced to the reaction flask via cannula. After stirring for 5 min, the light brown diethyl ether solution was transferred away from the remaining solid material into a new Schlenk vessel via cannula filtration. Removal of the diethyl ether solution in vacuo yielded 2-2a as an analytically pure off-white, microcrystalline powder (7.82 g, 28.4 mmol, 93%). Anal. calcd. for C_{17}H_{26}N_1P_1 (275.37 g mol^{−1}) (%): C 74.15, H 9.52, N 5.09; found: C 73.96, H 9.58, N 5.06. \(^1\)H NMR (C\(_6\)D\(_6\)): δ 7.27-7.16 (m, 2H, Ar-Hs), 7.02-6.93 (m, 2H, Ar-Hs), 5.40 (s, 1H, C(3)-H), 3.78 (d, \(^3\)J\(_{PH}\) = 4.0 Hz, 1H, C(1)-H), 2.60 (s, 6H, NMe\(_2\)), 2.22 (m, 1H, P(CHMe\(_2\))), 1.44 (m, 1H, P(CHMe\(_2\))), 1.20 (d of d, \(^3\)J\(_{PH}\) = 12.5 Hz, \(^3\)J\(_{HH}\) = 7.0 Hz, 3H, P(CHMe\(_2\))), 1.03 (d of d, \(^3\)J\(_{PH}\) = 15.6 Hz, \(^3\)J\(_{HH}\) = 6.7 Hz, 3H, P(CHMe\(_2\))), 0.91 (d of d, \(^3\)J\(_{PH}\) = 17.1 Hz, \(^3\)J\(_{HH}\) = 7.3 Hz, 3H, P(CHMe\(_2\))), 0.59 (pseudo t, \(^3\)J = 7.6 Hz, 3H, P(CHMe\(_2\))); \(^{13}\)C\({}^1\)H NMR (C\(_6\)D\(_6\)): δ 161.1 (d, \(J_\text{PC} = 5\) Hz), 147.2, 140.2 (d, \(J_\text{PC} = 4\) Hz), 127.8, 123.3, 121.0, 118.9, 101.1 (d, \(J_\text{PC} = 38\) Hz), 45.9 (d, \(J_\text{PC} = 32\) Hz), 42.1 (d, \(J_\text{PC} = 6\) Hz), 24.2 (d, \(J_\text{PC} = 27\) Hz), 22.2–21.1 (4 overlapping signals), 19.3 (d, \(J_\text{PC} = 2\) Hz); \(^{31}\)P\({}^1\)H NMR (C\(_6\)D\(_6\)): δ 19.6. The general connectivity in 2-2a was also qualitatively confirmed on the basis of X-ray crystallographic data. However, the poor quality of the data and lack of suitable refinement (R ~ 22%) precludes an
indepth discussion of the derived metrical parameters: \( P2_1/c \ a = 6.934(1) \ \text{Å}, \ b = 15.736(3) \ \text{Å}, \ c = 29.501(6) \ \text{Å}, \ \beta = 91.63(4) \).

**Synthesis of 1-diphenylphosphino-2-dimethylaminoindene (2-2c).** Compound 2-2c was prepared on the basis of the literature preparation of 2-2a. To a Schlenk flask containing a magnetic stir bar was added 2-dimethylaminoindene (0.66 g, 4.17 mmol) and THF (20 mL). The flask was then sealed with a septum and cooled to -80 °C. Magnetic stirring was initiated and a hexanes solution of \( nBuLi \) (2.6 mL of a 1.6 M solution, 4.2 mmol) was added dropwise over 3 min via syringe, after which the reaction mixture was allowed to warm to room temperature over 3 h. Subsequently, the reaction flask was again cooled to -80 °C and chlorodiphenylphosphine (0.75 mL, 4.17 mmol) was added via syringe over 2 min. The resulting clear tan solution was allowed to warm to room temperature and was stirred for 15 h. The THF and other volatile materials were then removed *in vacuo*, and the residue was washed with diethyl ether (15 mL) and dried *in vacuo*, leaving a cream-colored solid. Treatment of this solid with toluene (15 mL) generated a pale yellow solution, which was transferred away from the remaining insoluble materials via cannula filtration. Removal of the toluene and any other volatile materials *in vacuo* yielded 2-2c (0.86 g, 2.52 mmol, 61%). Anal. calcd. for C_{23}H_{22}N_1P_1 (\%): C 80.44, H 6.46, N 4.08, found: C 80.51, H 6.60, N 3.99. \(^1\)H NMR (C\(_6\)D\(_6\)): \( \delta \) 7.42-7.37 (m, 2H, Ar-H's), 7.22-6.92 (m, 10H, Ar-H's), 6.71-6.69 (m, 2H, Ar-H's), 5.13 (s, 1H, C3-H), 4.26 (d, \(^2\)J\(_{PH} = 5.2 \text{ Hz}, 1H, C1-H), 2.56 (s, 6H, NMe\(_2\)); \(^{13}\)C{\(^1\)H} NMR (C\(_6\)D\(_6\)): \( \delta \) 148.1 (d, \( J_{PC} = 4.8 \text{ Hz, } sp^2\text{C}, 136.5 (sp^2\text{C}), 128.8 (sp^2\text{C}), 125.6 (d, \( J_{PC} = 23.4 \text{ Hz, } sp^2\text{C}), 122.2 (d, \( J_{PC} = 16.2 \text{ Hz, } sp^2\text{C}), 119.8 (sp^2\text{C}, 118.3 (d, \( J_{PC} = 4.3 \text{ Hz, } sp^2\text{C}), 117.8-117.4 \).
(sp$^2$C's), 116.9 (sp$^2$C), 112.8 (sp$^2$C), 110.3 (sp$^2$C), 107.8 (sp$^2$C), 91.4 (sp$^2$C), 38.1 (d, J$_{PC}$ = 29.1 Hz, Cl), 31.3 (d, J$_{PC}$ = 4.3 Hz, N(CH$_3$)$_2$); $^{31}$P{¹H} NMR (C$_6$D$_6$): δ 8.1.

**Isomerization of 2-2a to 2-2b.** Within the glovebox, a 0.02 g sample of 2-2a was dissolved in C$_6$D$_6$ (2 mL) within a glass vial equipped with a magnetic stir bar. The initial $^{31}$P NMR spectrum of this solution revealed only one signal at 19.6 ppm. To this solution was added alumina (2 g) and the vial was subsequently sealed with a PTFE-lined cap. After stirring the mixture for 2 h, a $^{31}$P NMR spectrum was obtained of the decanted yellow solution, which revealed two resonances at chemical shifts of 19.6 ppm (2-2a) and −2.9 ppm (tentatively assigned as 2-2b) in an approximate ratio of 3:1. The mixture was allowed to stir for two weeks with periodic monitoring by using $^{31}$P NMR spectroscopy; no further changes in the peak ratios were observed.

**Isomerization of 2-2c to 2-2d.** Using a protocol analogous to that described for the attempted isomerization of 2-2a, a freshly prepared sample of 2-2c (0.02 g) dissolved in C$_6$D$_6$ (2 mL) was stirred over alumina (2 g). After 2 h, a $^{31}$P NMR spectrum obtained from a decanted aliquot of the reaction mixture revealed two resonances at chemical shifts of 8.1 ppm (2-2c) and −24.8 ppm (2-2d) in an approximate ratio of 1:3. The mixture was allowed to stir for 72 h with periodic monitoring by using $^{31}$P NMR spectroscopy; no further changes in the peak ratios were observed. $^1$H NMR (C$_6$D$_6$) for 2-2d: δ 7.74−7.71 (m, 2H, Ar-H's), 7.21−6.91 (m, 10H, Ar-H's), 6.87−6.83 (m, 2H, Ar-H's), 3.09 (s, 2H, CH$_2$), 2.71 (s, 6H, NMe$_2$).

**Synthesis of (COD)RhCl(κ¹-P,N-2-2a) (2-3a).** A solution of 2-2a (0.348 g, 1.26 mmol) in CH$_2$Cl$_2$ (3 mL) was added via Pasteur pipette over 1 min to a glass vial containing a small magnetic stir bar and a light orange solution of [CODRhCl]$_2$ (0.312 g, 0.633 mmol)
in CH₂Cl₂ (3 mL). The vial was then sealed with a PTFE-lined cap and the resulting dark orange solution was magnetically stirred for 1 h. \(^{31}\text{P}\) NMR data collected on an aliquot of this crude reaction solution indicated the quantitative formation of 2-3a. The reaction mixture was then filtered through Celite and the CH₂Cl₂ solvent and other volatile materials were removed in vacuo, yielding 2-3a as an analytically pure bright yellow powder (0.633 g, 1.21 mmol, 96%). Anal. calcd. for C₅₂H₃₈N₇P₇Cl₁Rh₁ (521.91 gmol⁻¹) (%): C 57.53, H 7.34, N 2.68, found: C 57.18, H 7.22, N 2.39. \(^1\text{H}\) NMR (CDCl₃, 250.1 MHz): \(\delta\) 8.90 (d, \(^3\text{J}_{\text{HH}} = 7.3\) Hz, 1H, Ar-H), 7.20-7.04 (m, 3H, Ar-Hs), 5.78 (s, 1H, C₃-H), 5.47-5.34 (m, 3H, COD and C1-H), 3.74 (broad m, 2H, COD), 3.00 (m, 1H, P(CHMe₂)), 2.73 (s, 6H, NMe₂), 2.38 (m, 5H, COD and P(CHMe₂)), 1.96 (m, 4H, COD), 1.70 (d of d, \(^3\text{J}_{\text{PH}} = 15.8\) Hz, \(^3\text{J}_{\text{HH}} = 6.8\) Hz, 3H, P(CHMe₂)), 1.32 (d of d, \(^3\text{J}_{\text{PH}} = 14.1\) Hz, \(^3\text{J}_{\text{HH}} = 7.3\) Hz, 3H, P(CHMe₂)), 1.02 (d of d, \(^3\text{J}_{\text{PH}} = 11.5\) Hz, \(^3\text{J}_{\text{HH}} = 7.3\) Hz, 3H, P(CHMe₂)), 0.44 (d of d, \(^3\text{J}_{\text{PH}} = 13.7\) Hz, \(^3\text{J}_{\text{HH}} = 7.3\) Hz, 3H, P(CHMe₂)); \(^{13}\text{C} \{^{1}\text{H}\} \) NMR (CDCl₃, 62.9 MHz): \(\delta\) 161.7 (d, \(J = 9\) Hz, C2), 144.9 (d, \(J = 4\) Hz, C3a or C7a), 139.7 (C7a or C3a), 126.7, 126.5 (2Cs), 121.6 (C4, C5, C6, and C7), 118.3 (C3), 108.5 (COD), 101.0 (m, COD), 68.6 (m, COD), 43.8 (NMe₂), 43.2 (m, C1), 33.2 (COD), 33.1 (COD), 28.3 (COD), 28.2 (COD), 24.0 (m, PCHMe₂), 23.0 (d, \(J = 16\) Hz, PCHMe₂), 21.9 (d, \(J = 15\) Hz, PCHMe₂), 20.1 (PCHMe₂), 19.3 (PCHMe₂), 18.0 (m, PCHMe₂); \(^{31}\text{P} \{^{1}\text{H}\} \) NMR (CDCl₃, 101.3 MHz): \(\delta\) 48.2 (d, \(J_{\text{rhp}} = 144\) Hz). Crystals of 2-3a·C₆H₆ suitable for use in a single crystal X-ray diffraction experiment were grown from a concentrated benzene solution stored at 24 °C.

**Synthesis of [Cl(NBD)Rh(κ¹-(P,N)-2-2a)] (2-3b).** A protocol analogous to that described for 2-3a was used with 2-2a (0.076 g, 0.28 mmol) in CH₂Cl₂ (2 mL) and [NBDRhCl]₂ (0.064 g, 0.14 mmol) in CH₂Cl₂ (2 mL) to yield 2-3b as a bright yellow
powder (0.121 g, 0.24 mmol, 86%). Anal. calcd. for C_{24}H_{34}N_{1}P_{1}Cl_{1}Rh_{1} (505.87 g mol^{-1}) (%): C 56.98, H 6.77, N 2.77, found: C 56.05, H 6.50, N 2.53. ^1 H NMR (CDCl₃): δ 8.56 (d, J_{HH} = 7.9 Hz, 1H, Ar-H), 7.38-7.04 (m, 3H, Ar-Hs), 5.75 (s, 1H, C(3)-H), 4.97 (d, J_{HH} = 11.0 Hz, 1H, C(1)-H), 4.36 (m, 2H, vinyl C-Hs), 3.77 (m, 2H, vinyl C-Hs), 2.78 (s, 6H, NMe₂), 2.70 (m, 1H, P(CHMe₂)), 1.61 (m, 1H, P(CHMe₂)), 1.51-1.21 (m, 10H, aliphatic C-Hs), 1.10 (d of d, J_{PH} = 11.6 Hz, J_{HH} = 6.7 Hz, 3H, P(CHMe₂)), 0.59 (d of d, J_{PH} = 14.6 Hz, J_{HH} = 7.3 Hz, 3H, P(CHMe₂)); ^13 C{^1 H} NMR (CDCl₃): δ 161.6 (d, J = 8 Hz), 144.9 (d, J = 3 Hz), 139.2, 126.9, 125.8 (d, J = 5 Hz), 121.8, 118.4, 108.1 (d, J = 2 Hz), 63.6, 50.7, 43.9, 43.5 (d, J = 5 Hz), 23.2, 22.9, 22.6 (m), 22.5 (m), 19.1 (m), 18.1 (m); ^31 P{^1 H} NMR (CDCl₃): δ 50.2 (d, J_{RhP} = 168 Hz).

**Synthesis of 1-diisopropylphosphinoindene (2-4a).** To a Schlenk flask containing a magnetic stir bar was added indene (1.0 mL, 8.6 mmol) and diethyl ether (30 mL). The reaction flask was sealed with a septum and the mixture was cooled to -80 °C. Magnetic stirring was initiated and a hexanes solution of nBuLi (5.4 mL of a 1.6 M solution, 8.6 mmol) was added dropwise over 5 min via syringe after which the reaction mixture was allowed to warm to room temperature over 15 h. The clear yellow solution was subsequently cooled to -80 °C and Pr₂PCl (1.4 mL, 8.6 mmol) was added via syringe over 3 min. Immediately, a cream-colored precipitate formed from the yellow-brown reaction mixture. After 20 min, magnetic stirring was arrested and the reaction mixture allowed to warm to room temperature over 5 h. The pale yellow solution was then transferred away from the precipitated solid via cannula filtration and subsequently dried *in vacuo* to remove solvent and any other volatile materials, yielding 2-4a as a pale yellow oil (1.85 g, 7.97 mmol, 92%). Since compound 2-4a slowly rearranges to 2-4b on
standing, only elemental analysis data for 2-4b are provided (vide infra). $^1$H NMR (C$_6$D$_6$): δ 7.69 (d, $^3$J$_{HH}$ = 7.0 Hz, 1H, C4-H or C7-H), 7.30-7.05 (m, 3H, C5-H, C6-H, and either C7-H or C4-H), 6.71 (m, 1H, C2-H or C3-H), 6.48 (m, 1H, C3-H or C2-H), 3.71 (m, 1H, C1-H), 1.76 (m, 1H, P(CHMe$_2$)), 1.46 (m, 1H, P(CHMe$_2$)), 1.03-0.98 (m, 6H, P(CHMe$_2$)), 0.78 (d of d, $^2$J$_{PH}$ = 11.9 Hz, $^3$J$_{HH}$ = 7.0 Hz, 3H, P(CHMe$_2$)), 0.58 (d of d, $^2$J$_{PH}$ = 14.0 Hz, $^3$J$_{HH}$ = 7.0 Hz, 3H, P(CHMe$_2$)); $^{13}$C{ $^1$H} NMR (C$_6$D$_6$): δ 147.2 (d, $^1$J$_{PC}$ = 8.6 Hz, C3a or C7a), 144.6 (d, $^1$J$_{PC}$ = 1.9 Hz, C7a or C3a), 137.1 (sp$^2$C-H), 131.2 (sp$^2$C-H), 126.8 (sp$^2$C-H), 125.3 (sp$^2$C-H), 124.7 (d, $^1$J$_{PC}$ = 7.6 Hz, sp$^2$C-H), 121.9 (sp$^2$C-H), 47.0 (d, $^1$J$_{PC}$ = 28.6 Hz, C1), 23.5 (d, $^1$J$_{PC}$ = 17.6 Hz, P(CHMe$_2$)), 22.6 (d, $^1$J$_{PC}$ = 18.6 Hz, P(CHMe$_2$)), 21.6 (d, $^2$J$_{PC}$ = 4.8 Hz, P(CHMe$_2$)), 21.3 (d, $^2$J$_{PC}$ = 5.3 Hz, P(CHMe$_2$)), 20.9 (d, $^2$J$_{PC}$ = 12.9 Hz, P(CHMe$_2$)), 20.7 (d, $^2$J$_{PC}$ = 9.5 Hz, P(CHMe$_2$)); $^{31}$P{ $^1$H} NMR (C$_6$D$_6$): δ 17.3.

**Synthesis of 3-diisopropylphosphinoindene (2-4b).** Within the glovebox, a freshly prepared solution of 2-4a (1.99 g, 8.60 mmol) in diethyl ether (30 mL) was passed down an alumina column (2 cm × 4 cm). The eluted yellow solution was dried in vacuo to remove the solvent and any other volatile materials, yielding 2-4b as a yellow oil (1.52 g, 6.53 mmol, 76%). Anal. calcd. for C$_{13}$H$_{21}$P$_1$: C 77.56, H 9.11, found: C 77.54, H 9.08. $^1$H NMR (C$_6$D$_6$): δ 7.82 (d, $^3$J$_{HH}$ = 7.6 Hz, 1H, C7-H or C4-H), 7.29-7.07 (m, 3H; C5-H, C6-H, and either C4-H or C7-H), 6.42 (m, 1H, C2-H), 3.10 (s, 2H, CH$_2$), 2.01 (d of septets, $^2$J$_{PH}$ = 2.1 Hz, $^3$J$_{HH}$ = 6.9 Hz, 2H, P(CHMe$_2$))$_2$), 1.08 (d of d, $^2$J$_{PH}$ = 14.7 Hz, $^3$J$_{HH}$ = 7.0 Hz, 6H, P(CHMe$_2$Me$_2$)$_2$); $^{13}$C{ $^1$H} NMR (C$_6$D$_6$): δ 148.7 (d, $^1$J$_{PC}$ = 18.6 Hz, quaternary), 144.6 (d, $^1$J$_{PC}$ = 3.8 Hz, quaternary), 141.8 (d, $^1$J$_{PC}$ = 5.7 Hz, sp$^2$C-H), 140.5 (d, $^1$J$_{PC}$ = 23.4 Hz, quaternary), 126.9 (sp$^2$C-H), 125.5 (sp$^2$C-H), 124.3 (sp$^2$C-H), 122.3 (d, $^1$J$_{PC}$ = 6.7 Hz, sp$^2$C-H), 40.3 (d,
$^{3}J_{\text{PC}} = 3.8$ Hz, CH$_2$), 23.3 (d, $J_{\text{PC}} = 11$ Hz, P(CHMe$_2$)), 21.0 (d, $J_{\text{PC}} = 17.6$ Hz, P(CHMe$_2$)), 19.9 (d, $J_{\text{PC}} = 10.0$ Hz, P(CHMe$_2$)); $^{31}$P{¹H} NMR (C$_6$D$_6$): δ -10.2.

**Synthesis of [Cl(COD)Rh(c^1-P-2-4b)] (2-5).** To a glass vial charged with a magnetic stir bar, 2-4b (0.038 g, 0.16 mmol) was dissolved in toluene (3 mL). In a separate glass vial, [CODRhCl]$_2$ (0.040 g, 0.08 mmol) was slurred in toluene (2 mL) and transferred via Pasteur pipette to the stirring solution of 2-4b, resulting in a clear yellow-orange solution. The reaction vial was then sealed with a PTFE-lined cap. After 10 min, a yellow solid formed. The reaction mixture was then stirred for an additional 1.5 h after which the supernatant was transferred away from the precipitated yellow solid via Pasteur pipette. By slightly concentrating the supernatant *in vacuo*, further yellow solid precipitated, which was isolated and combined with the original solid fraction. The combined solids were then dried *in vacuo* to remove the remaining solvent and any other volatile materials, yielding 2-5 (0.062 g, 0.13 mmol, 79%). Anal. calcd. for C$_{23}$H$_{33}$P$_1$Cl$_1$Rh$_1$ (%): C 57.69, H 6.95, found: C 57.45, H 7.00. $^{1}$H NMR (C$_6$D$_6$): δ 8.34 (d, $^{3}$J$_{HH} = 7.6$ Hz, 1H, C7-H or C4-H), 7.27-7.08 (m, 3H, C5-H, C6-H, and either C4-H or C7-H), 6.16 (m, 1H, C2-H), 5.77 (s, 2H, vinyl-CH$_2$), 3.46 (s, 2H, vinyl-CH$_2$), 2.96 (s, 2H, C1-H’s), 2.58 (m, 2H, P(CHMe$_3$Me$_2$)$_2$), 2.10 (d, $^{3}$J$_{HH} = 7.6$ Hz, 2H, CH$_2$CH$_2$), 1.56-1.68 (m, 4H, CH$_2$CH$_2$), 1.49 (d of d, $^{3}$J$_{PH} = 15.8$ Hz, $^{3}$J$_{HH} = 7.0$ Hz, 6H, P(CHMe$_3$Me$_2$)$_2$), 1.34 (m, 2H, CH$_2$CH$_2$), 1.06 (d of d, $^{3}$J$_{PH} = 13.7$ Hz, $^{3}$J$_{HH} = 6.7$ Hz, 6H, P(CHMe$_3$Me$_2$)$_2$); $^{13}$C{¹H} NMR (C$_6$D$_6$): δ 142.9 (sp$^2$C-H), 126.3 (sp$^2$C-H), 125.9 (sp$^2$C-H), 125.2 (sp$^2$C-H), 124.2 (sp$^2$C-H), 103.9 (d of d, $^{1}$J$_{RC}$ = 12.4 Hz, $^{2}$J$_{PC} = 7.2$ Hz, COD-vinyl-C’s), 71.0 (d, $^{1}$J$_{RC}$ = 13.3 Hz, COD-vinyl-C”s), 40.2 (d, $^{3}$J$_{PC} = 6.7$ Hz, C1), 33.5 (d, $J_{PC} = 2.9$ Hz, P(CHMe$_2$)), 24.5 (d, $J_{PC}$
= 23.8 Hz, P(CHMe₂), 21.1 (d, JPC = 3.8 Hz, P(CHMe₂)), 29.1 (s, COD-CH₂), 19.5 (s, COD-CH₂); 31P{1H} NMR (C₆D₆): δ 25.7 (d, 1JRP = 152 Hz).

**Synthesis of [(COD)Rh(κ²-(P,N)-2-2b)]⁺BF₄⁻ ([2-6a]⁺BF₄⁻).** Within the glovebox, a solution of freshly prepared 2-2a (0.20 g, 0.72 mmol) in THF (2 mL) was added to a glass vial containing a small magnetic stir bar and a light orange solution of [CODRhCl]₂ (0.18 g, 0.36 mmol) in THF (2 mL). The addition was carried out by use of a Pasteur pipette and was completed in 1 min, yielding a dark orange solution. The vial was then sealed with a PTFE-lined cap and the solution was magnetically stirred for 5 min. The cap was then removed and a solution of AgBF₄ (0.14 g, 0.72 mmol) in THF (2 mL) was added to the reaction mixture over 1 min by use of a Pasteur pipette; a precipitate formed immediately. The vial was again sealed with the PTFE-lined cap and the reaction mixture magnetically stirred for 1 h. 31P NMR data collected on an aliquot of this crude reaction mixture indicated the quantitative formation of [2-6a]⁺BF₄⁻. The reaction mixture was then filtered through Celite and the THF solvent and other volatile materials were removed in vacuo, yielding pure [2-6a]⁺BF₄⁻ as a bright orange powder (0.39 g, 0.68 mmol, 94%). Anal. calcd. for C₂₅H₃₈N₁P₂B₁F₄Rh₁ (573.27 gmol⁻¹) (%): C 52.38, H 6.68, N 2.44, found: C 51.70, H 6.66, N 2.40. ¹H NMR (CDCl₃): δ 7.47-7.16 (m, 4H, Ar-Hs), 5.16 (br m, 2H, vinyl C-Hs), 4.39 (br m, 2H, vinyl C-Hs), 3.74 (s, 2H, C(1)H₂), 3.06 (s, 6H, NMe₂), 2.79 (m, 2H, P(CHMe₂)₂), 2.49 (m, 4H, aliphatic C-Hs), 2.13 (m, 4H, aliphatic C-Hs), 1.39 (d of d, 3JP = 17.1 Hz, 3JHH = 7.3 Hz, 6H, P(CHMe₄Me₆)₂), 1.28 (d of d, 3JP = 15.9 Hz, 3JHH = 6.7 Hz, 6H, P(CHMe₆Me₆)₂); ¹³C{¹H} NMR (CDCl₃): δ 178.1 (d, J = 18 Hz), 143.4 (d, J = 6 Hz), 137.6, 127.9 (d, J = 28 Hz), 127.1, 126.8, 125.5, 122.7, 106.0 (m), 73.0 (d, J = 13 Hz), 51.3, 32.2, 31.4 (d, J = 10 Hz), 28.1, 24.8 (d,
$J = 23$ Hz), 19.6, 18.6 (d, $J = 4$ Hz); $^{31}$P ($^1$H) NMR (CDCl$_3$): δ 43.3 (d, $^1$J$_{RHP}$, 150 Hz).

Crystals suitable for single crystal X-ray diffraction analysis were obtained from a concentrated THF solution of [2-6a]$^+$BF$_4^-$ at room temperature.

**Synthesis of [(NBD)Rh($\kappa^2$-($P,N$)-2-2b)]$^+$BF$_4^-$ ([2-6b]$^+$BF$_4^-$).** A protocol analogous to that described for [2-6a]$^+$BF$_4^-$ was used with 2-2a (0.067 g, 0.24 mmol), [NBD]RhCl$_2$ (0.056 g, 0.12 mmol), and AgBF$_4$ (0.047 g, 0.24 mmol) to yield [2-6b]$^+$BF$_4^-$ as a bright orange powder (0.12 g, 0.21 mmol, 87%). Anal. calcd. for C$_{24}$H$_{34}$N$_1$P$_1$B$_1$F$_4$Rh$_1$ (557.22 g/mol) (%): C 51.76, H 6.15, N 2.51, found: C 52.05, H 6.40, N 2.24. $^1$H NMR (CDCl$_3$): δ 7.37 (m, 1H, Ar-H), 7.26-7.18 (m, 3H, Ar-Hs), 4.87 (m, 2H, vinyl C-Hs), 4.05 (m, 2H, vinyl C-Hs), 3.58 (s, 2H, C(1)H$_2$), 2.86 (s, 6H, NMe$_2$), 2.49 (m, 2H, P(CHMe$_2$)$_2$), 1.59 (s, 2H, aliphatic C-Hs), 1.30-1.15 (m, 14H, aliphatic C-Hs); $^{13}$C ($^1$H) NMR (CDCl$_3$): δ 177.8 (d, $J = 19$ Hz), 143.9 (d, $J = 6$ Hz), 138.1, 130.6 (d, $J = 27$ Hz), 127.3, 127.0, 125.8, 122.6, 68.1, 67.4 (d, $J = 6$ Hz), 53.7, 50.7, 31.1 (d, $J = 9$ Hz), 29.9, 25.8, 24.4 (d, $J = 23$ Hz), 19.9, 19.4 (d, $J = 6$ Hz); $^{31}$P ($^1$H) NMR (CDCl$_3$): δ 45.0 (d, $^1$J$_{RHP}$, 168 Hz). Crystals of [2-6b]$^+$BF$_4^-\cdot$C$_4$H$_8$O suitable for use in a single crystal X-ray diffraction experiment were grown from a concentrated THF solution stored at −30 °C.

**Synthesis of (COD)Rh($\kappa^2$-$P,N$)-2-2e) (2-7), Method A.** Within the glovebox, solid NaN$_2$S$_2$ (0.033 g, 0.18 mmol) was added all at once to a glass vial containing a magnetically stirred solution of freshly prepared [2-6a]$^+$BF$_4^-$ (0.10 g, 0.18 mmol) suspended in toluene (4 mL). A deep orange-red solution, along with some insoluble material, formed immediately upon addition. The vial was then sealed with a PTFE-lined cap and the solution was magnetically stirred for 1 h. $^{31}$P NMR data collected on an aliquot of this crude reaction mixture indicated the quantitative formation of 2-7. The
reaction mixture was then concentrated *in vacuo* to approximately 2 mL, filtered through Celite and stored at -30 °C in order to induce crystallization. After 24 h, crystals of 2-7 were isolated by transferring the supernatant solution to a new glass vial by using a Pasteur pipette; this solution was then concentrated *in vacuo* and stored at -30 °C to induce further crystallization. After repeating this procedure, the isolated crops of crystals were then combined and dried *in vacuo*, yielding 2-7 as an analytically pure orange-red microcrystalline solid (0.079 g, 0.16 mmol, 90%). **Method B.** Within the glovebox a mixture of [CODRhCl]₂ (0.044 g, 0.090 mmol) in toluene (3 mL) was transferred dropwise via Pasteur pipette to a glass vial containing a magnetically stirred slurry of 2-2e-Li²¹ (0.050 g, 0.18 mmol) suspended in toluene (3 mL). The reaction mixture immediately turned deep orange-red, accompanied by the formation of a fine precipitate. The vial was then sealed with a PTFE-lined cap and the solution was magnetically stirred for 45 min, after which time ³¹P NMR data collected on an aliquot of the crude reaction mixture indicated the quantitative formation of 2-7. The reaction mixture was then filtered through Celite, concentrated *in vacuo* and crystallized using the techniques described for Method A. Anal. calcd. for C₂₅H₂₅N₁P₁Rh₁ (485.45 gmol⁻¹) (%): C 61.85, H 7.68, N 2.89, found: C 61.68, H 7.62, N 2.76. ¹H NMR (C₆D₆): δ 7.97 (m, 1H, Ar-H), 7.75 (m, 1H, Ar-H), 7.32 (m, 2H, Ar-Hs), 6.31 (d, J = 3.7 Hz, 1H, C(1)-H), 4.23 (m, 2H, vinyl C-Hs), 3.95 (m, 2H, vinyl C-Hs), 2.66 (s, 6H, NMe₂), 2.48 (m, 2H, P(CHMe₂)₂), 2.09-1.45 (m, 8H, aliphatic C-Hs), 1.17 (d of d, ³Jₚₚ = 14.6 Hz, ³Jₜₜ = 7.3 Hz, 6H, P(CHMe₆Me₆)₂), 1.05 (d of d, ³Jₚₚ = 15.9 Hz, ³Jₜₜ = 7.3 Hz, 6H, P(CHMe₆Me₆)₂); ¹³C (¹H) NMR (C₆D₆): δ 181.1 (d, J = 10 Hz), 163.1 (m), 138.8 (m), 121.1, 120.0, 116.9, 116.6, 99.8 (m), 87.4 (d, J = 12 Hz), 69.1 (d, J = 13 Hz), 54.2, 32.6 (m), 28.3, 26.4 (d, J =
26 Hz), 19.7, 19.5 (d, J = 4 Hz); $^{31}$P{\(^1\)H} NMR (C\(_6\)D\(_6\)): δ 33.2 (d, $^{1}$J\(_{RHP}\), 145 Hz). Slow evaporation of a C\(_6\)H\(_6\) solution of 2-7 within the glovebox produced crystals suitable for single crystal X-ray diffraction analysis.

**Synthesis of [CODRh(η\(^5\)-2-1)] (2-8).** To a Schlenk flask containing a magnetic stir bar was added 2-1 (0.11 g, 0.67 mmol) and diethyl ether (10 mL), producing a light tan solution. The flask was then sealed with a septum and cooled to 0 °C. A hexanes solution of nBuLi (0.42 mL of a 1.6 M solution, 0.67 mmol) was added to the stirring solution over 5 min. The reaction flask was then allowed to warm to room temperature over 2 h, during which time a white solid precipitated. The flask was transferred to the glove box, and a slurry of [CODRhCl]\(_2\) (0.17 g, 0.34 mmol) in diethyl ether (4 mL) was added via Pasteur pipette. Immediately, a dark brown-red solution formed along with what appeared to be a fresh white precipitate. The reaction was stirred for 1 h followed by filtration through Celite. Fine brown fibers of 2-8 readily precipitated from the solution, which were isolated by transferring the supernatant away with a Pasteur pipette, and drying *in vacuo* to remove any remaining solvent and other volatile materials (0.13 g, 0.36 mmol, 53 %). Anal. calcd. for C\(_{19}\)H\(_{24}\)N\(_1\)Rh\(_1\) (%): C 61.79, H 6.55, N 3.79, found: C 60.43, H 6.50, N 3.61; repeat analyses consistently yielded low %C values. $^{1}$H NMR (CDCl\(_3\)): δ 7.30-7.21 (m, 4H, C4-H, C5-H, C6-H, and C7-H), 5.05 (s, 2H, C1-H and C3-H), 4.29 (s, 4H, vinyl-CH saga), 2.97 (s, 6H, N(CH\(_3\))\(_2\)), 2.18-1.97 (m, 8H, (CH\(_2\)CH\(_2\)CHCH\(_2\))\(_2\)), $^{13}$C{\(^1\)H} NMR (CDCl\(_3\)): δ 121.6 (C4 and C7 or C5 and C6), 118.0 (C5 and C6 or C4 and C7), 67.7 (d, $^{1}$J\(_{RHC}\) = 13.3 Hz, vinyl-C’s), 64.8 (d, $^{1}$J\(_{RHC}\) = 4.8 Hz, C1 and C3), 42.7 (N(CH\(_3\))\(_2\)), 31.8 ((CH\(_2\)CH\(_2\)CHCH\(_2\))\(_2\)).
Synthesis of [(COD)Rh(η⁵-2-4b)] (2-9). Within the glovebox, a hexanes solution of nBuLi (0.10 mL of a 1.6M solution, 0.16 mmol) was added to a stirring solution of 2-4b (0.037 g, 0.16 mmol) in diethyl ether (2 mL) and the vial was sealed with a PFTE-lined cap. A ³¹P NMR spectrum taken of this yellow reaction solution revealed the presence of 2-4e-Li as the only phosphorus-containing product.²¹ After 2 h, a slurry of [CODRhCl]₂ (0.040 g, 0.08 mmol) in diethyl ether (2 mL) was added to the reaction mixture via Pasteur pipette, whereupon the solution turned dark orange with the formation of a precipitate. After stirring for 16 h, the reaction mixture was filtered through Celite.³¹P NMR analysis of the clear brown-green filtrate revealed the presence of a single new phosphorus-containing product. Solvent and other volatile materials were then removed in vacuo, the resulting dark green greasy solid was washed once with pentane (1 mL), and the product (2-9) dried in vacuo (0.064 g, 0.14 mmol, 88%). Anal. calcd. for C₂₃H₃₂P₁Rh₁ (%): C 62.45, H 7.29, found: C 62.12, H 7.27.¹H NMR (C₆D₆): δ 7.45 (d, ³J_HH = 7.6 Hz, 1H, C4-H or C7-H), 7.28 (d, ³J_HH = 7.6 Hz, 1H, C7-H or C4-H), 7.08-6.96 (m, 2H, C5-H and C6-H), 5.77 (m, 1H, C2-H or C3-H), 4.77 (d, J = 2.4 Hz, 1H, C3-H or C2-H), 3.98 (m, 2H, vinyl-CH₃), 3.75 (m, 2H, vinyl-CH₃), 2.23 (m, 1H, P(CHMe₂)), 2.12-1.27 (m, 12H, P(CHMeMe) and (CH₂CH₂CHCH₂)₂), 1.15 (d of d, ³J_HH = 7.0 Hz, ³J_PH = 12.8 Hz, 3H, P(CHMeMe)), 0.90 (d of d, ³J_HH = 7.0 Hz, ³J_PH = 10.1 Hz, 3H, P(CHMeMe));¹³C{¹H} NMR (C₆D₆): δ 123.6 (sp²C-H), 122.2 (sp²C-H), 121.1 (sp²C-H), 120.3 (d, J = 5.7 Hz, sp²C-H), 96.3 (t, J = 4.3 Hz, sp²C-H), 76.5 (d, J = 4.3 Hz, sp²C-H), 70.6 (d, J_RHC = 13.8 Hz, vinyl-CH₃), 70.0 (d of d, J_PC = 4.3 Hz, J_RHC = 13.8 Hz, vinyl-CH₃), 32.2 ((CH₂CH₂CHCH₂)₂), 31.5 ((CH₂CH₂CHCH₂)₂), 25.9 (d, ¹J_PC = 16.2 Hz, P(CHMe₂)), 23.0
(d, $^1J_{PC} = 17.6$ Hz, P(CHMe$_2$)), 22.9 (d, $^2J_{PC} = 11.4$ Hz, P(CHMe$_2$)), 21.1 (d, $^2J_{PC} = 9.5$ Hz, P(CHMe$_2$)), 20.9 (d, $^2J_{PC} = 11.4$ Hz, P(CHMe$_2$)), 19.5 (d, $^2J_{PC} = 7.2$ Hz, P(CHMe$_2$));

$^{31}$P{$^1$H} NMR (CD$_6$D$_6$): $\delta$ -11.8.

**Formation of 2-10.** In a Schlenk flask equipped with a magnetic stir bar, 2-4b (0.12 g, 0.54 mmol) was dissolved in diethyl ether (10 mL) within the glove box. The reaction flask was sealed with a septum and transferred to the Schlenk line. The flask was then cooled to 0 °C and magnetic stirring was initiated. A hexanes solution of nBuLi (0.86 mL of a 1.6 M solution, 1.4 mmol) was subsequently added to the flask over 2 min via syringe and the yellow solution was then left to stir for 2 h as it warmed to room temperature. A $^{31}$P NMR spectrum taken of an aliquot of this yellow solution confirmed the clean formation of 2-4c-Li. The reaction flask was then taken back into the glovebox and a slurry of [CODRhCl]$_2$ (0.13 g, 0.26 mmol) in toluene (4 mL) was added via Pasteur pipette. Immediately, the reaction turned dark red-brown and a lightly colored precipitate formed. After 1 h, $^{31}$P NMR analysis of the reaction solution revealed the formation of 2-9 (δ -11.8) as the major product. The reaction mixture was then concentrated in vacuo and filtered through Celite into a glass vial. The vial was then sealed with a PFTE-lined cap and stored at -30 °C. Initially, no crystalline material was produced. However, after 3 months a minute quantity of red crystals was isolated by transferring the supernatant away via Pasteur pipette into a separate glass vial. Single-crystal X-ray analysis of the isolated crystals revealed their identity to be 2-10. A subsequent $^{31}$P NMR analysis of the supernatant from which the crystals had grown revealed a sharp singlet at δ -11.8 (attributable to 2-9) but also many new rhodium coupled products in the range δ 75.9 to 48.9. Satisfactory NMR data for the isolated crystals of 2-
could not be obtained, and no further material was isolated from this reaction mixture in pure form.

**Crystallographic Solution and Refinement Details.** X-Ray crystallographic data for 2-2d, 2-3•C₆H₆, 2-5, [2-6a⁺]BF₄⁻, [2-6b⁺]BF₄⁻, 2-7 and 2-10•C₇H₈ were collected on a Bruker PLATFORM/SMART 1000 CCD instrument at 193(2) K, using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å), employing samples that were mounted in inert oil and transferred to a cold gas stream on the diffractometer. Programs for diffractometer operation, data collection, data reduction and absorption correction were those supplied by Bruker. The structures were solved by use of direct methods (except for 2-7 where a Patterson search/structure expansion was employed), and refined by use of full-matrix least-squares procedures (on F²) with R₁ based on F₀² ≥ 2σ(F₀²) and wR₂ based on F₀² ≥ −3σ(F₀²). Structural refinement was carried out by using full-matrix least squares methods on F² with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were added at calculated positions and refined using a riding model. Complete experimental details for these compounds are available through the Cambridge Crystallographic Database. Select crystallographic data are provided in Table 2-1.
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Table 2-1 Continued. Crystallographic Data for [2-6b]⁺BF₄⁻, 2-7, and 2-10·C₇H₈

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<td>1.083</td>
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2.6 References and Endnotes


11. Mean deviation from the plane defined by C1, C2, C3, C3a, C4, C5, C6, C7, C7a, C8, C9, N and P in 2-2d is less than 0.05 Å. Within error, the sum of the angles around N in 2-2d is 360 degrees.

12. Whereas the pKₘ of the benzylic protons on indene itself is 20.1, the incorporation of a 2-(cyclo-C₄H₈N) substituent causes the pKₘ of the benzylic protons to rise to 24.5, see: Bordwell, F. G.; Satish, A.V. J. Am. Chem. Soc. 1992, 114, 10173.


21. Lithium salts of phosphinoindenes have been found to be rather unstable in the solid state. As such, the preparation of 2-2e-Li is carried out in situ by treating a solution of 2-2a with nBuLi. The single phosphorus resonance in the ³¹P NMR spectrum (δ = -9.6) of the resulting solution is attributed to 2-2e-Li. Similarly, the preparation of 2-4c-Li is carried out in a similar manner, with the single phosphorus resonance in the ³¹P NMR spectrum (δ = -8.9) of the resulting solution attributed to 2-4c-Li.
3.1 Introduction

Building on seminal investigations by Schrock and Osborn,¹ and later by Crabtree,² the development of cationic square-planar complexes of the heavier group 9 metals has emerged as an important theme in modern organometallic chemistry research, since such species are among the most active and widely used classes of homogeneous catalysts for the addition of E-H bonds (E = main group element) to unsaturated substrates, as discussed in Chapter 1.³ The groundbreaking work of Knowles⁴ and more recent discoveries by Pfaltz⁵ demonstrate that the rational development of such catalysts can enable significant breakthroughs in metal-mediated synthesis. However, the range of experimental conditions under which such cationic group 9 species can be employed is limited, since these catalysts commonly exhibit poor solubility in low-polarity media, and can be rendered inactive in strongly coordinating solvents.⁶ Furthermore, the systematic design of cationic catalysts is complicated by the fact that the choice of accompanying outer-sphere counteranion in such discrete salts can influence catalytic performance (i.e. activity, selectivity, lifetime, etc.), with some of the most effective counteranions (e.g. tetrakis(3,5-(trifluoromethyl)phenyl)borate, BAřF⁻) being costly to obtain from commercial sources and/or hazardous to prepare.⁷ In principle, the use of less polar neutral catalyst complexes represents a way in which to circumvent the aforementioned drawbacks associated with cationic species; however, neutral group 9 catalysts can be less
active than their cationic relatives. This trend is particularly evident in the case of Ir(I) alkene hydrogenation catalysts; while Crabtree’s catalyst ([(COD)Ir(PCy₃)(Py)]⁺PF₆⁻, 1-10 introduced initially in Chapter 1)² is capable of hydrogenating a much wider range of alkene substrates than can be reduced by use of Wilkinson’s catalyst ((PPh₃)₂RhCl, 1-1),⁸ the related neutral Ir(I) complex (PPh₃)₂IrCl is inactive for alkene hydrogenation.⁹

Zwitterionic group 9 complexes that feature formal charge separation between a cationic metal fragment and an associated anionic ancillary ligand represent appealing candidates for catalytic studies, since such species espouse the desirable traits of both discrete salts and traditional neutral complexes in offering a formally cationic metal fragment within an overall neutral molecular framework.¹⁰ However, given the challenges associated with the construction of such charge-separated species, formally zwitterionic group 9 complexes are much less common than their cationic relatives. The first zwitterionic Rh(I) complexes to be explored in catalytic applications were those supported by η⁶-coordinated tetraphenylborate and related ligands,¹¹ as discussed in Section 1.5.2. While such zwitterions have proven capable of mediating a wide range of substrate transformations involving E-H and/or E-E bond activation under mild conditions and with a high degree of selectivity,¹¹ it has been shown that these complexes can be transformed into conventional cationic [L₄Rh]⁺BPh₄⁻ species upon substitution of the η⁶-boratoarene ligand by more strongly coordinating Lewis bases.¹² Other classes of Rh(I) zwitterions featuring homobidentate or homotridentate anionic ancillary ligands on the basis of either P or N donors have also emerged, including those in which the anionic charge carrier is a substituted carborane,¹³ sulfate,¹⁴ or borate¹⁵ fragment. Notably, Betley and Peters¹⁵b,c have demonstrated that zwitterionic square-planar Rh(I) complexes
featuring either $\kappa^2$-[Ph$_2$B(CH$_2$PR$_2$)$_2$] or $\kappa^2$-[Ph$_2$B(CH$_2$NR$_2$)$_2$]$^-$ ancillary ligands are active catalysts for various E-H bond additions to alkenes in the presence of both high and low polarity solvents, as discussed in Section 1.5.2. However, a more recent report by Tilley and co-workers$^{15}$ highlights that this general class of zwitterions are also susceptible to decomposition by way of B-C bond cleavage to yield non-zwitterionic bis(phosphino)borane Rh(I) derivatives.$^{16}$ By comparison, zwitterionic complexes featuring formally cationic Ir centers are much less common than their Rh relatives, and while the synthetic utility of cationic Ir(I) catalysts such as 1-10 is well-established, the reactivity properties of related Ir(I) zwitterions have not been explored systematically.$^{15,17}$

In Chapter 2, synthetic routes to an entirely new zwitterionic Rh(I) complex derived from a donor-substituted indene was established. In contrast to the facial ($\eta^5$) binding of metal fragments that is commonly observed in indenyl rhodium chemistry,$^{18,19}$ this unusual zwitterion can be viewed as comprising a formally cationic metal fragment whose charge is counterbalanced by a sequestered, uncoordinated 10π-electron indenide unit that is built into the backbone of a bidentate ancillary ligand.$^{20}$ In light of the superior catalytic properties commonly exhibited by platinum-group metal complexes featuring $\kappa^2$-P,N ancillary ligands compared to analogous P,P or N,N species,$^{2,21}$ and given the general lack of heterobidentate group 9 zwitterions, studying the catalytic utility of this Rh(I) and related Ir(I) complexes of P,N-substituted indenides has been identified as a particularly important target. The ligand 1-P$_2$P$_2$-2-NMe$_2$-inden (2-2a) and related derivatives can be prepared easily in a high yielding and modular fashion via condensation of the commercially available reagents 2-indanone and HNR$_2$, followed by
deprotonation of the ensuing 2-aminoindene and finally quenching with a chlorophosphine (eq 2-1). While in solution the first-formed allylic indene 2-2a evolves slowly to an equilibrium mixture of 2-2a and the vinylic isomer 2-2b, both are readily deprotonated to afford cleanly the desired P,N-indenide 2-2e, which has proven to be an effective ancillary ligand for supporting a $\kappa^2$-P,N zwitterionic Rh complex, as discussed in Chapter 2.

In light of the relatively simple and high-yielding preparative route to the Rh(I) zwitterion bound by 2-2e that was discussed in Chapter 2, the development of an analogous Ir(I) zwitterion was one target of the research presented in this chapter. As well, a more extensive synthetic investigation of a series of isostructural Rh(I) and Ir(I) cations supported by 2-2a and 2-2b (in addition to the $[\kappa^2$-(P,N-2-2b)RhCOD]$^+$BF$_4^-$ cation introduced in Chapter 2), was conducted. In an effort to assess the extent to which these group 9 zwitterions supported by $\kappa^2$-P,N-2-2e compare with more conventional square-planar Rh(I) and Ir(I) cationic complexes, a series of structural and reactivity studies have been carried out in which cations supported by $\kappa^2$-P,N-2-2b have been compared with formally zwitterionic relatives that feature the anionic ligand, $\kappa^2$-P,N-2-2e. The interrogation of such structurally related complexes has afforded an opportunity to evaluate changes in the electronic characteristics of a formally cationic group 9 metal center on going from cationic complexes featuring $\kappa^2$-P,N-2-2b ligation, to isosteric neutral and formally zwitterionic species incorporating $\kappa^2$-P,N-2-2e. The hydrogenation and hydrosilylation of alkenes were exploited as representative E-H bond addition reactions to initially outline the potential synthetic utility of these new group 9 complexes. Their efficacy as hydrogenation and hydrosilylation catalysts was confirmed
and benchmarked against the prototypical group 9 catalysts, 1-1 and 1-10 during the course of this survey. The findings of this multi-faceted study involving $\kappa^2$-P,N Rh(I) and Ir(I) derivatives of 2-2e – the first formally zwitterionic analogues of ubiquitous heterobidentate $\kappa^2$-P,N square-planar group 9 cations – are described in this chapter.

3.2 Results and Discussion

3.2.1 Synthesis and Characterization of Neutral and Cationic Rh(I) and Ir(I) Complexes of 2-2a

In Chapter 2, an initial survey of the Rh(I) coordination chemistry was presented and the synthetic routes to attaining a neutral (2-3), a cationic tetrafluoroborate (BF$_4^-$) salt ([2-6a]$^+$BF$_4^-$), and a zwitterionic Rh(I) (2-7) complex were discussed. In this chapter, the Rh(I) coordination chemistry of 2-2 is examined more thoroughly and analogous Ir(I) chemistry is presented and compared to the Rh system. In addition, a survey of counteranions in the cationic complexes has been conducted in an attempt to correlate the nature of the counteranion to the catalytic reactivity of the resulting salts.

As discussed in Chapter 2, 2-2a can function effectively as a two-electron donor through the diisopropyl phosphine donor arm to form (κ$^1$-P,N-2-2a)(COD)RhCl (2-3a) in 96% yield (Scheme 3-1). Analogous reactions employing [CODIrCl]$_2$ resulted in the consumption of 2-2a, along with the clean formation of two phosphorus-containing products (δ $^{31}$P = 6.8 and 36.1). Although the isolation and unequivocal identification of these products has not been achieved, by analogy to the Rh system, these shifts could correspond to an isomeric mixture of (κ$^1$-P,N-2-2a)Ir(COD)Cl and (κ$^1$-P,N-2-
2b)Ir(COD)Cl. Alternatively, the high-frequency $^{31}$P NMR resonance is consistent with the formation of [(κ²-P,N-2-2b)Ir(COD)]⁺Cl⁻, ([3-2b]⁺Cl⁻, vide infra).

![Scheme 3-1. Synthesis of Rh(I) and Ir(I) Complexes Derived from 2-2a. Reagents: (i) 0.5 [CODRhCl]₂; (ii) 0.5 [(COD)MC]₂, AgX (M = Rh, X = PF₆; M = Ir, X = OTf); (iii) NEt₃; (iv) 0.5 [(COD)MC]₂, AgX (X = OTf, BF₄, or PF₆) then NEt₃ (except for M = Rh and X = BF₄); (v) NaN(SiMe₃)₂; (vi) n-BuLi, then 0.5 [(COD)MC]₂ (OTf = SO₃CF₃).](image)

In the pursuit of [(COD)M(κ²-P,N-2-2a)]⁺X⁻ ([3-1]⁺X⁻, M = Rh; [3-2a]⁺X⁻, M = Ir; X = SO₃CF₃, BF₄, or PF₆) complexes, appropriate [(COD)M(THF)]⁺X⁻ precursors were treated with 2-2a at 24 °C, and the progress of each reaction was monitored by use of $^{31}$P NMR spectroscopic methods. Notably, the nature of the metal/counteranion combination was found to figure importantly in determining the course of these transformations. For reactions featuring SO₃CF₃⁻ or PF₆⁻ counterions, [3-1]⁺X⁻ or [3-2a]⁺X⁻ and the corresponding [(COD)M(κ²-P,N-2-2b)]⁺X⁻ ([2-6a]⁺X⁻, M = Rh; [3-2b]⁺X⁻, M = Ir) isomer were observed in various proportions as the only products in the crude
reaction mixture, even after short reaction times (minutes). While a similar isomeric $[\text{3-2a,b}]^+X^-$ mixture was detected spectroscopically in reactions employing the BF$_4^-$ counteranion, under analogous conditions the Rh(I) cation $[\text{2-6a}]^+X^-$ was observed exclusively. Only for $[\text{3-1}]^+\text{PF}_6^-$ (14%) and $[\text{3-2a}]^+\text{SO}_3\text{CF}_3^-$ (41%) were the differing solubilities of the $\kappa^2-P,N$-$2-2a$ and $\kappa^2-P,N$-$2-2b$ isomers successfully exploited as a means of isolating pure samples of these complexes (Scheme 3-1). Data obtained from $^1\text{H}$ and $^{13}$C NMR experiments are in keeping with the $C_1$-symmetric nature of $[\text{3-1}]^+\text{PF}_6^-$ and $[\text{3-2a}]^+\text{SO}_3\text{CF}_3^-$, and confirm the allylic structure of the bound 2-2a ligand in these complexes. It is evident that $[\text{3-1}]^+X^-$ and $[\text{3-2a}]^+X^-$ species represent kinetic products in these reactions, and that the net 1,3-proton shift within the indene backbone of 2-2a, leading to thermodynamically favored $[\text{2-6a}]^+X^-$ or $[\text{3-2b}]^+X^-$ products featuring $\kappa^2-P,N$-$2-2b$ ligands, is facilitated upon coordination to $[(\text{COD})\text{M}]^+$ fragments in this system.

One interesting observation of these Rh and Ir systems is that while in solution the isomerization of isolated $[\text{3-1}]^+\text{PF}_6^-$ or $[\text{3-2a}]^+\text{SO}_3\text{CF}_3^-$ to the corresponding $\kappa^2-P,N$-$2-2b$ complex is slow and does not proceed to completion after several days at 24 °C, under similar conditions such transformations are rendered rapid (hours) and quantititative in the presence of NEt$_3$. In contrast, uncoordinated 2-2a is not transformed cleanly into 2-2b upon treatment with amine, as outlined in Chapter 2.

The incomplete rearrangement of 2-2a to 2-2b in solution prevents the direct use of the latter in the synthesis of $\kappa^2-P,N$-$2-2b$ metal complexes. However, the target complexes $[\text{2-6a}]^+X^-$ and $[\text{3-2b}]^+X^-$ are formed quantitatively ($^3\text{P}$ NMR) upon addition of 2-2a to in-situ prepared $[(\text{COD})\text{M(THF)}_2]^+X^-$, followed by treatment with NEt$_3$ (Scheme 3-1); $[\text{2-6a}]^+\text{BF}_4^-$ is generated cleanly from $[(\text{COD})\text{Rh(THF)}_2]^+\text{BF}_4^-$ and 2-2a.
even in the absence of added amine (vide supra). After workup, [2-6a]$^+\!X^-$ (X = SO$_2$CF$_3$, 87%; BF$_4$, 94%; PF$_6$, 73%) or [3-2b]$^+\!X^-$ (X = SO$_2$CF$_3$, 89%; BF$_4$, 37%; PF$_6$, 78%) were isolated as analytically pure orange solids. Attempts to prepare [3-2b]$^+\!B(C_6F_5)_4^-$ by employing Li(Et$_2$O)$_{2.5}$B(C$_6$F$_5$)$_4$ as the halide abstracting reagent under analogous conditions produced dark solids that exhibited numerous $^{31}$P NMR resonances, and from which no pure Ir(I) complexes could be isolated. The $^1$H, $^{13}$C, and $^{31}$P NMR data obtained for [2-6a]$^+\!X^-$ and [3-2b]$^+\!X^-$ are in each case consistent with a square-planar [(COD)M(κ$^2$-P,N-2-2b)]$^+\!X^-$ complex possessing $C_4$ symmetry. As well, NMR resonances associated with the respective Rh(I) and Ir(I) cations are not influenced by the nature of the accompanying counteranion, in keeping with the proposed outer-sphere nature of X in these salts.

For [2-6a]$^+\!BF_4^-$ (prepared and presented in Chapter 2), [3-2b]$^+\!SO_2$CF$_3^-$ and [3-2b]$^+\!PF_6^-$, the solution structural characterization of these complexes was confirmed on the basis of data obtained from single-crystal X-ray diffraction experiments (Figure 3-1; Tables 3-1 and 3-2 (for Ir compounds)). For all other COD-containing crystallographically characterized compounds that are reported in this chapter, a structural diagram is also provided in Figure 3-1, and selected metrical parameters and relevant X-ray experimental data are collected in Tables 3-1 and 3-2, respectively. Table 3-2 appears in the experimental section following a description of the crystallographic solution and refinement details. The metrical parameters associated with the cationic fragments in these complexes are indistinguishable, and no short contacts are observed between M and X,$^{23}$ or between M and the adjacent C2=C3 unit. As well, the interatomic distances within the metal coordination sphere of these complexes fall within the range of those observed in
related group 9 complexes,\textsuperscript{7b,24} with the M-alkene distances trans to P being significantly longer than those trans to N.

![Diagram of molecular structures](Image)

**Figure 3-1.** The crystallographically determined structures of [3-2b]\textsuperscript{+}SO\textsubscript{3}CF\textsubscript{3}, [3-2b]\textsuperscript{+}PF\textsubscript{6}, 3-3 and 3-4 shown with 50% displacement ellipsoids and with the atomic numbering scheme depicted. Selected hydrogen atoms have been omitted for clarity. Only one of the two crystallographically independent molecules of [3-2b]\textsuperscript{+}PF\textsubscript{6} is shown.

Selected bond lengths (Å) and angles (°) are provided in Table 3-1, except for 3-4 since the metal coordination sphere in 3-4 is not analogous to the other complexes in Fig 3-1; selected bond lengths (Å) and angles (°) for 3-4 are provided here: Ir-P 2.314(7); Ir-N 3.064; Ir-C\textsubscript{alkene}\textsuperscript{b} 2.168(3); Ir-C\textsubscript{alkene}\textsuperscript{b} 2.156(3); Ir-C\textsubscript{alkene}\textsuperscript{c} 2.200(3); Ir-C\textsubscript{alkene}\textsuperscript{c} 2.181(3); Ir-C\textsubscript{C7} 2.088(3); N-C\textsubscript{C7} 1.471(4); N-C2 1.341(4); C1-C2 1.519(4); C2-C3 1.383(4); C3-C3a 1.470(4); C3a-C4 1.390(4); C4-C5 1.398(4); C5-C6 1.381(4); C6-C7 1.388(5); C7-C7a 1.377(4); C7a-C1 1.499(4); P-Ir-C27 85.08(9); Ir-C27-N 117.8(2); C27-N-C2 120.1(2); N-C2-C3 127.6(3); C2-C3-P 123.8(2); C3-P-Ir 111.52(9). Trans-annular distance measured in the final refined structure.\textsuperscript{b} The Ir-cyclooctadiene distances trans to phosphorus.\textsuperscript{c} The Ir-cyclooctadiene distances trans to C27.
Table 3-1. Bond Lengths (Å) and Angles (°) for [3-2b]^+OTf, [3-2b]^+PF₆⁻, and 3-3

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<tr>
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<td>1.406(7)</td>
<td>1.394(7)</td>
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</tr>
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</tr>
</tbody>
</table>

\(^{a,b}\)Within the first and second independent molecules of [3-2b]^+PF₆⁻, respectively. \(^c\)The metal-COD distances trans to phosphorus. \(^d\)The metal-COD distances trans to nitrogen or chloride. \(^e\)Trans-annular distance measured in the final refined structure.

3.2.2 Synthesis and Characterization of the Formally Zwitterionic Complexes 2-7 and 3-3

While the ability of the indenyl fragment to coordinate metals in an \(\eta^5\) fashion is well-known,\(^{18}\) other binding modes are also commonly observed, and entirely new coordination motifs for this versatile ligand are continuing to emerge.\(^{25}\) Alternatively, the use of donor-substituted variants of this anionic hydrocarbon in the construction of
formally zwitterionic $\kappa^2$-$P,N$ group 9 metal complexes, in which the uncoordinated indenide unit serves as a sequestered anionic charge reservoir, rather than as a site for metal binding, was unexplored prior to this work. Having successfully prepared cationic square-planar group 9 complexes supported by $\kappa^2$-$P,N$-2-2b, the synthesis of structurally analogous and formally zwitterionic species featuring $\kappa^2$-$P,N$-2-2e ligation was the next challenge. While the synthesis of the Rh zwitterion 2-7 was introduced in Chapter 2, this methodology has been extended to the preparation of the Ir(I) congener, which is discussed here.

Similar to the conversion of [2-6a]$^+X^-$ to 2-7 observed upon exposure to NaN(SiMe$_3$)$_2$, [3-2b]$^+X^-$ is also transformed quantitatively ($^{31}$P NMR) into the desired $\kappa^2$-$P,N$-2-2e complex 3-3 (Scheme 3-1) under comparable reaction conditions.

Additionally, 3-3 can be isolated as an analytically pure orange-red solid in high yield (M = Ir, 93%) from the introduction of 0.5 equiv of [CODIrCl]$_2$ to 2-2e, as reported for 2-7 in Chapter 2. The exclusive formation of 2-7 and 3-3 in these transformations is unusual, given the established propensity of (COD)M$^+$ fragments for $\eta^5$ binding to indenyl ligands.$^{19}$ The connectivity in 2-7 and 3-3 that was initially determined by use of $^1$H, $^{13}$C, and $^{31}$P NMR methods was subsequently ascertained by use of X-ray crystallographic techniques (Fig 2-7 for 2-7 and Fig 3-1 for 3-3). A comparison of the structural features of the Rh cation [2-6a]$^+BF_4^-$ and zwitterion 2-7 was presented in Section 2.3.2, in which the isosteric relationship of the reactive metal coordination sphere between the cationic and zwitterionic complexes was discussed, in addition to the very apparent delocalization of the 10π indenide fragment in the Rh zwitterion. A similar structural comparison is obvious upon examination of the structural features of [3-2b]$^+X^-$ and 3-3 presented in this
chapter (Table 3-1), and warrant no further discussion. Interestingly, the Ir zwitterion 3-3 displays the same sort of contracted P-C3 and C1-C2 distances observed in 2-7 (Section 2.3.2) relative to its cationic counterparts [3-2b]+X⁻, and is supportive of a methylene phosphide-type resonance structure such as that depicted in Scheme 2-6.²⁶

3.2.3 Solubility and Substrate Reactivity of the Cationic and Formally Zwitterionic Complexes

The solubility of the discrete salts [2-6a]+X⁻ and [3-2b]+X⁻ along with the neutral complexes 2-7 and 3-3 in various organic media was assessed so as to determine the scope of solvents in which such complexes may be potentially utilized as catalysts.²⁷ All complexes were found to be fully soluble in both CH₂Cl₂ and THF with the exception of [3-2b]+X⁻, which exhibited only limited solubility in the latter solvent. In contrast, while these cationic species proved insoluble in all hydrocarbons, complexes 2-7 and 3-3 were observed to dissolve fully in benzene and toluene, and even proved soluble to a limited extent in hexanes and pentane. This observation is significant, given the possible activity and selectivity advantages that might be achieved by conducting metal-mediated E-H addition reactions in low-polarity media.

The reactivity of the cationic and formally zwitterionic Rh and Ir complexes toward E-H containing small molecules was surveyed prior to catalytic studies; unfortunately, such reactions proved rather uninformative. Exposure of [2-6a]+X⁻, [3-2b]+X⁻, 2-7, or 3-3, to Et₃SiH or Ph₃SiH₂ (1 or 10 equiv in THF) at 24 °C or 60 °C led to the formation of a complex mixture of products, including in some cases 2-2a and 2-2b (³¹P NMR). Similarly, though exposure of Crabtree’s catalyst, 1-10, to an atmosphere of H₂ is known to generate the trinuclear cluster [Ir₃H₇(PCy₃)₃(Py)₃]²⁺,² treatment of 3-3 in
C₆D₆ with H₂ produced an intractable dark brown precipitate. While these complexes clearly react with silanes and dihydrogen respectively, detailed information relating to the possible structure of potential catalytic intermediates could not be obtained.

### 3.2.4 Thermal Stability of the Cationic and Formally Zwitterionic Complexes

In addition to surveying the reactivity of the cationic and formally zwitterionic Rh(I) and Ir(I) species prepared in this work towards small molecules containing E-H bonds, the stability of the complexes in various solvents that may potentially be used as catalytic reaction media was also assessed to determine if the potential catalysts might access a common intermediate upon heating in solution. In this regard, after heating formally zwitterionic 3-3 in THF at 60 °C for 72 h, there was partial conversion (ca. 25%) to a single new phosphorus-containing species (3-4, δ ³¹P = 14). Significant quantities of 3-4, along with another as-yet-unidentified phosphorus-containing species (δ ³¹P = 61), were also produced in toluene under similar conditions. Although efforts to isolate sufficient amounts of analytically pure 3-4 to allow for the comprehensive characterization of this complex have been met with limited success, in one instance a minute quantity of pure 3-4 in crystalline form was obtained from pentane, which allowed for the spectroscopic (¹H and ³¹P NMR)²⁸ and X-ray crystallographic identification of 3-4 as the cyclometallation product depicted in equation 3-1.

The crystallographically determined structure of 3-4 is provided in Figure 3-1, while X-ray experimental data are presented in Table 3-2. In 3-4, the Ir-alkene distances trans to P are comparable to those trans to NCH₂, suggesting that these fragments exert a similar trans-influence in this complex. In addition, the planarity at nitrogen (Σ angles at N ~ 360°) and the contracted N-C2 distance (1.341(4) Å) relative to the other N-C distances in
3-4 (1.471(4) Å, 1.444(4) Å), indicate that the nitrogen fragment is in partial conjugation with the adjacent indene framework. The generation of 3-4 from 3-3 can be viewed as proceeding by way of an initial C-H activation step involving the NMe₂ fragment, followed by formal transfer of a proton (either intra- or intermolecular) from the formally cationic Ir center to the indene backbone of the ancillary ligand. Similar cyclometallation processes have been observed by other researchers in the Stradiotto group in the examination of Pt and Ru coordination complexes of P,N-substituted indenes.²⁹b-d

![Chemical Structure](image)

Whereas the cationic complex [3-2b]⁺PF₆⁻ proved to be more thermally robust than 3-3, with only 10% decomposition observed after 72 h at 60 °C in THF or toluene (³¹P NMR), once again 3-4 was identified as one of the thermolysis products. In this case, 3-4 can be viewed as arising from an initial insertion of Ir into a C-H bond of the NMe₂ unit in [3-2b]⁺PF₆⁻, followed by net loss of HPF₆. Notably, treatment of either [3-2b]⁺PF₆⁻ or 3-3 with NEt₃ for 12 h at room temperature in THF resulted in the consumption of the Ir starting complex, along with the formation of 3-4 as the major product. Nonetheless, all efforts to isolate pure 3-4 from such reactions have met with only limited success and as such the catalytic competence of 3-4 can not be commented on. Unlike [3-2b]⁺PF₆⁻ and 3-3, both Rh complexes [2-6a]⁺PF₆⁻ and 2-7 exhibited excellent thermal stability under similar experimental conditions, with no decomposition observed for [2-6a]⁺PF₆⁻, and < 5% decomposition detected in the case of 2-7 (³¹P NMR). As well, no reaction was
observed upon treatment of [2-6a]$^+$PF$_6^-$ or 2-7 with NEt$_3$ for 12 h at room temperature in THF.

3.2.5 Assessing the Binding Affinity of Neutral and Anionic $\kappa^2$-$P,N$-2-2b and $\kappa^2$-$P,N$-2-2e

To compare further the behavior of the Rh complexes presented here and in Chapter 2, a study targeted at qualitatively assessing the binding affinity of the neutral $\kappa^2$-$P,N$-2-2b ligand in [2-6a]$^+$BF$_4^-$ relative to the anionic $\kappa^2$-$P,N$-2-2e ligand in 2-7 was undertaken. To facilitate this investigation, a series of neutral phosphine donor molecules (PCy$_3$, PMePh$_2$, and PPh$_3$) were added to solutions of [2-6a]$^+$BF$_4^-$ and 2-7 to determine if any substitution chemistry of the existing P,N-bound ligand and/or the COD fragment on Rh occurs.

Clean reactivity was observed for reactions employing PMePh$_2$; addition of 10 equiv of this phosphine to [2-6a]$^+$BF$_4^-$ resulted in the quantitative consumption of the starting Rh(I) complex in 1 hour, with concomitant formation of [Rh(PMePh$_2$_4)]$^+$, 2-2a, and 2-2b as the only phosphorus-containing products (eq 3-2) by $^{31}$P NMR spectroscopy. Whereas both the neutral $\kappa^2$-$P,N$-2-2b ligand and COD were displaced by PMePh$_2$ in this reaction featuring [2-6a]$^+$BF$_4^-$, under similar experimental conditions employing the formally zwitterionic 2-7, only the COD ligand underwent substitution, affording (PMePh$_2$_2)Rh($\kappa^2$-$P,N$-2-2e), 3-5 (eq 3-3).
Complex 3-5 was obtained subsequently as an analytically pure light brown powder in 66% isolated yield. In the absence of significant steric differences between $\kappa^2$-$P,N$-2-2b and $\kappa^2$-$P,N$-2-2e (vide supra), and given the possible hemilabile character of these P,N-ligands whereby the P-donor may serve as an anchor to the group 9 metal, it is plausible that the divergent reactivity of [2-6a]$^+$BF$_4^-$ and 2-7 with PMePh$_2$ may be attributable in part to the ease with which the N-donor can dissociate from the formally cationic Rh(I) center; this presumes that such a process is of relevance to the reaction pathway leading to substitution of the P,N-ligand in these complexes. In this vein, and consistent with the observed reluctance of the $\kappa^2$-$P,N$-2-2e ligand in 2-7 to undergo substitution by PMePh$_2$, the dissociation of a ligand arm in [2-6a]$^+$ to give a $[(\text{COD})\text{M}(\kappa^1-P,N$-2-2b)]$^+$ intermediate is anticipated to be more facile than an analogous dechelation process involving 2-7 given the heightened attractive electrostatic forces that are likely to exist between the formally anionic P,N-ligand and the formally cationic $[(\text{COD})\text{M}]^+$ fragment in 2-7, relative to those in [2-6a]$^+$. The retention of the anionic ancillary ligand in 2-7 following treatment with PMePh$_2$ contrasts the previously documented loss of BPh$_4^-$ from formally zwitterionic ($\eta^6$-PhBPh$_3$)RhL$_2$ species upon exposure to phosphines.$^{12}$

In the course of characterizing 3-5 at 300 K, the $^1$H and $^{13}$C{$^1$H} NMR resonances associated with the PPh$_2$, P$^\prime$Pr$_2$, and NMe$_2$ fragments were found to be broadened.
significantly relative to the indenide and the PMePh$_2$ signals, as can be seen in Figure 3-2. Furthermore, the observation of two unique P(CHMe$_2$)$_2$ resonances in both the $^1$H and $^{13}$C{$^1$H} NMR spectra at this temperature is consistent with 3-5 adopting an effective $C_1$-symmetric solution structure on the NMR timescale, in contrast to the apparent $C_S$ symmetry exhibited by [2-6a]$^+$X, [3-2b]$^+$X, 2-7, and 3-3. The $^1$H NMR lineshape changes that occur on going from 240 K to 350 K, including the apparent simplification of the PPh$_2$ and P$^t$Pr$_2$ regions of the spectrum as well as coalescence ($T_c = 298$ K) of the initially well-resolved NMe$_2$ resonances, are consistent with a dynamic process involving restricted rotation about the Rh-PMePh$_2$ bonds in 3-5. Although signal overlap within the PPh$_2$ and P$^t$Pr$_2$ regions of the $^1$H NMR spectrum rendered these resonances too complex to interpret in terms of lineshape analysis, evaluation of the temperature-dependent $^1$H NMR lineshape changes for the NMe$_2$ unit employing the Gutowsky-Holm approximation$^{32}$ yielded a value for $\Delta G^2_{Tc}$ of ca. 14 kcal/mol. It is unclear whether the calculated $\Delta G^2_{Tc}$ on the basis of the coalescence of the NMe$_2$ signals provides a measure of the barrier associated with the proposed Rh-PMePh$_2$ restricted rotation process, since an alternative dynamic process involving Rh-N dissociation, rotation about the C2-NMe$_2$ linkage, inversion at N, and re-coordination to Rh, would also render equivalent the two N-Me environments in 3-5, if rapid on the NMR timescale.$^{33}$ However, such a process alone cannot account for the temperature-dependent lineshape changes that are observed within the PPh$_2$ and P$^t$Pr$_2$ regions of the $^1$H NMR spectra of 3-5.
Figure 3-2. Variable Temperature $^1$H NMR Plot of 3-5 in Toluene-d$^8$
Donor competition experiments conducted with 10 equiv of PCy₃ in place of PMePh₂ revealed that neither [2-6a]⁺BF₄⁻ nor 2-7 exhibited decomposition or a change in the coordination environment of the Rh(I) fragment (³¹P NMR), even after prolonged heating of the sample at 60 °C in THF solvent. The sterically less encumbered PPh₃ yielded clean reactivity with 2-7 after heating a toluene solution at 60 °C for 5 days, in contrast to the fast reactivity of the complexes with PMePh₂. The differing reactivity amongst the phosphines examined can be attributed to the differences in their steric and/or electronic profiles; whereas PCy₃ is a more electron-rich donor relative to PPh₃ and PMePh₂, and would be anticipated to be more nucleophilic and react faster, it is by far the most sterically-encumbered of these donors with a cone angle of 170°.³⁴ The reduced steric demands of PPh₃ (cone angle of 145°) would seemingly make it a much better candidate to access the metal coordination sphere, and this is observed in the slow, but quantitative substitution chemistry observed with [2-6a]⁺BF₄⁻ and 2-7. The much faster reaction with PMePh₂ can be attributed to the enhanced Lewis basicity of this donor versus PPh₃ and the slightly smaller space (cone angle of 136°) it requires to access the metal centre and displace one of the bound ligands.

3.2.6 Pursuit of Rh Carbonyl Complexes

Related to the phosphine-competition studies described in Section 3.2.5, carbon monoxide was viewed as an alternative donor molecule that could provide qualitative information on the relative binding affinity of the indene versus indenide ligands to the group 9 metals under scrutiny in this work. In addition, the dicarbonyl analogues of the cyclooctadiene-Rh complexes [2-6a]⁺PF₆⁻ and 2-7 are attractive target molecules since
infrared spectroscopic techniques could be used to compare the electron-donating abilities of the P,N-ligands in these complexes.35

In exploring the reactivity of 2-2a with 0.5 equiv of [(CO)2RhCl]2 in THF, complete consumption of 2-2a was noted after 10 min, along with the formation of multiple phosphorus-containing products (31P NMR). However, subsequent treatment of this reaction mixture with anhydrous K2CO3 resulted in the clean formation of a single phosphorus-containing species (3-6, δ31P = 72), which was isolated as an analytically pure yellow-orange solid in 43% yield (eq 3-4). The crystallographically determined structure of 3-6 is presented in Figure 3-3, which reveals trans-disposed phosphorus and chloride ligands in this square planar complex, a bonding motif that has been observed in related crystallographically characterized (κ2-P,N)Rh(CO)Cl species.36

![Chemical structure of 2-2a and 3-6](image)

Initial attempts to prepare the cationic dicarbonyl complex 3-7 (eq 3-5) via treatment of 2-2a with 0.5 equiv of [(CO)2RhCl]2 in the presence of AgPF6 generated a complex mixture of products. While similarly complex product distributions were obtained upon exposure of a THF solution of [2-6a]PF6 to an atmosphere of CO, clean conversion to a single phosphorus-containing species (3-7, δ31P = 63) was achieved under similar conditions in CH2Cl2, allowing for the subsequent isolation of this product.
in 66% yield. The structure proposed for 3-7 is supported by elemental analysis data as well as NMR spectroscopic ($^1$H, $^{13}$C{$^1$H}, and $^{31}$P{$^1$H}) data, with the exception that $^{13}$C NMR resonances attributable to the CO groups were not observed, despite prolonged data acquisition times.

![Figure 3-3](image)

**Figure 3-3.** The crystallographically determined structures of 3-6 and 3-9 shown with 50% displacement ellipsoids and with the atomic numbering scheme depicted; selected hydrogen atoms have been omitted for clarity. Crystallographic data is available in Table 3-2 in the experimental section. Selected bond lengths (Å) and angles (°) for 3-6: Rh-P 2.219(1); Rh-N 2.202(4); Rh-C31 1.790(5); Rh-Cl 2.397(1); C31-O31 1.162(5); C1-C2 1.513(6); C2-C3 1.343(6); P-Rh-N 85.3(1); C3-P-Rh 102.3(2); C2-N-Rh 111.8(3); C3-C2-N 123.3(4); C2-C3-P 117.3(4). Selected bond lengths (Å) and angles (°) for 3-9: Rh-P1 2.3107(9); Rh-P2 2.3292(8); Rh-O1 2.088(2); Rh-C41 1.793(3); C41-O41 1.158(4); P-Rh-O1 84.47(6); C3-P1-Rh 98.8(1); C2-O1-Rh 114.8(2); O1-Rh-P2 87.60(6); P1-Rh-P2 172.00(3); P1-Rh-C41 94.3(1); O1-Rh-C41 176.0(1); Rh-P2-C11 109.4(1).

Moreover, while only two IR-active CO vibrations are predicted for 3-7, three vibrations (2100, 2030, and 1990 cm$^{-1}$) were detected for this complex. Scheme 3-2 illustrates the possible arrangements of CO ligands that would give rise to IR active stretches in metal complexes containing two or three carbonyl ligands; although definitive experimental data needed to confirm the connectivity in 3-7 and to rationalize such IR-spectroscopic observations, such as a solid state structure are unavailable, it is possible
that the third IR band arises from an isomeric relative of 3-7 that possesses a linear OC-M-CO linkage, but which is not detected by use of NMR spectroscopy, even at low temperatures. This is possibly due to the much slower observation time scale of the NMR experiment compared to the IR. A second alternative is that some in-situ dimeric structure forms where a CO from a second molecule temporarily bridges between two metal centers to generate a situation where there are three CO ligands interacting with the metal that then gives rise to three IR active bands, as in Scheme 3-2 (c).

\[ L = \text{neutral 2-electron donor ligand} \]

\[
\begin{array}{c}
\text{OC-}M-\text{CO} \\
L \\
\hline \\
\text{OC-}M-\text{CO} \\
L \\
\hline \\
\text{OC-}M-\text{CO} \\
L \\
\hline \\
\end{array}
\]

\# and type of IR active stretches: 
<table>
<thead>
<tr>
<th>(a)</th>
<th>(b)</th>
<th>(c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>one asymmetric</td>
<td>one symmetric, one asymmetric</td>
<td>one symmetric, two asymmetric</td>
</tr>
</tbody>
</table>

Scheme 3-2. Depiction of Possible Geometries that would Give Rise to Metal-Carbonyl Complexes Displaying (a) One, (b) Two, or (c) Three IR Active Stretches

The preparation of the formally zwitterionic dicarbonyl Rh complex (3-8) was examined subsequently. Although lithiation of 2-2a followed by addition of 0.5 equiv of [CODRhCl]₂ afforded 2-7 quantitatively, under similar conditions employing [(CO)₂RhCl]₂ a complicated mixture of products was generated (³¹P NMR). Similarly complex product distributions were observed upon exposure of THF, CH₂Cl₂, or toluene solutions of 2-7 to an atmosphere of CO (Scheme 3-3). In the case of the reaction carried out in toluene, the crude reaction mixture was dried in vacuo and washed with pentane. On standing, a crystal separated from this pentane solution, which was identified as the monocarbonyl complex (3-9) on the basis of data obtained from X-ray diffraction analysis; the crystallographically determined structure of 3-9 is provided in Figure 3-2.

The formation of 3-9 from 2-7 in the presence of CO requires a number of decomposition
events, including hydrolysis of the enamine ligand in 2-7,\textsuperscript{39} and net transfer of 2-2a between Rh complexes. Efforts to isolate or identify other Rh-containing products from these reactions have thus far not been fruitful.

![Scheme 3-3. Attempted Synthesis of 3-8](image)

3.2.7 Alkene Hydrogenation Studies

In an initial effort to compare and contrast the catalytic abilities of the Rh(I) and Ir(I) cations [2-6a]\textsuperscript{+}PF\textsubscript{6}\textsuperscript{-} and [3-2b]\textsuperscript{+}PF\textsubscript{6}\textsuperscript{-} with those of the structurally related and formally zwitterionic complexes 2-7 and 3-3, the metal-mediated hydrogenation of styrene (24 °C, ~1 atm H\textsubscript{2}) was examined; catalytic results are collected in Table 3-3. The catalytic behavior of [2-6a]\textsuperscript{+}PF\textsubscript{6}\textsuperscript{-} and 2-7 were found to be similar, with both of these Rh(I) catalysts exhibiting an induction period\textsuperscript{40a} that was not observed for Wilkinson’s catalyst 1-1 or the Ir(I) catalysts examined in this reactivity survey (\textit{vide infra}). While both [2-6a]\textsuperscript{+}PF\textsubscript{6}\textsuperscript{-} and 2-7 exhibited only modest activity in CH\textsubscript{2}Cl\textsubscript{2} (entries 3-3.1 and 3-3.4), improved catalytic performance was noted in THF (entries 3-3.2 and 3-3.5), especially when a catalyst loading of 5.0 mol% was employed (entries 3-3.3 and 3-3.6). By comparison, 1-1 proved superior to both [2-6a]\textsuperscript{+}PF\textsubscript{6}\textsuperscript{-} and 2-7 in THF, affording
ethylbenzene quantitatively after only 4 h (entry 3-3.7). Although the styrene conversions achieved by use of [2-6a]PF₆⁻ in THF were consistently greater than those obtained by use of 2-7 as a catalyst under similar conditions, the latter formally zwitterionic species provided quantitative styrene conversion in benzene (entry 3-3.8), a solvent in which [2-6a]PF₆⁻ is not soluble.

Table 3-3. Hydrogenation of Styrene

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Loading (mol%)</th>
<th>Solvent</th>
<th>Yield (%)</th>
<th>t (h)⁵</th>
</tr>
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<tbody>
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<td>24</td>
</tr>
<tr>
<td>3-3.2</td>
<td>[2-6a]PF₆⁻</td>
<td>1.0</td>
<td>THF</td>
<td>97</td>
<td>24</td>
</tr>
<tr>
<td>3-3.3</td>
<td>[2-6a]PF₆⁻</td>
<td>5.0</td>
<td>THF</td>
<td>&gt;99</td>
<td>24</td>
</tr>
<tr>
<td>3-3.4</td>
<td>2-7</td>
<td>1.0</td>
<td>CH₂Cl₂</td>
<td>17</td>
<td>24</td>
</tr>
<tr>
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<td>THF</td>
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</tr>
<tr>
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<td>2-7</td>
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<td>THF</td>
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</tr>
<tr>
<td>3-3.7</td>
<td>1-1</td>
<td>5.0</td>
<td>THF</td>
<td>&gt;99</td>
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</tr>
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<td>3-3.8</td>
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<td>5.0</td>
<td>benzene</td>
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<td>24</td>
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<tr>
<td>3-3.9</td>
<td>[3-2b]PF₆⁻</td>
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<td>0.5</td>
<td>CH₂Cl₂</td>
<td>&gt;99</td>
<td>4</td>
</tr>
<tr>
<td>3-3.11</td>
<td>[3-2b]PF₆⁻</td>
<td>0.5</td>
<td>THF</td>
<td>&gt;99</td>
<td>4</td>
</tr>
<tr>
<td>3-3.12⁺</td>
<td>1-10</td>
<td>0.5</td>
<td>THF</td>
<td>91</td>
<td>4</td>
</tr>
<tr>
<td>3-3.13</td>
<td>3-3</td>
<td>0.5</td>
<td>CH₂Cl₂</td>
<td>56</td>
<td>4</td>
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<td>3-3.14</td>
<td>3-3</td>
<td>1.0</td>
<td>CH₂Cl₂</td>
<td>54</td>
<td>4</td>
</tr>
<tr>
<td>3.3-15</td>
<td>3-3</td>
<td>5.0</td>
<td>CH₂Cl₂</td>
<td>76</td>
<td>24</td>
</tr>
<tr>
<td>3-3.16</td>
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<td>0.5</td>
<td>THF</td>
<td>58</td>
<td>4</td>
</tr>
<tr>
<td>3-3.17</td>
<td>3-3</td>
<td>0.5</td>
<td>benzene</td>
<td>37</td>
<td>4</td>
</tr>
<tr>
<td>3-3.18</td>
<td>3-3</td>
<td>0.5</td>
<td>hexanes</td>
<td>17</td>
<td>4</td>
</tr>
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<td>3-3.19</td>
<td>[3-2b]PF₆⁻</td>
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<td>CH₂Cl₂</td>
<td>&gt;99</td>
<td>0.25</td>
</tr>
<tr>
<td>3-3.20</td>
<td>[3-2b]BF₄⁻</td>
<td>1.0</td>
<td>CH₂Cl₂</td>
<td>&gt;99</td>
<td>0.5</td>
</tr>
<tr>
<td>3-3.21</td>
<td>[3-2a]OTf⁻</td>
<td>1.0</td>
<td>CH₂Cl₂</td>
<td>97</td>
<td>4</td>
</tr>
<tr>
<td>3-3.22</td>
<td>[3-2b]OTf⁻</td>
<td>1.0</td>
<td>CH₂Cl₂</td>
<td>96</td>
<td>4</td>
</tr>
</tbody>
</table>

¹Conditions: 24 °C and −1 atm H₂. ²Time at which the quoted conversion (yield) was achieved on the basis of GC-MS and GC-FID data, rounded to the nearest percent. ³Catalyst was not completely soluble in this solvent.

Whereas cationic square-planar Ir(I) complexes, including Crabtree’s catalyst (1-10) and related [(COD)Ir(P,N)]⁺X⁻ species, are among the most active homogeneous
catalysts for alkene hydrogenation,\textsuperscript{21a} effective neutral Ir(I) alkene hydrogenation catalysts are still rare. In this regard, benchmarking the catalytic abilities of the neutral and formally zwitterionic complex 3-3 against those of the more traditional cationic complexes [3-2b]\textsuperscript{−}X\textsuperscript{−} and 1-10 were of considerable interest. In keeping with the well-documented affinity of [(COD)Ir(P,N)]\textsuperscript{−}X\textsuperscript{−} alkene hydrogenation catalysts for chlorocarbon reaction media,\textsuperscript{2,21a} the reduction of styrene mediated by [3-2b]\textsuperscript{+}PF\textsubscript{6}\textsuperscript{−} or 1-10 (0.5 mol%) occurred quantitatively in CH\textsubscript{2}Cl\textsubscript{2} after 0.5 h or 4 h, respectively (entries 3-3.9 and 3-3.10). The noteworthy catalytic activity displayed by [3-2b]\textsuperscript{+}PF\textsubscript{6}\textsuperscript{−} in CH\textsubscript{2}Cl\textsubscript{2} contrasts the apparent deactivating effect that this solvent has on the related Rh(I) species, [2-6a]\textsuperscript{+}PF\textsubscript{6}\textsuperscript{−} and 2-7 (\textit{vide supra}). While [3-2b]\textsuperscript{+}PF\textsubscript{6}\textsuperscript{−} also out-performed both [2-6a]\textsuperscript{+}PF\textsubscript{6}\textsuperscript{−} and 2-7 in THF, affording ethylbenzene quantitatively after only 4 h at the 0.5 mol% catalyst loading level (entry 3-3.11), incomplete conversion was noted for analogous reactions employing 1-10 as a catalyst in THF, even after 24 h (entry 3-3.12). Unlike [2-6a]\textsuperscript{+}PF\textsubscript{6}\textsuperscript{−} and 2-7, which exhibited comparable catalytic abilities, the formally zwitterionic 3-3 proved to be a considerably less effective styrene hydrogenation catalyst than both [3-2b]\textsuperscript{+}PF\textsubscript{6}\textsuperscript{−} and 1-10. When employing 0.5 mol\% 3-3 as a catalyst in CH\textsubscript{2}Cl\textsubscript{2}, a maximum conversion of 56\% was achieved after 4 h (entry 3-3.13), and only 54\% conversion was noted by use of 1.0 mol\% 3-3 after 4 h (entry 3-3.14). With an even higher catalyst loading of 5.0 mol\% 3-3, only 76\% conversion was realized after a 24 h period (entry 3-3.15). However, given that reasonable initial styrene hydrogenation rates are observed for 3-3 (210 h\textsuperscript{−1}, \textit{cf} 170 h\textsuperscript{−1} for [3-2b]\textsuperscript{+}OTf\textsuperscript{−} and 400 h\textsuperscript{−1} for [3-2b]\textsuperscript{+}PF\textsubscript{6}\textsuperscript{−}),\textsuperscript{40b} it is feasible that the lower styrene conversions obtained by use of 3-3 as a catalyst, as compared to reactions employing [3-2b]\textsuperscript{+}PF\textsubscript{6}\textsuperscript{−}, may reflect the instability of 3-3 under these experimental conditions, rather than the inherent catalytic activity of this formally
zwitterionic species. In exploring further the effect of solvent on the catalytic performance of 3-3, the production of ethylbenzene in THF (entry 3-3.16) was found to be similar to that obtained in CH₂Cl₂. In addition, while both [3-2b]⁺PF₆⁻ and 1-10 are not soluble in hydrocarbons, complex 3-3 exhibited modest catalytic activity in benzene (entry 3-3.17), as well as in hexanes (entry 3-3.18).

While the catalytic survey focused on comparing and contrasting [3-2b]⁺PF₆⁻ and 3-3, an exploration of potential counteranion effects on the catalytic ability of the metal complex to effectively reduce styrene was examined using 1 mol% [3-2b]⁺X⁻. While [3-2b]⁺PF₆⁻ provided clean conversion to ethylbenzene after only 15 min (entry 3-3.19), quantitative reduction was also achieved after 30 min by employing [3-2b]⁺BF₄⁻ (entry 3-3.20). In contrast, complete consumption of styrene was not observed for hydrogenations mediated by [3-2b]⁺SO₃CF₃⁻ even after 4 h (entry 3-3.21). The dependence of the counteranion (i.e. PF₆⁻ > BF₄⁻ > SO₃CF₃⁻) on catalytic activity in this series of complexes mirrors that noted in some other [(COD)Ir(κ²-P,N)]⁺X⁻ catalyst systems.⁷a

The existence of two possible isomeric forms of the indene fragment (2-2a and 2-2b) in the cationic complexes under scrutiny also led to an examination of the possible effect this may have on their catalytic potential. In the case of the isolated [3-2a]⁺SO₃CF₃⁻ and [3-2b]⁺SO₃CF₃⁻ pair, a set of experiments revealed that there is no discernable difference between a coordinated 2-2a or 2-2b on the ability of the cationic Ir fragment to reduce styrene (entries 3-3.21 and 3-3.22). This suggests that either the rearrangement of 2-2a to 2-2b under the experimental conditions employed is fast, generating only [3-
$2b)^{+}\text{SO}_3\text{CF}_3^{-}$ in the catalytic reaction mixture, or that the geometry of the coordinated donor-substituted indene ligand does not affect the reactivity of the complex.

Other differences in the catalytic abilities of $[3-2b)^{+}\text{PF}_6^{-}$ and 3-3 were brought to light through the study of more highly substituted alkene substrates (Table 3-4). Whereas the cationic Ir(I) complex $[3-2b)^{+}\text{PF}_6^{-}$ proved capable of reducing cyclohexene quantitatively and competitively with 1-10 (entry 3-4.1 and 3-4.2), only 26% conversion of cyclohexene was achieved by use of 3-3 as a catalyst under similar conditions (entry 3-4.3). In contrast, while 1-10 remained efficient at reducing the more sterically hindered 1-methylcyclohexene in CH$_2$Cl$_2$, and $[3-2b)^{+}\text{PF}_6^{-}$ achieved significant conversion (entry 3-4.5), no zwitterion-mediated reduction of the aforementioned tri-substituted alkene was observed in CH$_2$Cl$_2$ or benzene (entry 3-4.6).

Table 3-4. Hydrogenation of Substituted Alkenes at 0.5 mol% Catalyst Loading.*

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Alkene</th>
<th>Yield (%)</th>
<th>$t$ (h)$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-4.1</td>
<td>1-10</td>
<td>Cyclohexene</td>
<td>&gt;99</td>
<td>0.25</td>
</tr>
<tr>
<td>3-4.2</td>
<td>$[3-2b)^{+}\text{PF}_6^{-}$</td>
<td>Cyclohexene</td>
<td>&gt;99</td>
<td>0.5</td>
</tr>
<tr>
<td>3-4.3</td>
<td>3-3</td>
<td>Cyclohexene</td>
<td>26</td>
<td>4</td>
</tr>
<tr>
<td>3-4.4</td>
<td>1-10</td>
<td>1-methylcyclohexene</td>
<td>97</td>
<td>4</td>
</tr>
<tr>
<td>3-4.5</td>
<td>$[3-2b)^{+}\text{PF}_6^{-}$</td>
<td>1-methylcyclohexene</td>
<td>83</td>
<td>4</td>
</tr>
<tr>
<td>3-4.6</td>
<td>3-3</td>
<td>1-methylcyclohexene</td>
<td>&lt;1</td>
<td>4</td>
</tr>
</tbody>
</table>

*Conditions: CH$_2$Cl$_2$ solvent, 24 °C and ~1 atm H$_2$. $^b$Time at which the quoted conversion (yield) was achieved on the basis of GC-MS and GC-FID data, rounded to the nearest percent.

3.2.8 Styrene Hydrosilylation Studies

In continuing the head-to-head reactivity comparison of the structurally related cationic and formally zwitterionic Rh(I) and Ir(I) species reported herein, the catalytic addition of triethylsilane to styrene mediated by $[2-6a)^{+}\text{PF}_6^{-}$, $[3-2b)^{+}\text{PF}_6^{-}$, 2-7, or 3-3 was
chosen as a second test reaction (24 °C or 60 °C, 5.0 mol% catalyst, excess styrene); selected experimental results are provided in Table 3-5.

![Chemical reaction](image)

As well as representing a widely employed chemical transformation that provides access to synthetically useful organosilicon compounds, metal-catalyzed alkene hydrosilylation can serve as a prototype for E-H addition reactions in which product selectivity can be a challenge. In contrast to the relative simplicity of alkene hydrogenation, the metal-mediated addition of silanes to substituted olefins can generate a range of organosilicon species; the predominant products of this reaction in the case of triethylsilane and styrene are depicted in eq 3-6. Beyond the two possible regioisomers that can arise from simple Si-H addition (3-10a and 3-10c), vinylsilanes formed via dehydrogenative silylation (3-10b, 3-10d, and 3-10e) are also commonly observed. Selectivity towards the dehydrogenative silylation of alkenes has been achieved through the use of some group 9 catalysts, including Wilkinson’s catalyst, 1-1.43

In contrast to the standard Chalk-Harrod mechanism for hydrosilylation, in which a coordinated alkene in an intermediate of the type \( L_n M(H)(\text{SiR}_3)(\text{alkene}) \) undergoes a 1,2-insertion into the M-H bond followed by Si-C reductive elimination, vinylsilanes are presumed to arise by way of the modified Chalk-Harrod mechanism, which involves alkene 1,2-insertion into the M-Si bond, followed by \( \beta \)-hydrogen elimination.44 Notably,
3-10b is often generated as the major product in such metal-catalyzed reactions where an excess of styrene is employed as a sacrificial H₂ acceptor.⁴³

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Solvent</th>
<th>Temp. (°C)</th>
<th>Yield (%)</th>
<th>3-10a</th>
<th>3-10b</th>
<th>3-10c</th>
<th>other</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-5.1</td>
<td>[2-6a]⁺PF₆⁻</td>
<td>DCE</td>
<td>60</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
</tr>
<tr>
<td>3-5.2</td>
<td>2-7</td>
<td>DCE</td>
<td>60</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
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<td>3-5.3</td>
<td>1-1</td>
<td>DCE</td>
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<td>&gt;99</td>
<td>4</td>
<td>93</td>
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<td>&lt;1</td>
</tr>
<tr>
<td>3-5.4</td>
<td>[2-6a]⁺PF₆⁻</td>
<td>THF</td>
<td>60</td>
<td>37</td>
<td>5</td>
<td>32</td>
<td>&lt;1</td>
<td>&lt;1</td>
</tr>
<tr>
<td>3-5.5</td>
<td>2-7</td>
<td>THF</td>
<td>60</td>
<td>&gt;99</td>
<td>10</td>
<td>90</td>
<td>&lt;1</td>
<td>&lt;1</td>
</tr>
<tr>
<td>3-5.6</td>
<td>2-7</td>
<td>toluene</td>
<td>60</td>
<td>98</td>
<td>2</td>
<td>96</td>
<td>&lt;1</td>
<td>&lt;1</td>
</tr>
<tr>
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<td>[3-2b]⁺PF₆⁻</td>
<td>DCE</td>
<td>60</td>
<td>66</td>
<td>66</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
</tr>
<tr>
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<td>3-3</td>
<td>DCE</td>
<td>60</td>
<td>&gt;99</td>
<td>99</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
</tr>
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<td>3-3</td>
<td>DCE</td>
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<td>86</td>
<td>86</td>
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<td>&lt;1</td>
<td>&lt;1</td>
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<td>1-10</td>
<td>DCE</td>
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<td>&gt;99</td>
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<td>40</td>
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<td>&lt;1</td>
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<tr>
<td>3-5.11</td>
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<td>THF</td>
<td>60</td>
<td>&gt;99</td>
<td>91</td>
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<td>8</td>
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<tr>
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<td>35</td>
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<td>&lt;1</td>
<td>&lt;1</td>
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<td>THF</td>
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<td>98</td>
<td>94</td>
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<td>&lt;1</td>
<td>&lt;1</td>
</tr>
<tr>
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<td>3-3</td>
<td>toluene</td>
<td>60</td>
<td>64</td>
<td>55</td>
<td>2</td>
<td>&lt;1</td>
<td>7</td>
</tr>
</tbody>
</table>

*Conditions: 60 °C (except where noted); 5.0 mol% catalyst; styrene-to-silane ratio of 5:1; DCE = 1,2-dichloroethane; control experiments confirmed that solutions of [2-6a]⁺PF₆⁻, [3-2b]⁺PF₆⁻, 2-7, or 3-3 are each stable upon heating at 60 °C for a minimum of 24 h (³¹P NMR). On the basis of the consumption of triethyilsilane at 24 h, except for entry 3-5.3 where the yield is quoted after 4 h. Product distribution on the basis of GC-MS and GC-FID data, rounded to the nearest percent; other silicon-containing products including 3-10d and 3-10e.

In keeping with the poor alkene hydrogenation activity noted for [2-6a]⁺PF₆⁻ and 2-7 in CH₂Cl₂, no hydrosilylation chemistry was observed for reactions conducted in 1,2-dichloroethane employing either of these Rh(I) catalyst complexes (entries 3-5.1 and 3-5.2). However, the ability of Rh(I) species to mediate alkene hydrosilylations under these conditions was confirmed through the use of 1-1. Complete consumption of the silane was achieved after 4 h in 1,2-dichloroethane, along with excellent selectivity for the vinylsilane 3-10b (entry 3-5.3); similar results were obtained in benzene. While upon changing the solvent to THF only modest catalytic productivity was exhibited by [2-
6a]PF₆⁻ (37%, entry 3-5.4), quantitative consumption of the silane was achieved under similar conditions employing 2-7, affording 3-10b along with the anti-Markovnikov addition product 3-10a in a 90:10 ratio (entry 3-5.5). Similarly high conversions and even greater selectivity were achieved by use of 2-7 as a catalyst in toluene (entry 3-5.6), a solvent in which the structurally related cationic complex [2-6a]PF₆⁻ is not soluble.

In contrast to some of the other platinum-group metals, the use of Ir complexes as alkene hydrosilylation catalysts has received relatively little attention. However, evidence for the selectivity advantages that can be brought about by use of Ir catalysts in such transformations is provided in a report by Uemura and co-workers. These workers observed that whereas analogous chiral κ²-P,N Rh and Ir species both proved capable of mediating the asymmetric hydrosilylation of acetophenone in nearly quantitative yield and with high enantioselectivity, the chiral alcohol products obtained upon workup from the respective reactions were found to possess different absolute configurations.

The lack of catalytic activity observed for both [2-6a]PF₆⁻ and 2-7 in 1,2-dichloroethane contrasts the substantial silane conversion (66%) and complete selectivity for 3-10a that was achieved by using catalytic amounts of the Ir(I) cation [3-2b]PF₆⁻ in this solvent (entry 3-5.7). Even more remarkable is the catalytic performance exhibited by the formally zwitterionic species 3-3, which under analogous conditions afforded 3-10a quantitatively, despite the four-fold excess of styrene employed (entry 3-5.8). High yields of 3-10a were also achieved by use of 3-3 as a catalyst in 1,2-dichloroethane on lowering the reaction temperature from 60 °C to 24 °C, with no loss in selectivity (entry 3-5.9). While hydrosilylation reactions mediated by Crabtree’s catalyst (1-10) at 60 °C were also quantitative, very poor selectivity was observed (entry 3-5.10).
In examining the effect of solvent on the catalytic behavior of \([3-2b]^+\text{PF}_6^-\) and 3-3, hydrosilylation reactions were conducted in THF. Nearly quantitative silane conversions and good selectivity for 3-10a were achieved by use of \([3-2b]^+\text{PF}_6^-\) or 3-3 in this solvent at 60 °C (entries 3-5.11 and 3-5.13). While on lowering the temperature to 24 °C both of these Ir(I) catalyst complexes displayed complete selectivity for 3-10a in THF, the formally zwitterionic 3-3 out-performed the analogous cation in terms of yield (entries 3-5.12 and 3-5.14). In contrast to the excellent catalytic performance that was exhibited by the formally zwitterionic Rh(I) complex 2-7 in toluene (entry 3-5.6), the Ir(I) analogue 3-3 proved much less effective in this solvent relative to the others surveyed (entry 3-5.15). The catalytic abilities of the discrete salts \([3-2b]^+\text{PF}_6^-\) and 1-10 in toluene could not be surveyed, due to the poor solubility of these complexes in hydrocarbon media.

### 3.3 Summary and Conclusions

The versatility of 1-P^iPr_2-2-NMe_2-indene (2-2a) has been demonstrated through the use of this ligand in the synthesis of neutral, cationic, and formally zwitterionic Rh(I) and Ir(I) complexes. Whereas the facile rearrangement of 2-2a to 3-P^iPr_2-2-NMe_2-indene (2-2b) within the coordination sphere of these group 9 metals presented a challenge with regard to the isolation of \(\kappa^2-P,N\cdot2\cdot2\) derivatives (\([3-1]^+X^-\) and \([3-2a]^+X^-\)) in high yield, such an isomerization process has been exploited successfully in the preparation of \(\kappa^2-P,N\cdot2\cdot2\) complexes (\([2-6a]^+X^-\) and \([3-2b]^+X^-\)), with the isolated yields of these salts ranging from 37-94% on the basis of the metal and the counteranion involved. The formally zwitterionic \(\kappa^2-3-P^iPr_2-2-NMe_2\)-indenide (\(\kappa^2-2-2\)) complexes 2-7 and 3-3 were prepared in high isolated yield, either upon extrusion of HX from \([2-6a]^+X^-\) or \([3-2b]^+X^-\), or by addition of 2-2e-Li to 0.5 equiv of [(COD)MCl]_2. The formally zwitterionic species
2-7 and 3-3 constitute an unusual new class of formally charge-separated Rh(I) and Ir(I) species that are distinct from more traditional \( \eta^5 \)-indenyl and \([(\text{COD})M(\kappa^2-P,N)]^+X^-\) group 9 complexes.

Data obtained from X-ray crystallographic experiments revealed that the steric and electronic characteristics of the metal coordination environments in these cationic \( \kappa^2-P,N\text{-}2\text{-}2b \) and formally zwitterionic \( \kappa^2-P,N\text{-}2\text{-}2e \) group 9 complexes are strikingly similar, and confirm that there is a significant degree of charge separation in the formally zwitterionic \( \kappa^2-P,N\text{-}2\text{-}2e \) species, on the basis of delocalization of the anionic charge over the indenide unit. Despite these apparent similarities, divergent catalytic behavior both within and between the cation/zwitterion pairs \([2\text{-}6a]^+X^-/2\text{-}7\) and \([3\text{-}2b]^+X^-/3\text{-}3\) was observed. Amongst these four complexes, the Ir(I) cation \([3\text{-}2b]^+\text{PF}_6^-\) proved to be the most effective styrene hydrogenation catalyst in CH\(_2\)Cl\(_2\) or THF, exhibiting catalytic activity rivaling that of the well-known and common benchmark for Ir(I) cations, Crabtree's catalyst (1-10), under similar conditions.

While the catalytic performance of 3-3 proved vastly inferior to that of \([3\text{-}2b]^+\text{PF}_6^-\) in these solvents, the initial hydrogenation rates noted for 3-3 in CH\(_2\)Cl\(_2\), as well as the modest catalytic activity exhibited by this formally zwitterionic species in hydrocarbon media, suggest that alterations to the ancillary P,N-ligand architecture in 3-3 may provide access to more active and long-lived Ir(I) hydrogenation catalysts of this type. Although \([3\text{-}2b]^+\text{PF}_6^-\) proved superior to both \([2\text{-}6a]^+\text{PF}_6^-\) and 2-7 in terms of styrene hydrogenation activity in CH\(_2\)Cl\(_2\) or THF, high conversion to ethylbenzene was achieved by use of 2-7 as a catalyst in benzene, in which \([2\text{-}6a]^+\text{PF}_6^-\) and \([3\text{-}2b]^+\text{PF}_6^-\) are not soluble.
The catalytic utility of these formally zwitterionic Rh(I) and Ir(I) species was also demonstrated in hydrosilylation reactions employing triethylsilane and styrene. Remarkably, while reactions mediated by either 2-7 (in toluene or THF) or 3-3 (in 1,2-dichloroethane or THF) were observed to occur in nearly quantitative yield and with high selectivity, a different organosilane product was obtained in each case; the use of 2-7 as a catalyst afforded E-1-triethylsilyl-2-phenylethene (3-10b) selectively, whereas 1-triethylsilyl-2-phenylethane (3-10a) was the only organosilane product detected in reactions employing 3-3 as a catalyst in 1,2-dichloroethane. The complete selectivity for 3-10a exhibited by this formally zwitterionic Ir(I) complex in the presence of excess styrene is noteworthy, especially in light of the observation that a nearly equimolar ratio of 3-10a and 3-10b was generated in reactions employing 1-10 under similar conditions.

On the basis of the results of this preliminary catalytic survey, \([2-6a]^+PF_6^-, [3-2b]^+PF_6^-, 2-7, 3-3\), and their derivatives constitute a complementary family of catalyst complexes for the addition of E-H bonds to alkenes, when issues of catalytic activity/selectivity and solvent compatibility are considered. Notably, these catalytic studies also confirm that formally zwitterionic species such as 2-7 and 3-3 represent a unique and effective class of neutral catalyst complexes for the addition of E-H bonds to unsaturated substrates, whose solubility and reactivity properties are in some cases divergent from those of more traditional Rh(I) and Ir(I) \([(\text{COD})M(\kappa^2-P,N)]^+X^-\) salts. Presently, the specific origins of the reactivity differences noted between structurally related cationic group 9 complexes supported by \(\kappa^2-P,N\)-2-2b and their formally zwitterionic relatives are unknown; the observation that \([2-6a]^+BF_4^-\) was cleanly transformed into \([\text{Rh}(\text{PMePh}_2)_4]^+BF_4^-\) upon exposure to excess PMePh_2, while under
similar conditions only the COD ligand in 2-7 was displaced to form 3-5, suggests that
the more tightly bound anionic κ²-P,N-2-2e ligand in 2-7 and 3-3 may represent a
potential source of such divergent reactivity. Temperature-dependent ¹H NMR lineshape
changes observed for 3-5 were rationalized in terms of the operation of at least one
dynamic process in this complex (ΔG‡298 ≈ 14 kcal/mol).

Preparation of dicarbonyl analogues of 2-3, [2-6a]⁺PF₆⁻ and 2-7 was attempted in
an effort to examine the relative strength of the P-M bond in the cationic complexes
compared to the formal zwitterions through the use of infrared spectroscopic techniques.
While the neutral species 3-6 (κ²-P,N-2-2b-Rh(CO)(Cl)) and cationic species 3-7 (κ²-
P,N-2-2b-Rh(CO)₂) were readily prepared, the zwitterionic counterpart 3-8 was
unattainable, leading instead to the isolation of decomposition product 3-9 in a minute
quantity. While no useful IR spectroscopic data was obtained, the synthetic survey
revealed the importance of choice in the reactive ligands on the ultimate stability of the
resulting metal complexes; the cyclooctadiene-containing complexes are relatively easy
to prepare and are robust to a variety of solvents and conditions. The observation of the
thermolysis cyclometallation product 3-4 from [3-2b]⁺X⁻ or 3-3 suggests that at elevated
temperatures for an extended period of time the efficiency of the Ir(I) catalysts may be
diminished or not representatively of the initial catalytic species, although a similar
decomposition pathway is not observed for the Rh(I) catalyst complexes [2-6a]⁺X⁻.

In the absence of complete formal charge separation within 2-7 and 3-3, the
electrophilicity of the associated metal center in each of these complexes should be
attenuated relative to [2-6a]⁺PF₆⁻ and [3-2b]⁺PF₆⁻, which in turn could also influence the
catalytic behavior displayed by these species. As well, the participation of the backbone
indenide unit in these formally zwitterionic species during the course of catalytic transformations cannot be discounted. In this regard, synthetic and mechanistic experiments directed towards addressing these questions are future targets to be examined by other members of the Stradiotto research group.

3.4 Experimental Section

General Considerations. See Section 2.5 for a description of general experimental conditions. Any changes or additions to those procedures are described here: The non-deuterated solvents tetrahydrofuran, dichloromethane, diethyl ether, toluene, benzene, hexanes, and pentane were deoxygenated and dried by sparging with dinitrogen gas, followed by passage through a double-column solvent purification system purchased from mBraun Inc. Tetrahydrofuran, dichloromethane, and diethyl ether were purified over two alumina-packed columns, while toluene, benzene, hexanes, and pentane were purified over one alumina-packed column and one column packed with copper-Q5 reactant and stored as described in Section 2.5. CD₂Cl₂ (Cambridge Isotopes) was degassed by using three repeated freeze-pump-thaw cycles, dried over CaH₂ for 7 days, distilled in vacuo and stored over 3 Å molecular sieves for 24 h prior to use. Purification of NEt₃ was achieved by stirring over KOH for 7 d, followed by distillation; the distilled NEt₃ was then refluxed over CaH₂ for 3 d under dinitrogen, followed by distillation. All other liquid solvents or reagents (Aldrich) were degassed by using three repeated freeze-pump-thaw cycles and then dried over 3 Å molecular sieves for 24 h prior to use. K₂CO₃ was obtained from Aldrich and dried in vacuo for 12 h prior to use. Carbon monoxide gas (99.5%, chemically pure grade) and Hydrogen gas (99.999%, UHP Grade) were obtained from Air
Liquide and used as received. All silver salts (Aldrich) were dried in vacuo for 12 h prior to use. Compounds $[\text{CODRhCl}_2]$, $[\text{CODIrCl}_2]$, $[\text{PPh}_3\text{RhCl}]$ (1-1) and $[(\text{CO})_2\text{RhCl}]_2$ were prepared using literature methods and dried in vacuo for 24 h prior to use, while $[(\text{COD})\text{Ir(PCy}_3\text{(Py)}])PF_6^-$ (1-10) was obtained from Strem. All $^1\text{H}$, $^{13}\text{C}$, and $^{31}\text{P}$ NMR characterization data were collected at 300 K on a either a Bruker AC-250 spectrometer operating at 250.1 MHz, 62.9 MHz and 101.3 MHz, for $^1\text{H}$, $^{13}\text{C}$ and $^{31}\text{P}$ (respectively) or a Bruker AV-500 spectrometer operating at 500.1, 125.8, and 202.5 MHz (respectively) with chemical shifts reported in parts per million downfield of SiMe$_4$ (for $^1\text{H}$ and $^{13}\text{C}$) or 85% H$_3$PO$_4$ in D$_2$O (for $^{31}\text{P}$). In some cases, slightly fewer than expected independent $^1\text{H}$ and/or $^{13}\text{C}$ NMR resonances were observed, despite prolonged data acquisition times. In some cases, $^1\text{H}$ and $^{13}\text{C}$ NMR chemical shift assignments are on the basis of data obtained from $^{13}\text{C}$-DEPT, $^1\text{H}-^1\text{H}$ COSY, $^1\text{H}-^{13}\text{C}$ HSQC, $^1\text{H}-^{13}\text{C}$ HMBC, and/or 1D $^1\text{H}$ nOe NMR experiments. Variable-temperature NMR studies involving 3-5 were conducted on a Bruker AC-250 spectrometer, with temperature calibrations carried out using an external MeOH/MeOD standard. GC-FID analyses were performed on a Perkin-Elmer Autosystem Gas Chromatograph, while GC-MS analyses were performed on a Varian Saturn-2000 system. All GC analyses were carried out using a 30 m x 0.53 mm J&W DB5 column, with helium as the carrier gas. Elemental analyses were performed either by Desert Analytics, Tucson, Arizona, (USA) or by Canadian Microanalytical Service Ltd., Delta, British Columbia (Canada). Single crystal X-ray diffraction experiments were performed by Dr R. McDonald and Dr. M. J. Ferguson at the X-Ray Crystallography Laboratory, University of Alberta, Department of Chemistry, Edmonton, Alberta (Canada) or by Dr. G. Schatte at the Saskatchewan Structural
Synthesis of [(COD)Rh(κ²-P,N-2-2a)]⁺PF₆⁻ ([3-1⁺PF₆⁻]). To a solution of [CODRhCl]₂ (0.120 g, 0.244 mmol) in THF (2 mL) was added a solution of AgPF₆ (0.123 g, 0.487 mmol) in THF (2 mL) via Pasteur pipette. The vial was sealed with a PTFE-lined cap and the mixture shaken vigorously for ~30 sec; the immediate formation of a white precipitate was observed. After 5 min, a solution of 2-2a (0.134 g, 0.487 mmol) in THF (3 mL) was added, affording a yellow-orange solution. The reaction vial was sealed and shaken vigorously for 30 sec, after which the precipitate was allowed to settle over 15 min. The reaction mixture was filtered through Celite to remove the precipitated solids, which were discarded. From the initially homogeneous filtrate a yellow micro-crystalline precipitate formed at room temperature. This solid was isolated by decanting away the supernatant (which was found to contain a mixture of [3-1⁺PF₆⁻] and [2-6a⁺PF₆⁻] as identified by ³¹P NMR analysis), and dried in vacuo to leave [3-1⁺PF₆⁻] as an analytically pure orange powder (0.041 g, 0.066 mmol, 14 %). Anal. calcd. for C₂₃H₃₈P₂N₁Rh₁F₆ (631.4 gmol⁻¹) (%): C 47.55; H 6.07; N 2.22. found: C 47.70; H 6.06; N 2.23. ¹H NMR (CD₂Cl₂, 500.1 MHz): δ 7.36-7.29 (m, 3H, Ar-Hs), 7.24 (m, 1H, Ar-H), 6.37 (broad s, 1H, C3-H), 5.22 (broad s, 1H, COD), 4.94 (broad s, 1H, COD), 4.42 (d, ²Jₚₕ = 12.0 Hz, 1H, C1-H), 4.32 (broad s, 1H, COD), 4.15 (broad s, 1H, COD), 3.25 (s, 3H, NC₆₆Me₆₆), 2.79 (s, 3H, NC₆₆Me₆₆), 2.62-2.37 (m, 4H, COD), 2.32-2.15 (m, 3H, COD and P(CH₆₆Me₆₆)(CH₆₆Me₆₆)), 2.14-2.01 (m, 3H, COD and P(CH₆₆Me₆₆)(CH₆₆Me₆₆)), 1.71 (d of d, ³Jₚₕ = 17.8 Hz, ³J₁₁ = 7.2 Hz, 3H, P(CH₆₆Me₆₆)(CH₆₆Me₆₆)), 1.50 (d of d, ³Jₚₕ = 12.5 Hz, ³J₁₁ = 6.9 Hz, 3H, P(CH₆₆Me₆₆)(CH₆₆Me₆₆)), 1.08 (d of d, ³Jₚₕ =
15.0 Hz, $^3J_{HH} = 7.4$ Hz, 3H, P(CHMe$_a$Me$_b$)(CHMe$_c$Me$_d$)), 0.82 (d of d, $^3J_{PH} = 17.8$ Hz, $^3J_{HH} = 6.9$ Hz, 3H, P(CHMe$_a$Me$_b$)(CHMe$_c$Me$_d$)); $^{13}$C{${^1}$H} NMR (CD$_2$Cl$_2$, 125.8 MHz): δ 165.1 (C2), 143.2 (C3a or C7a), 134.9 (d, $J = 6.7$ Hz, C7a or C3a), 128.9, 126.4, 125.3, 122.9 (C4, C5, C6, and C7), 116.7 (d, $J = 9.4$ Hz, C3), 108.4 (COD), 105.1 (COD), 76.0 (d, $J_{RhC} = 12.8$ Hz, COD), 72.1 (d, $J_{RhC} = 12.4$ Hz, COD), 51.7 (NMe$_a$Me$_b$), 48.1 (NMe$_a$Me$_b$), 42.9 (d, $^1J_{PC} = 10.8$ Hz, C1), 33.2 (COD), 32.0 (COD), 28.6 (COD), 28.3 (COD), 25.7 (d, $^1J_{PC} = 19.4$ Hz, P(CHMe$_a$Me$_b$)(CHMe$_c$Me$_d$)), 23.8 (d, $^1J_{PC} = 17.0$, P(CHMe$_a$Me$_b$)(CHMe$_c$Me$_d$)), 20.5 (d, $^2J_{PC} = 4.8$ Hz, P(CHMe$_a$Me$_b$)(CHMe$_c$Me$_d$)), 19.1 (d, $^2J_{PC} = 4.2$ Hz, P(CHMe$_a$Me$_b$)(CHMe$_c$Me$_d$)), 18.7 (d, $^2J_{PC} = 6.1$ Hz, P(CHMe$_a$Me$_b$)(CHMe$_c$Me$_d$)), 18.4 (P(CHMe$_a$Me$_b$)(CHMe$_c$Me$_d$)); $^{31}$P{${^1}$H} NMR (CD$_2$Cl$_2$, 202.5 MHz): δ 25.7 (d, $^1J_{RhP} = 147.0$ Hz, P(CHMe$_2$)$_2$), -143.2 (septet, $^1J_{PF} = 709.3$ Hz, PF$_6$).

**Synthesis of [(COD)Rh(κ$_2$-P,N-2-2b)]$^+$SO$_3$CF$_3^{-}$ ([2-6a]$^+$SO$_3$CF$_3^{-}$).** To a solution of [CODRhCl]$_2$ (0.048 g, 0.098 mmol) in THF (1 mL) was added via Pasteur pipette to a solution of AgSO$_3$CF$_3$ (0.050 g, 0.20 mmol) in THF (2 mL). The vial was sealed with a PTFE-lined cap and the mixture shaken vigorously for ~30 sec. A white precipitate formed immediately, which was allowed to settle over 15 min and was removed from the reaction mixture by filtration over Celite and discarded. A solution of 2-2a (0.054 g, 0.195 mmol) in THF (2 mL) was added to the filtrate, with immediate formation of an orange solution. The reaction vial was sealed, manually shaken for 30 sec, and then left to stand for 2.5 h. $^{31}$P NMR data collected on an aliquot of the reaction mixture at this stage revealed a ~ 90:10 isomeric mixture of [3-1]$^+$SO$_3$CF$_3^{-}$ and [2-6a]$^+$SO$_3$CF$_3^{-}$. To facilitate the rearrangement of [3-1]$^+$SO$_3$CF$_3^{-}$ to [2-6a]$^+$SO$_3$CF$_3^{-}$, NEt$_3$ (0.08 mL) was added to the
reaction mixture. The vial was sealed and manually shaken for 10 sec. After 5 min, the solvent and other volatile materials were removed in vacuo to leave an orange solid. This solid was dried in vacuo, affording [2-6a]+SO₃CF₃ as an analytically pure orange powder (0.105 g, 0.169 mmol, 87 %). Anal. calcd. for C₂₆H₃₈P₁N₁S₃Rh₁F₃ (619.55 gmol⁻¹) (%): C 49.12, H 6.03, N 2.20, found: C 48.98, H 6.20, N 2.25. ¹H NMR (CD₂Cl₂, 500.1 MHz): δ 7.53 (m, 1H, Ar-H), 7.49 (m, 1H, Ar-H), 7.39-7.36 (m, 2H, Ar-H), 5.14 (broad s, 2H, COD), 4.49 (broad s, 2H, COD), 3.72 (s, 2H, Cl₁(H)₂), 3.03 (s, 6H, NMe₂), 2.83 (m, 2H, P(C₂H₃Me₂Me₅)₂), 2.54-2.49 (m, 4H, COD), 2.26-2.18 (m, 4H, COD), 1.45 (d of d, 3JPH = 17.1 Hz, 3JHH = 7.2 Hz, 6H, P(CH₃Me₅Me₅)₂), 1.35 (d of d, 3JPH = 15.9 Hz, 3JHH = 7.0 Hz, 6H, P(CH₃Me₅Me₅)₂); ¹³C{¹H} NMR (CD₂Cl₂, 125.8 MHz): δ 195.9 (SO₃CF₃), 177.3 (d, J = 17.9 Hz, C2), 143.5 (C3a or C7a), 137.7 (C7a or C3a), 128.8 (d, ¹JPC = 26.3, C3), 127.1, 126.9, 125.3, 123.0 (C4, C5, C6, or C7), 105.9 (m, COD), 73.3 (d, ¹JRhC = 12.4 Hz, COD), 51.1 (NMe₂), 32.3 (COD), 31.2 (d, J = 10.1 Hz, C1), 28.1 (COD), 24.9 (d, ¹JPC = 24.5 Hz, P(CH₃Me₅Me₅)₂), 19.4 (P(CH₃Me₅Me₅)₂), 18.5 (P(CH₃Me₅Me₅)₂). ³¹P{¹H} NMR (CD₂Cl₂, 202.5 MHz): δ 43.1 (d, ¹JRHP = 150.6 Hz).

**Synthesis of [(COD)Rh(κ²-P,N-2-2b)]+PF₆⁻ ([2-6a]+PF₆⁻).** To a solution of [CODRhCl]₂ (0.060 g, 0.244 mmol) in THF (2 mL) was added a solution of AgPF₆ (0.123 g, 0.487 mmol) in THF (2 mL) via Pasteur pipette. The vial was sealed with a PTFE-lined cap and the mixture shaken vigorously for ~30 sec. Immediate formation of a white precipitate was observed. After 5 min, a solution of 2-2a (0.134 g, 0.487 mmol) in THF (3 mL) was added, which resulted in the formation of a yellow-orange solution. The reaction vial was sealed and shaken vigorously for 30 sec, after which the precipitate was allowed to settle over 15 min. The reaction mixture was filtered through Celite to remove
the precipitated solids, which were discarded. From the initially homogeneous filtrate some amount of yellow micro-crystalline material precipitated ([3-1]PF₆⁻), which was separated from the supernatant. At this stage, ³¹P NMR data collected on an aliquot of the supernatant solution indicated the presence of an isomeric mixture of [3-1]PF₆⁻ and [2-6a]PF₆⁻. To the isolated supernatant, NEt₃ (0.070 mL) was added to facilitate the rearrangement of [3-1]PF₆⁻ to [2-6a]PF₆⁻. The vial was sealed and manually shaken for 10 sec, and after standing for an additional 5 min, the solvent and other volatile materials were removed in vacuo to leave a sticky dark yellow-orange solid. The solid was washed with toluene (2 x 1 mL) and subsequently dried in vacuo to leave [2-6a]PF₆⁻ as an analytically pure orange powder (0.189 g, 0.300 mmol, 62 %). Anal. calcd. for C₂₅H₃₈P₂N₁Rh₁F₆ (631.4 gmol⁻¹) (%): C 47.55; H 6.07; N 2.22. found: C 47.49; H 6.02; N 2.40. All ¹H, ¹³C{¹H}, and ³¹P{¹H} NMR data for the cation were identical to those reported for [2-6a]⁺SO₃CF₃⁻. NB: If precipitated [3-1]PF₆⁻ is not separated from the supernatant in the aforementioned procedure, analytically pure [2-6a]⁺PF₆⁻ is obtained in 73% isolated yield.

**Synthesis of [(COD)Ir(κ²-P,N-2-2a)]⁺SO₃CF₃⁻ ([3-2a]⁺SO₃CF₃⁻).** To a solution of [CODIrCl]₂ (0.080 g, 0.12 mmol) in THF (5 mL) was added a solution of AgSO₃CF₃ (0.061 g, 0.24 mmol) in THF (2 mL) via Pasteur pipette. Immediate formation of a white precipitate was observed. After 1 h, the reaction mixture was filtered through Celite to yield a clear bright yellow solution, to which a solution of 2-2a (0.065 g, 0.24 mmol) in THF (1.5 mL) was added; the solution turned dark red immediately. The reaction vial was sealed with a PTFE-lined cap, shaken vigorously for 30 sec and allowed to sit undisturbed for 1 h. Over this time, an orange crystalline solid had formed in the reaction vial. The
supernatant (which was found to contain a mixture of [3-2a]+SO₃CF₃⁻ and [3-2b]+SO₃CF₃⁻ as identified by ³¹P NMR analysis) was decanted away from the solid product. In turn, this solid was dried in vacuo to afford [3-2a]+SO₃CF₃⁻ as an analytically pure bright orange solid (0.071 g, 0.098 mmol, 41 %). Anal. Calcd. for

C₂₆H₃₈P₁N₁Ir₁O₃S₁F₃ (724.8 gmol⁻¹) (%): C 43.08; H 5.28; N 1.93. found: C 43.08; H 5.55; N 1.95. ¹H NMR (CD₂Cl₂, 500.1 MHz): δ 7.43-7.32 (m, 4H, Ar-Hs), 6.57 (s, 1H, C3-H), 4.98 (m, 1H, COD), 4.78 (m, 1H, COD), 4.62 (d, ²JₚH = 13.0 Hz, 1H, C1-H), 4.20 (m, 1H, COD), 3.94 (m, 1H, COD), 3.27 (s, 3H, NMe₃Me₉), 3.16 (s, 3H, NMe₃Me₉), 2.56-2.41 (m, 3H, COD and P(CHMe₃Me₉)(CHMe₃Me₉) and

P(CHMe₃Me₉)(CHMe₃Me₉), 2.38-2.21 (m, 3H, COD), 2.13-2.03 (m, 2H, COD), 1.89-1.86 (m, 2H, COD), 1.73 (d of d, ³JₚH = 13.1 Hz, ³JₕH = 7.2 Hz, 3H,

P(CHMe₃Me₉)(CHMe₃Me₉), 1.59 (d of d, ³JₚH = 13.1 Hz, ³JₕH = 6.9 Hz, 3H,
P(CHMe₃Me₉)(CHMe₃Me₉), 1.16 (d of d, ³JₚH = 15.3 Hz, ³JₕH = 7.3 Hz, 3H,
P(CHMe₃Me₉)(CHMe₃Me₉), 0.79 (d of d, ³JₚH = 17.9 Hz, ³JₕH = 7.0 Hz, 3H,
P(CHMe₃Me₉)(CHMe₃Me₉); ¹³C {¹H} NMR (CD₂Cl₂, 125.8 MHz): δ 166.9 (C2), 143.5 (C3a or C7a), 134.7 (C7a or C3a), 129.1, 126.9, 125.6, 123.6 (C4, C5, C6, and C7), 118.1 (d, ³JₚC = 8.7 Hz, C3), 96.8 (d, ²JₚC = 11.5 Hz, COD), 93.6 (d, ²JₚC = 11.1 Hz, COD), 61.4 (COD), 58.2 (COD), 53.0 (NMe₃Me₉), 49.1 (NMe₃Me₉), 42.9 (d, ¹JₚC = 17.3 Hz, C1).

34.3 (broad s, COD), 32.3 (broad s, COD), 29.7 (COD), 28.7 (COD), 26.2 (d, ¹JₚC = 25.6 Hz, P(CHMe₃Me₉)(CHMe₃Me₉), 24.3 (d, ¹JₚC = 23.4, P(CHMe₃Me₉)(CHMe₃Me₉), 20.7 (d, ²JₚC = 3.1 Hz, P(CHMe₃Me₉)(CHMe₃Me₉), 19.3 (d, ²JₚC = 2.5 Hz,
P(CHMe₃Me₉)(CHMe₃Me₉), 19.1 (d, ²JₚC = 5.6 Hz, P(CHMe₃Me₉)(CHMe₃Me₉), 18.5 (P(CHMe₃Me₉)(CHMe₃Me₉); ³¹P {¹H} NMR (CD₂Cl₂, 202.5 MHz): δ 15.0.

110
Synthesis of [(COD)Ir(κ²-P,N-2-2b)]⁺SO₃CF₃⁻ ([3-2b]⁺SO₃CF₃⁻). To a solution of [CODIrCl]₂ (0.10 g, 0.15 mmol) in THF (3 mL) was added a solution of AgSO₃CF₃ (0.076 g, 0.30 mmol) in THF (2 mL) via Pasteur pipette. Immediate formation of a white precipitate was observed. After 1 h, the reaction mixture was filtered through Celite to yield a clear bright yellow solution, to which a solution of 2-2a (0.082 g, 0.30 mmol) in THF (1.5 mL) was added; a dark red solution immediately formed. After magnetically stirring the mixture for 1 h, the supernatant was decanted away from any precipitate that had formed (identified as [3-2a]⁺SO₃CF₃⁻ on the basis of ³¹P NMR analysis) and NEt₃ (0.4 mL) was added to the solution to facilitate the rearrangement of [3-2a]⁺SO₃CF₃⁻ to [3-2b]⁺SO₃CF₃⁻. After 30 min, the solvent and other volatile materials were removed in vacuo to leave a dark brown sticky solid. This solid was washed with toluene (2 x 2 mL) and pentane (2 mL) to leave [3-2b]⁺SO₃CF₃⁻ as an analytically pure orange solid (0.10 g, 0.14 mmol, 47 %). Anal. calcd. for C₂₆H₃₆P₁N₁Ir₁O₃S₁F₃ (724.8 gmol⁻¹) (%): C 43.08; H 5.28; N 1.93. found: C 42.96; H 5.09; N 1.78. ¹H NMR (CD₂Cl₂, 500.1 MHz): δ 7.52-7.48 (m, 2H, Ar-Hs), 7.38-7.34 (m, 2H, Ar-Hs), 4.81-4.76 (m, 2H, COD), 4.26-4.20 (m, 2H, COD), 3.80 (s, 2H, C₁(H₂)), 3.13 (s, 6H, NMe₂), 3.06-2.99 (m, 2H, P(CHMe₂)₂), 2.32-2.26 (m, 4H, COD), 1.94-1.90 (m, 4H, COD), 1.38 (d of d, ³Jₚₗ = 17.5 Hz, ³Jₜₜ = 7.5 Hz, 6H, P(CHMe₃Me₃)₂), 1.30 (d of d, ³Jₚₗ = 15.5 Hz, ³Jₜₜ = 7.0 Hz, 6H, P(CHMe₃Me₃)₂); ¹³C {¹H} NMR (CD₂Cl₂, 125.8 MHz): δ 195.9 (SO₃CF₃), 179.5 (d, ²Jₚₗ = 16.0 Hz, C₂), 144.2 (d, ²Jₚₗ = 6.0 Hz, C₃a), 136.9 (C₇a), 130.7 (d, ¹Jₚₗ = 34.8 Hz, C₃), 127.4, 127.2, 125.9, 122.6 (C₄, C₅, C₆, C₇), 93.4 (d, ²Jₚₗ = 11.3 Hz, COD), 59.8 (COD), 52.2 (NMe₂), 33.0 (d, ³Jₚₗ = 2.6 Hz, COD), 31.6 (d, ³Jₚₗ = 9.5 Hz, C₁), 28.8 (COD), 25.4 (d, ¹Jₚₗ = 30.4 Hz, P(CHMe₂)₂), 19.7 (P(CHMe₃Me₃)₂), 18.5 (P(CHMe₃Me₃)₂); ³¹P {¹H}
NMR (CD$_2$Cl$_2$, 202.5 MHz): $\delta$ 35.9. Crystals suitable for single crystal X-ray diffraction analysis were obtained from a concentrated THF solution of $[3\text{-}2\text{b}]^+\text{SO}_3\text{CF}_3^-$ at room temperature. *NB:* If in using the procedure above the precipitated $[3\text{-}2\text{a}]^+\text{SO}_3\text{CF}_3^-$ is not separated from the supernatant containing a mixture of $[3\text{-}2\text{a}]^+\text{SO}_3\text{CF}_3^-$ and $[3\text{-}2\text{b}]^+\text{SO}_3\text{CF}_3^-$, then NEt$_3$ can be added to the mixture to afford analytically pure $[3\text{-}2\text{b}]^+\text{SO}_3\text{CF}_3^-$ in 89% isolated yield.

**Synthesis of** $[(\text{COD})\text{Ir}(\kappa^2\text{-}P,N\text{-}2\text{-}2\text{b})]^+\text{BF}_4^-$ $([3\text{-}2\text{b}]^+\text{BF}_4^-)$. To a solution of $[\text{COD}\text{IrCl}]_2$ (0.050 g, 0.075 mmol) in THF (3 mL) was added a solution of AgBF$_4$ (0.032 g, 0.16 mmol) in THF (2 mL) via Pasteur pipette. Immediate formation of a white precipitate was observed. After 1 h, the reaction mixture was filtered through Celite to afford a clear bright yellow solution, to which a solution of 2-2a (0.041 g, 0.15 mmol) in THF (1.5 mL) was added, with formation of an orange solution. After 1.5 h, the solvent and other volatile materials were removed in vacuo to leave a sticky brown solid. The solid was washed with toluene (2 mL) and subsequently with pentane (2 mL) to leave $[3\text{-}2\text{b}]^+\text{BF}_4^-$ as an analytically pure orange powder (0.037 g, 0.056 mmol, 37%). Anal. calcd. for C$_{25}$H$_{38}$P$_1$N$_1$Ir$_1$B$_1$F$_4$ (662.6 g mol$^{-1}$) (%): C 45.32; H 5.78; N 2.11. found: C 45.39; H 5.70; N 2.15. All $^1$H, $^{13}$C{$^1$H}, and $^{31}$P{$^1$H} NMR data for the cation were identical to those reported for $[3\text{-}2\text{b}]^+\text{SO}_3\text{CF}_3^-$. Whereas a much higher apparent isolated yield of $[3\text{-}2\text{b}]^+\text{BF}_4^-$ is obtained by use of less toluene and pentane in the washing procedure, the resulting solids thereby obtained did not reliably provide satisfactory combustion analysis.

**Synthesis of** $[(\text{COD})\text{Ir}(\kappa^2\text{-}P,N\text{-}2\text{-}2\text{b})]^+\text{PF}_6^-$ $([3\text{-}2\text{b}]^+\text{PF}_6^-)$. To a solution of $[\text{COD}\text{IrCl}]_2$ (0.060 g, 0.090 mmol) in THF (3 mL) was added a solution of AgPF$_6$ (0.045 g, 0.18
mmol) in THF (2 mL) via Pasteur pipette. A white precipitate formed immediately, and after 5 min a solution of 2-2a (0.049 g, 0.18 mmol) in THF (3 mL) was added, with immediate darkening of the solution to dark red. The reaction vial was then sealed and shaken vigorously for 30 sec, after which the precipitate was allowed to settle over 15 min. The reaction mixture was filtered through Celite, and to the filtrate was added NEt₃ (0.075 mL). The reaction mixture was sealed and manually shaken for 10 sec, and then was left to settle for 5 min. The solvent and other volatile materials were then removed in vacuo to leave a sticky orange-brown solid. The crude product was extracted into CH₂Cl₂ (5 mL) and the mixture filtered over Celite in order to remove a fine black insoluble material. The filtrate was then dried in vacuo, and the resulting sticky orange solid was washed once with pentane (2 mL). The remaining solid was dried in vacuo to leave [3-2b]+PF₆⁻ as an analytically pure orange powder (0.101 g, 0.140 mmol, 78 %). Anal. calcd. for C₂₅H₃₈P₂N₁Ir₁F₆ (720.7 gmol⁻¹) (%): C 41.66; H 5.31; N 1.94. found: C 41.44; H 5.41; N 2.11. All ¹H, ¹³C{¹H}, and ³¹P{¹H} NMR data for the cation were identical to those reported for [3-2b]+SO₃CF₃⁻. Crystals suitable for single crystal X-ray diffraction analysis were obtained from a concentrated THF solution of [3-2b]+PF₆⁻ at room temperature.

**Synthesis of (COD)Ir(κ²-P,N-2-2e) (3-3).** A solution of [CODIrCl]₂ (0.099 g, 0.15 mmol) in toluene (3 mL) was added to a slurry of 2-2e-Li (0.081 g, 0.29 mmol) in toluene (3 mL) via Pasteur pipette; the solution instantly darkened to ruby red. After 40 min, the reaction mixture was filtered through Celite to remove any precipitate. At this stage, ³¹P NMR data collected on an aliquot of the crude reaction mixture indicated the quantitative formation of 3-3. The solvent and any other volatile materials were then removed in vacuo to yield 3-3 as an analytically pure dark orange solid (0.16 g, 0.27 mmol, 93 %).
Anal. calcd. for C_{25}H_{37}P_{1}N_{1}Ir_{1} (574.8 gmol^{-1}) (%): C 52.24; H 6.49; N 2.44. found: C 52.53; H 6.44; N 2.68. \textsuperscript{1}H NMR (C_{6}D_{6}, 500.1 MHz): \delta 7.98 (d, \textsuperscript{3}J_{HH} = 11.0, 1H, C7-H), 7.80 (d, \textsuperscript{3}J_{HH} = 8.0, 1H, C4-H), 7.39-7.32 (m, 2H, C6-H and C5-H), 6.30 (d, J = 3.7 Hz, 1H, C1-H), 3.88-3.84 (m, 4H, COD), 2.75 (s, 6H, NMe_{2}), 2.74-2.68 (m, 2H, P(CHMe_{2})_{2}), 1.95-1.79 (m, 4H, COD), 1.41-1.36 (m, 2H, COD), 1.33-1.26 (m, 2H, COD), 1.18 (d of d, \textsuperscript{3}J_{PH} = 15.1 Hz, \textsuperscript{3}J_{HH} = 7.0 Hz, 6H, P(CHMe_{2}Me_{2})_{2}), 1.05 (d of d, \textsuperscript{3}J_{PH} = 15.9 Hz, \textsuperscript{3}J_{HH} = 7.2 Hz, 6H, P(CHMe_{2}Me_{2})_{2}); \textsuperscript{13}C\{(\textsuperscript{1}H) NMR (C_{6}D_{6}, 125.8 MHz): \delta 164.5 (d, \textsuperscript{2}J_{PC} = 22.8 Hz, C2), 139.3 (d, J = 10.2 Hz, C3, C3a, or C7a), 130.6 (C3, C3a, or C7a), 121.5, 119.8, 116.9, 116.7 (C4, C5, C6, and C7), 87.3 (d, \textsuperscript{3}J_{PC} = 11.2 Hz, C1), 84.7 (d, J_{PC} = 11.8 Hz, COD), 54.8 (NMe_{2}), 54.6 (COD), 32.8 (d, J_{PC} = 2.3 Hz, COD), 28.7 (COD), 26.4 (d, \textsuperscript{1}J_{PC} = 33.8 Hz, P(CHMe_{2})_{2}), 19.6 (P(CHMe_{2}Me_{2})_{2}), 19.1 (P(CHMe_{2}Me_{2})_{2}); \textsuperscript{31}P\{(\textsuperscript{1}H) NMR (C_{6}D_{6}, 202.5 MHz): \delta 25.0. Crystals suitable for single crystal X-ray diffraction analysis were grown from a concentrated toluene solution of 3-3 at room temperature.

Synthesis of (PPh_{2}Me)_{2}Rh(κ^{2}-P,N-2-2e) (3-5). A dark red solution of 2-7 (0.096 g, 0.20 mmol) in toluene (5 mL) was cooled to -35 °C after which PPh_{2}Me (0.19 mL, 0.99 mmol) was added via Eppendorf pipette. The solution immediately darkened to brown-red. The vial was sealed with a PTFE-lined cap and the mixture was left to magnetically stir for 36 h; \textsuperscript{31}P NMR analysis of the reaction at this stage confirmed the quantitative conversion of 2-7 to 3-5. The solvent was removed in vacuo and the dark brown solid was washed with pentane (3 × 2 mL). The resulting solid was dried in vacuo for 16 h to leave 3-5 as an analytically pure light brown powder (0.11 g, 0.14 mmol, 66%). Anal. calcd. for C_{43}H_{51}P_{3}N_{1}Rh_{1} (777.7 gmol^{-1}) (%): C 66.41; H 6.61; N 1.80. found: C 66.21; H 6.49; N 1.60. NB: Signals in the \textsuperscript{1}H NMR spectrum of 3-5 are broadened at 300 K, in keeping...
with the observed dynamic behavior of this complex (vide supra). Some $^{13}$C NMR resonances are also broadened, and thus the observation of the NMe$_2$ resonances in the $^{13}$C-$^1$H NMR spectrum of this complex was not possible. Data reported here were obtained at 300 K, unless otherwise indicated. $^1$H NMR (C$_6$D$_6$, 500.1 MHz): δ 7.84 (d, $^3$J$_{HH}$ = 7.6 Hz, 1H, C4-H), 7.73 (m, 1H, C5-H or C6-H), 7.59 (m, 1H, C6-H or C5-H), 7.51 (d, $^3$J$_{HH}$ = 7.5 Hz, C7-H), 7.39-7.26 (m, 5H, Ar-Hs), 7.16-6.92 (m, some resonances obscured by reference solvent, Ar-Hs), 6.18 (s, 1H, C1-H), 3.50-2.10 (very broad resonance at 300 K; upon cooling to 240 K, this resolved into two singlets at 3.34 ppm (3H, NMe$_2$) and 2.52 ppm (3H, NMe$_2$)), 3.00 (m, 1H, P(CHMe$_2$Me)$_2$)(CHMe$_2$Me$_2$), 2.79 (m, 1H, P(CHMe$_2$Me)$_2$)(CHMe$_2$Me$_2$), 1.58 (d, $^2$J$_{PH}$ = 6.2 Hz, 3H, P(C$_6$H$_5$)$_2$Me), 1.29-1.12 (m, 6H, P(CHMe$_2$Me)$_2$), 1.10 (d, $^2$J$_{PH}$ = 6.8 Hz, 3H, P(C$_6$H$_5$)$_2$Me), 0.95-0.83 (m, 6H, P(CHMe$_2$Me)$_2$); $^{13}$C-$^1$H NMR (C$_6$D$_6$, 125.8 MHz): δ 167.3 (C2), 147.6 (C3a or C7a), 144.1, 143.4 (P(C(CH)$_3$)$_2$Me)$_2$, 142.3 (C7a or C3a), 140.4, 139.4 (P(C(CH)$_3$)$_2$Me)$_2$, 133.8, 133.6, 132.9, 132.7, 132.1, 131.9, 131.8 (P(C(CH)$_3$)$_2$Me), 123.7 (C4), 121.5 (C5 or C6), 118.2, 118.1 (C7 and C6 or C7 and C5), 103.2 (C1), 37.3 (d, $^1$J$_{PC}$ = 112.3 Hz, C3), 27.7 (broad s, P(CHMe$_2$Me)$_2$)(CHMe$_2$Me$_2$), 26.9 (broad s, P(CHMe$_2$Me)$_2$)(CHMe$_2$Me$_2$), 22.3 (P(CHMe$_2$Me)$_2$), 21.5 (d, $^1$J$_{PC}$ = 20.9 Hz, P(C$_6$H$_5$)$_2$Me), 20.1, 20.0 (P(CHMe$_2$Me)$_2$), 14.5 (d, $^1$J$_{PC}$ = 23.1 Hz, P(C$_6$H$_5$)$_2$Me); $^{31}$P-$^1$H NMR (C$_6$D$_6$, 202.5 MHz): δ 35.8 (d of d of d, $^1$J$_{PRh}$ = 113.8 Hz, $^2$J$_{PaPb}$ = 31.6 Hz, $^2$J$_{PaPind}$ = 237.4 Hz, P(C$_6$H$_5$)$_2$Me, cis to N), 24.2 (d of d of d, $^1$J$_{PRh}$ = 189.8 Hz, $^2$J$_{PbPa}$ = 31.1 Hz, $^2$J$_{PbPind}$ = 26.6 Hz, P(C$_6$H$_5$)$_2$Me, trans to N), 15.6 (d of d of d, $^1$J$_{PRh}$ = 177.0 Hz, $^2$J$_{PindPb}$ = 26.0 Hz, $^2$J$_{PindPa}$ = 237.2 Hz, P(CHMe$_2$)$_2$).
[Cl(CO)Rh(κ²-P,N-2-2b)] (3-6). To a solution of 2-2a (0.050 g, 0.18 mmol) in THF (2 mL), a solution of [CO]RhCl]₂ (0.016 g, 0.091 mmol) in THF (1 mL) was added via Pasteur pipette. The clear yellow solution was magnetically stirred for 10 min, upon which K₂CO₃ (0.050 g, 0.36 mmol) was added. After magnetically stirring the heterogeneous mixture for 30 min, the slurry was filtered through celite to leave a clear orange filtrate. The solvent was removed in vacuo to leave an oily residue, from which some product was extracted into Et₂O (2 x 2 mL); orange crystals suitable for X-ray crystallographic analysis were obtained from this fraction. Additional product was obtained by dissolution of the remaining oily residue in benzene (2 mL), from which brown impurities were precipitated out by addition of pentane (1 mL) to leave a yellow solution. The solution was filtered through celite and the product was isolated by removal of the solvent in vacuo. The product was dried in vacuo 18 h (0.034 g, 0.077 mmol, 43%).

Anal. Calcd. for C₁₈H₂₆PNOCIRh (%): C 48.94, H 5.93, N 3.17. Found: C 49.07, H 6.26, N 3.29. 'H NMR (C₆D₆, 500.1 MHz): δ 7.11 - 7.06 (m, 2H, C5-H and C6-H), 7.03 (d, 3JHH = 6.8 Hz, 1H, C4-H), 7.00 (d, 3JHH = 6.8 Hz, 1H, C7-H), 2.59 (s, 6H, NMe₂), 2.46 (s, 2H, C1-H₂), 2.06 – 1.97 (m, 2H, P(CHMe₃Me₆)₂), 1.06 (d of d, 3JPH = 17.8 Hz, 3JHH = 6.9 Hz, 6H, P(CHMe₃Me₆)₂), 0.81 (d of d, 3JPH = 16.7 Hz, 3JHH = 6.9 Hz, 6H, P(CHMe₃Me₆)₂);

¹³C{¹H} NMR (C₆D₆, 125.8 MHz): δ189.7 (d of d, ¹JRhC = 73.2 Hz, ²JPC = 18.5 Hz, CO), 175.3 (d, J = 18.9 Hz, C2), 143.4 (C3a or C7a), 138.3 (C7a or C3a), 132.4 (d, ¹JPC = 29.2 Hz, C3), 126.8 (C5 or C6), 125.8 (C6 or C5), 124.9 (C7), 121.6 (C4), 48.8 (NMe₂), 29.8 (d, J = 10.2 Hz, C1), 26.5 (d, J = 30.8 Hz, P(CHMe₃Me₆)₂), 19.7 (d, ²JPC = 5.3 Hz, P(CHMe₃Me₆)₂), 19.5 (P(CHMe₃Me₆)₂); ³¹P{¹H} NMR (C₆D₆, 202.5 MHz): δ 72.2 (d, ¹JRhP = 161.5 Hz). IR (C₆H₆/ Csl) (cm⁻¹): 1977 (Rh(CO)Cl), 1459 (P-C).
[(CO)2Rh(k2-P,N-2-2b)][PF6] (3-7). [2-6a]PF6\(^{-}\) (0.054 g, 0.085 mmol) was dissolved in CH2Cl2 (4 mL) in a Schlenk flask equipped with a magnetic stir bar. The flask was transferred to a Schlenk line and the orange solution was degassed by three repeated cycles of freeze-pump-thaw. Magnetic stirring of the solution was initiated and the flask was backfilled with carbon monoxide (~1 atm). Within 30 sec, the solution turned bright yellow in color. After 90 min, the flask was purged for 20 min using N2(g) to remove CO(g) remaining in the headspace of the flask. The reaction vessel was transferred back to the glovebox whereupon pentane (2 mL) was added to cause precipitation of the fluffy yellow product from the reaction mixture. The solid product was isolated by filtration through a Büchner funnel equipped with a fine porosity filter paper. Additional product was isolated by concentrating the filtrate to approximately half the original volume in vacuo followed by adding a further aliquot of pentane (2 mL) to precipitate a second crop of product. This process was repeated until the filtrate was essentially colorless. All isolated yellow solid was combined and dried in vacuo 5 h to leave analytically pure 3-7 (0.033 g, 0.056 mmol, 66%). Anal. Calcd. for C19H26P2NO2F3Rh (%): C 39.39, H 4.52, N 2.42. Found: C 39.23, H 4.88, N 2.38. \(^1\)H NMR (CD2Cl2, 500.1 MHz): \(\delta\) 7.62 (m, 1H, C7-H), 7.46-7.44 (m, 3H, C4-H, C5-H, and C6-H), 3.79 (s, 2H, C1-H2), 3.30 (s, 6H, NMe2), 2.89-2.82 (m, 2H, P(CHMeaMeb)\(_2\)), 1.51 (d of d, \(^3\)J_{PH} = 19.4 Hz, \(^2\)J_{HH} = 7.0 Hz, 6H, P(CHMeaMeb)\(_2\)), 1.32 (d of d, \(^3\)J_{PH} = 18.1 Hz, \(^2\)J_{HH} = 7.0 Hz, 6H, P(CHMeaMeb)\(_2\)); \(^{13}\)C\(^{\text{\textsuperscript{1}}}\)H NMR (CD2Cl2, 125.8 MHz): \(\delta\) 175.7 (d, \(J = 16.5\) Hz, C2), 144.2 (d, \(J = 6.4\) Hz, C3a or C7a), 136.2 (C7a or C3a), 130.0 (d, \(^1\)J_{PC} = 34.0 Hz, C3), 127.9, 127.7, 122.2 (C4, C5, C6), 125.8 (C7), 54.8 (NMe2), 30.9 (d, \(J = 10.8\) Hz, C1), 26.1 (d, \(^1\)J_{PC} = 29.6 Hz, P(CH(MeaMeb)\(_2\)), 19.9 (P(CHMeaMeb)\(_2\) or P(CHMeaMeb)\(_2\)), 19.8 (d, \(^2\)J_{PC} = 3.7 Hz,
\( P(\text{CHMe}_2\text{Me}_b)_2 \) or \( P(\text{CHMe}_2\text{Me}_b)_2 \); \(^{31}\text{P} \{^1\text{H} \} \) NMR (CD\(_2\)Cl\(_2\), 202.3 MHz): \( \delta \) 62.7 (d, \(^1J_{\text{Rh-P}} = 123.5 \text{ Hz} \), \( P(\text{CHMe}_2\text{Me}_b)_2 \)), \(-144.5 \) (septet, \(^1J_{\text{PF-PF}} = 710.7 \text{ Hz} \), PF\(_6^-\)). IR (CH\(_2\)Cl\(_2\)/CsI) (cm\(^{-1}\)): 2100 (s), 2030 (s), (Rh(CO))\(_2\), 1990 (m), 1460 (P-C), 839 (PF\(_6^-\)).

**General Protocol for Hydrogenation Experiments.** The protocol used for hydrogenation reactions employing 0.5 mol% catalyst loading in CH\(_2\)Cl\(_2\) is provided as a representative procedure. A solution of catalyst compound in CH\(_2\)Cl\(_2\) (0.014 mmol in 7 mL to give a 0.002 M solution) was allowed to equilibrate for 5 min, at which point the alkene (2.8 mmol) was added by use of an Eppendorf pipette. The vial was then sealed and shaken vigorously. Subsequently, 1 mL aliquots of the mixture were placed in glass reactor cells, which were each equipped with a magnetic stir bar and sealed under nitrogen with a PTFE valve. The cells were transferred immediately to a Schlenk line and degassed by use of three freeze-pump-thaw cycles employing liquid nitrogen. Magnetic stirring of the solutions was initiated and the evacuated cells were backfilled with hydrogen gas (~1 atm, UHP grade). With the exception of the noted experiments in which the catalyst was not fully soluble, clear yellow homogeneous solutions were observed throughout. At the desired sampling time, the reactor cell was opened to air and 2 mL of hexanes (or pentane in the case of the hydrogenation of cyclohexene) was added via Pasteur pipette. The resultant slurries were then filtered through a short Al\(_2\)O\(_3\) column (2 cm) from which clear, colorless solutions eluted. These solutions were transferred to GC vials and sealed. Products of each reaction were identified by use of GC-MS and quantitative data were obtained from GC-FID analysis; tabulated data represent the average of at least two runs.
General Protocol for Hydrosilylation Experiments. The protocol used for these reactions employing 5.0 mol% catalyst loading (relative to Et$_3$SiH) in benzene with a styrene to silane ratio of 5:1 run at 60 °C is provided as a representative procedure. A solution of catalyst compound in benzene (0.0225 mmol in 4.5 mL to give a 0.005 M solution) was allowed to equilibrate for 5 min, at which point the alkene (2.25 mmol) was added by use of an Eppendorf pipette. The vial was then sealed and shaken vigorously. Subsequently, Et$_3$SiH (0.45 mmol) was added by use of an Eppendorf pipette to the reaction mixture, and the vial was then sealed and shaken as before. Aliquots (1 mL) of the mixture were placed in glass reactor cells, which were each equipped with a magnetic stir bar and sealed under nitrogen with a PTFE valve. The cells were transferred immediately to a Schlenk line and magnetic stirring of the solutions was initiated. At the desired sampling time, the reactor cell was opened to air and ~1 mL of pentane was added via Pasteur pipette. The resultant mixtures were then filtered through a short Al$_2$O$_3$ column (2 cm) from which clear, colorless solutions eluted. These solutions were transferred to GC vials and sealed. Products of each reaction were identified by use of GC-MS, while quantitative data were obtained from GC-FID analysis; tabulated data represent the average of at least two runs. Due to the complex nature of the product mixture that could be obtained from these experiments, each product was prepared independently and characterized by GC-MS and GC-FID to determine their retention times.$^{33b}$ These data were then used to identify which products were formed in the catalytic reactions.

Crystallographic Solution and Refinement Details. Crystallographic data (Table 3-2) were obtained at 193(±2) K on a Bruker PLATFORM/SMART 1000 CCD diffractometer using a graphite-monochromated Mo Kα ($\lambda = 0.71073$ Å) radiation, employing samples
that were mounted in inert oil and transferred to a cold gas stream on the diffractometer. Programs for diffractometer operation, data collection, data reduction, and absorption correction (including SAINT and SADABS) were supplied by Bruker. The structures were solved by use of direct methods and refined by use of full-matrix least-squares procedures (on $F^2$) with $R_1$ on the basis of $F_o^2 \geq 2\sigma(F_o^2)$ and $wR_2$ on the basis of $F_o^2 \geq -3\sigma(F_o^2)$. Anisotropic displacement parameters were employed throughout for the non-hydrogen atoms, and all hydrogen atoms were added at calculated positions and refined by use of a riding model employing isotropic displacement parameters on the basis of the isotropic displacement parameter of the attached atom. Structural disorder was noted during the refinement of [3-2h]$^+$PF$_6^-$, which was treated in a satisfactory manner by employing a model featuring two half-occupied formula units of the complex within the asymmetric unit. The crystallographically determined structures of the complexes reported in this chapter were generated as ORTEP diagrams.$^{52}$ Complete experimental details for these compounds are available through the Cambridge Crystallographic Database. Further crystallographic data are provided in Table 3-2.
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3.5 References and Endnotes


10. For the purposes of the discussions herein, formally zwitterionic complexes are defined as those species lacking conventional resonance structures that place an anionic charge onto one of the donor atoms of the ancillary ligand.


16. The related degradation of a (phosphino)borate ligand has also been observed in the context of Cu(I) chemistry: Thomas, J. C.; Peters, J. C. *Polyhedron* **2004**, *23*, 2901.


23. The shortest cation-anion contacts: (a) [2-6a]+BF4−, 2.78 Å between F and C(1)H2; (b) [3-2b]+SO3CF3−, 2.44 Å between F and C(1)H2; (c) [3-2b]+PF6−, 2.48 Å between F and C4-H.


27. A combination of 6 mg complex and 0.8 mL solvent was utilized in these qualitative visual solubility tests. The solubility of [2-6a]+X and [3-2b]+X complexes was not found to vary significantly for X = SO3CF3, BF4, and PF6.

28. Spectroscopic data for 3-4: 1H NMR (CD2Cl2) δ: 7.24 (d, 3JHH = 8.0 Hz, 1H, C4-H or C7-H), 7.18 (d, 3JHH = 6.50 Hz, 1H, C7-H or C4-H), 7.02 (t, 3JHH = 7.8 Hz, 1H, C5-H or C6-H), 6.76 (t, 3JHH = 7.3 Hz, 1H, C6-H or C5-H), 4.11 (br m, 2H, COD), 3.91 (br m, 2H, COD), 3.51 (s, 2H, C1(H)2 or N-CH2-Br), 3.47 (s, 2H, N-CH2-Br or C1(H)2), 3.18-2.98 (m, 5H, NMe and P(CHMe2Me)2), 2.13-2.05 (m, 4H, COD), 1.85 (m, 2H, COD), 1.74 (m, 2H, COD), 1.27 (d of d, 6H, 3JHH = 7.0 Hz, 3JPH = 15.0 Hz, P(CHMe2Me)2), 1.14 (d of d, 6H, 3JHH = 7.0 Hz, 3JPH = 15.0 Hz, P(CHMe2Me)2). 31P{1H} NMR (CD2Cl2) δ: 13.7.


33. (a) A similar dynamic process has been proposed to account for the temperature-dependent $^1$H NMR lineshape changes observed for $[(COD)M(\kappa^2-1-P(S)Pr_2-2-NMe_2$-indene)]$^+BF_4^-$ (M = Rh, Ir), the analysis of which also yielded $\Delta G^{\ddagger,T}$ of ca. 14 kcal/mol: Wechsler, D.; Myers, A.; McDonald, R.; Ferguson, M. J.; Stradiotto, M. *Inorg. Chem.* 2006, 45, 4562; (b) see reference 25 within this *Inorg. Chem.* paper which describes the preparation and identification of the hydrosilylation and dehydrogenative silylation products.


35. A comparative IR spectroscopic study of an alternative class of structurally related cationic and formally zwitterionic Rh complexes has been reported by Betley and Peters; see references 15b,c herein.


40. (a) For styrene hydrogenation reactions employing either $[2-6a]^+$PF$_6^-$ or 2-7 as a catalyst, <1% conversion was observed after 0.5 h, and in the case of reactions employing 5.0 mol% catalyst loadings, only 5-10% conversion was achieved after 4 h. (b) Initial rates (TOF) are defined as (moles ethylbenzene produced/moles catalyst)/time, and are measured at 0.25 h for reactions employing 1.0 mol% catalyst.
41. While the hydrogenation of alkenes catalyzed by \([\text{COD})\text{Ir}(\kappa^2-\text{Pt}_{2}\text{CH}_2\text{CH}_2\text{NMe}_2)\text{BF}_4\] has been reported, the data provided do not allow for a direct comparison with \([3-2b]\text{BF}_4\]: Estebuelas, M. A.; López, A. M.; Oro, L. A.; Pérez, A.; Schulz, M.; Werner, H. *Organometallics* 1993, 12, 1823.


44. For a detailed discussion of the differences in Pt- and Rh-catalyzed hydrosilylation mechanisms, see: Sakaki, S.; Sumimoto, M.; Fukuhara, M.; Sugimoto, M.; Fujimoto, H.; Matsuzaki, S. *Organometallics* 2002, 21, 3788.


Chapter 4: Synthesis and Crystallographic Characterization of New Mn(I) Complexes of Donor-Functionalized Indenes

4.1 Introduction

With the goal of identifying new classes of transition metal complexes that are capable of mediating synthetically useful chemical transformations, the Rh(I) and Ir(I) coordination chemistry and catalytic potential of the corresponding metal complexes have been explored for complexes featuring new ligands derived from 2-dimethylaminoindene, including the P,N ligand 2-2, as discussed in Chapters 2 and 3. Other members of the Stradiotto research group have focused on exploring the coordination behavior and reactivity properties of metal complexes supported by an oxidized version of 2-2, such as the P(S),N ligand, 4-1 (eq 4-1).\(^1\) These new multifunctional ligands incorporate hard (N) and soft (P or S) donor fragments fused to an unsaturated carbocyclic backbone,\(^2\) in anticipation that such a combination of chemically diverse donor groups will allow for the binding of a range of metal fragments, as well as allowing for the rational construction of heteropolynuclear metal complexes.\(^3\)

![Diagram](image)

In the synthetic survey involving Rh(I) that was discussed in Chapters 2 and 3, it was established that 2-2 can be used in the preparation of cationic \(\kappa^2-P,N\)-Rh(I) complexes, as well as the zwitterionic complex, 2-7, \(\kappa^2-(P,N-2-2e)\)Rh(COD).
Interestingly, in the latter species, the carbocyclic backbone serves as an anionic charge reservoir, rather than as a locale for metal binding. In an attempt to undertake a thorough examination of the coordination properties of the ligands 2-2, a synthetic survey aiming to incorporate metal fragments from across the transition series is ongoing; in the context of Mn(I), work in the Stradiotto group has demonstrated that 4-1b-Li reacts cleanly with BrMn(CO)₅ to yield η⁵-(4-1b)Mn(CO)₃.¹ Building upon these results, the progress towards developing further the Mn(I) coordination chemistry of 2-2 and related ligands is the topic of this chapter.

4.2 Results and Discussion

4.2.1 The Synthesis of κ²-P,N-Mn Complexes

In light of the established ability of coordinatively and electronically unsaturated Mn(CO)₅ complexes to bind and/or activate E-H bonds (E = H, B, C, Si, etc.),⁴ five-coordinate Mn cations supported by 2-2a or 2-2b were identified as appealing synthetic targets that might also function as precursors to the 16-electron zwitterion, κ²-(P,N-2-2c)Mn(CO)₃.⁵ Treatment of 2-2a with BrMn(CO)₅ provides 4-2 as an analytically pure orange solid in 73% isolated yield (Scheme 4-1). The single-crystal X-ray structure of 4-2·0.5C₇H₈ is presented in Figure 4-1 and relevant crystallographic parameters are collected in Table 4-1, which appears in Section 4.4 after details of the crystallographic experiments. Both NMR spectroscopic and X-ray crystallographic data confirm that 2-2a has undergone a structural rearrangement, such that the ligand 2-2b is coordinated to Mn through the P- and N-donors in 4-2, similar to what was observed in the case of Rh(I) (Chapter 2 and 3). Although an analogous crystallographically characterized κ²-
(P,N)Mn(I) chelate complex has yet to be identified from the literature, the interatomic distances within the Mn coordination sphere in 4-2 are comparable to reported values. In keeping with the greater trans-influence of P-donors relative to N-donors, the Mn-C12 distance (trans to P) in 4-2 is lengthened relative to the Mn-C13 distance (trans to N).

Scheme 4-1. Reagents: (i) BrMn(CO)₅; (ii) AgBF₄; (iii) AgSO₃CF₃; (iv) BrMn(CO)₅/AgBF₄.

Figure 4-1. The crystallographically determined structure of 4-2•0.5C₇H₈, shown with 50% displacement ellipsoids. Selected hydrogen atoms and the toluene solvate have been omitted for clarity. Selected bond lengths (Å) for 4-2•0.5C₇H₈: Mn-Br 2.5218(8); Mn-P 2.346(1); Mn-N 2.211(4); Mn-C11 1.805(6); Mn-C12 1.877(5); Mn-C13 1.791(5); C1-C2 1.505(6); C2-C3 1.340(5); N-C2 1.457(5); P-C3 1.803(4).
In an attempt to access cationic, 16-electron Mn(I) complexes, compound 4-2 was treated with either AgBF₄ or AgSO₂CF₃ in toluene (Scheme 4-1). Monitoring $^{31}$P NMR) of the reaction mixtures allowed for the loss of the signal attributable to 4-2 (59.8 ppm) and the appearance of a new signal associated with either 4-3a (63.5 ppm) or 4-3b (62.6 ppm) to be observed; these complexes were subsequently isolated as analytically pure yellow solids in 62% and 65% yield, respectively. Crystallographic analysis of 4-3a·0.5C₇H₈ and 4-3b (Figures 4-2 and 4-3; Table 4-1) revealed both of these complexes to be neutral, six-coordinate 18-electron species, in which the counteranion is coordinated directly to the Mn center. Although Mn(I) complexes featuring either inner-sphere tetrafluoroborate or triflate complexes are known,⁷ no crystallographically characterized compounds of this type have been reported previous to these complexes. Since the geometric features of the three crystallographically independent molecules of 4-3a are similar, the following discussion will be limited to the independent molecule that is depicted in Figure 4-2. The Mn-F1a distance in 4-3a (2.070(3) Å) is only slightly elongated relative to the corresponding distance in FMn(dppe)(CO)₃ (2.028(2) Å).⁸ As well, the B-F_bridging distance (1.465(7) Å) in 4-3a is significantly longer than the corresponding B-F_terminal distances (ave ≈ 1.33 Å), resulting in a distorted tetrahedral geometry at boron. Taken collectively, these metrical parameters suggest that 4-3a is perhaps most appropriately described as a MnF•BF₃ adduct, which can be compared to other crystallographically characterized MF•BF₃ species.⁹ The observation of two resonances at -152.3 and -293.5 ppm (~3:1 ratio) in the $^{19}$F NMR spectrum of 4-3a suggests that this structural motif is also maintained in a 1:1 toluene/THF solution.⁷e,¹⁰
For comparative purposes, the 18-electron cationic species \([\kappa^2-P,N-(2-2b)\text{Mn(CO)}_4]^+\)BF\(_4^-\) (4-4) was also prepared and crystallographically characterized (Figure 4-4; Table 4-1). In contrast to 4-3a, complex 4-4 exhibits a single \(^{19}\text{F}\) NMR resonance at -153.1 ppm in dichloromethane. Moreover, the \(^{11}\text{B}\) NMR signal for the coordinated tetrafluoroborate in 4-3a (0.31 ppm, \(\Delta v_{1/2} = 63\) Hz) is broadened relative to the signal observed for the uncoordinated anion (-0.84 ppm, \(\Delta v_{1/2} = 29\) Hz) in 4-4, in keeping with the reduced local symmetry at the boron center in 4-3a.

![Crystal structure of 4-3a•0.5C\(_7\)H\(_8\)](image)

**Figure 4-2.** The crystallographically determined structure of 4-3a•0.5C\(_7\)H\(_8\), shown with 50% displacement ellipsoids (only one of three crystallographically independent molecules is shown). Selected hydrogen atoms and the toluene solvate have been omitted for clarity. Selected bond lengths (Å) for 4-3a•0.5C\(_7\)H\(_8\): Mn1a-P1a 2.340(1); Mn1a-N1a 2.175(4); Mn1a-F1a 2.070(3); Mn1a-C11a 1.857(5); Mn1a-C12a 1.808(5); Mn1a-C13a 1.776(5); C1a-C2a 1.523(6); C2a-C3a 1.336(6); N1a-C2a 1.454(5); P1a-C3a 1.808(4); B1a-F1a 1.465(7); B1a-F2a 1.35(1); B1a-F3a 1.330(8); B1a-F4a 1.323(9).

While a crystallographically characterized inner-sphere Mn(I) triflate complex from the literature was not found, the Mn-O1 distance (2.094(2)Å) in 4-3b can be compared with the related distance (2.04(1) Å) in (F\(_5\)TeO)Mn(CO)\(_5\). The Mn-P, Mn-N, and Mn-C distances in 4-3a•0.5C\(_7\)H\(_8\), 4-3b, and 4-4 are in general similar to those found in 4-2•0.5C\(_7\)H\(_8\), while the carbonyl stretching bands in the IR spectrum of 4-2 (1895,
1926, and 2013 cm$^{-1}$) appear at lower energy than those observed in the IR spectra of 4-3a (1912, 1952, and 2038 cm$^{-1}$) and 4-3b (1916, 1957, and 2036 cm$^{-1}$),$^{12}$ in keeping with the greater electron-withdrawing power of the tetrafluoroborate and triflate anions relative to bromide.

**Figure 4-3.** The crystallographically determined structure of 4-3b, shown with 50% displacement ellipsoids. Selected hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) for 4-3b: Mn-P 2.3419(6); Mn-N 2.209(2); Mn-O1 2.094(2); Mn-C11 1.859(2); Mn-C12 1.806(2); Mn-C13 1.779(3); C1-C2 1.516(3); C2-C3 1.342(3); N-C2 1.450(3); P-C3 1.805(2).

**Figure 4-4.** The crystallographically determined structure of 4-4, shown with 50% displacement ellipsoids. Selected hydrogen atoms and the BF$_4^-$ counterion have been omitted for clarity. Selected bond lengths (Å) for 4-4: Mn-P 2.3340(7); Mn-N 2.196(2); Mn-C11 1.855(3); Mn-C12 1.803(3); Mn-C13 1.858(3); Mn-C14 1.879(3); C1-C2 1.509(3); C2-C3 1.341(3); N-C2 1.460(3); P-C3 1.789(2).
4.2.2 Reactivity of $\kappa^2-P,N$-Mn Complexes Towards Neutral Donors

In an effort to assess the lability of the coordinated anions in 4-3a and 4-3b, these complexes were treated with various two-electron donors (L). Although no changes were observed in the $^{31}$P{${}^1$H} NMR spectra of either 4-3a or 4-3b upon dissolution in THF, the addition of one equiv of PPh$_3$ to 4-3a generated a complex mixture of phosphorus-containing products. Compound 4-3b did not react with PPh$_3$ (one or two equiv) at ambient temperature, and upon heating at 60 °C the only new $^{31}$P NMR signals observed were those attributable to 2-2a (19.6 ppm) and 2-2b (-2.9 ppm). Complex reactivity was also observed when solutions of 4-3a or 4-3b were treated with either CH$_3$CN or 4-dimethylaminopyridine. In contrast, it is known that (F$_3$CSO$_2$O)Mn(CO)$_5$ reacts cleanly and rapidly with a variety of two-electron donors including THF, CH$_3$CN, and P(nBu)$_3$ to yield the corresponding [LMn(CO)$_5$]$^+$SO$_3$CF$_3$$^-$ salts.$^7$ Given that treatment of (F$_3$BF)Mn(CO)$_5$ with 2-2a successfully produces 4-4, it is possible that steric factors inhibit the clean formation of the analogous [$\kappa^2-P,N$-(2-2b)Mn(CO)$_5$L]$^+$X$^-$ complexes upon addition of L to either 4-3a or 4-3b. An additional attempt to prepare a cationic, five-coordinate Mn(I) species by treatment of 4-2 with Li(2EtO)$_2$B(C$_6$F$_5$)$_4$ generated a complex mixture of products, including 2-2a and 2-2b. Moreover, efforts to prepare the coordinatively unsaturated zwitterion, $\kappa^2-P,N$-(2-2e)Mn(CO)$_3$, via treatment of 4-2, 4-3a, or 4-3b with either nBuLi, NEt$_3$, or K$_2$CO$_3$ were unsuccessful.

4.2.3 Developing Synthetic Routes to $\eta^5$-(2-2e)Mn(CO)$_3$

Donor-functionalized planar-chiral cymantrene (i.e. $\eta^5$-CpMn(CO)$_3$) derivatives are emerging as effective ancillary supports for a variety of metal-mediated asymmetric
transformations. In an effort to prepare $\eta^5$-(2-2e)Mn(CO)$_3$, BrMn(CO)$_3$ was treated with 2-2e-Li in toluene (Scheme 4-2). Analysis of the crude reaction mixture ($^{31}$P NMR) after 20 h revealed the formation of multiple phosphorus-containing products, including those giving rise to resonances at 60 ppm (4-2, ~20%), 53 ppm (~70%), -2 ppm (2-2, ~5%), and -6 ppm (~5%). A similar product distribution was obtained in toluene and control experiments ruled out hydrolysis of 2-2e-Li by trace moisture. Although the major product of this reaction could not be isolated in pure form, storage of this reaction mixture at -35 °C for an extended period (>10 months) resulted in the formation of a small quantity of crystalline material that gives rise to $^{31}$P resonances at 69 and 217 ppm. The lower frequency resonance coincides with the signal observed for the cationic species, 4-4. This structural formulation was further substantiated by data obtained from a single-crystal X-ray diffraction study; the crystal structure of this complex (4-5*0.5C$_7$H$_8$) is presented in Figure 4-5, and relevant crystallographic data are provided in Table 4-1.

The metrical parameters within the cationic portion of 4-5 are identical to those found in 4-4 and do not warrant further commentary. The $[\text{Mn}_2(\text{CO})_8(\mu-P\text{Pr}_2)]^+$ counteranion in 4-5 accounts for the observed high frequency $^{31}$P NMR signal, and can be compared with the analogous $[\text{Mn}_2(\text{CO})_8(\mu-P\text{Ph}_2)]^+$ anion reported by Mays and co-workers. Efforts to isolate more of 4-5 from this reaction mixture were unsuccessful, and thus additional characterization data for this species can not be provided. Given the complexity of the reaction mixture that produced 4-5, and the lack of supporting experimental data, a detailed mechanistic route to 4-5 can not be proposed. However, it is possible to envisage the initial formation of the zwitterionic species, $\kappa^2-(P,N-2-2e)$Mn(CO)$_4$ (by analogy with 2-7), which decomposes to yield a dimeric form of 2-2.
(vide infra) along with the unsaturated Mn₂(CO)₈ fragment; the latter could ultimately go on to form the observed [Mn₂P]⁻ counteranion, via some ill-defined P-C bond activation process involving a free or ligated form of 2-2. Although slow hydrolysis by trace moisture over extended periods can not be ruled out as being involved in the formation of 4-5, it is worthy of mention that the highly air- and moisture-sensitive 2-2e-Li was not hydrolyzed under analogous experimental conditions.

\[
\text{BrMn(CO)₅} \xrightarrow{2-2e-Li} 4-2 + \begin{array}{c}
\text{\textbf{Scheme 4-2. Formation of 4-5}} \\
+ \text{other P-containing products}
\end{array}
\]

\[
\text{Figure 4-5. The crystallographically determined structure of the cation (left) and the anion (right) in 4-5•0.5C₇H₈, shown with 50% displacement ellipsoids. Selected hydrogen atoms and the toluene solvate have been omitted for clarity. Selected bond lengths (Å) for 4-5•0.5C₇H₈: Mn1-P1 2.3373(8); Mn1-N1 2.195(2); Mn1-C11 1.856(3); Mn1-C12 1.856(3); Mn1-C13 1.816(3); Mn1-C14 1.777(3); N-C2 1.454(3); P-C3 1.797(3); Mn2-Mn3 2.8472(6); Mn2-P2 2.2728(8); Mn3-P2 2.2571(8).}
\]
So as to circumvent the use of aggressive lithium-based ligand transfer reagents such as 2-2e-Li, a silylated derivative of 2-2 was targeted in anticipation that treatment with BrMn(CO)₅ would result in loss of bromosilane, thus directing metal coordination to the carbocyclic ring to give η⁵-(2-2e)Mn(CO)₃.¹⁷ Treatment of 2-1b-Li with ClSiMe₃ provided 4-6 in 93% isolated yield as an analytically pure brown solid, which in turn was lithiated followed by quenching with ClPr₂ (Scheme 4-3). Analysis of the resulting product mixture (¹H and ³¹P NMR) confirmed the consumption of the starting materials, and the two new ³¹P NMR signals observed at 11.8 and -3.2 ppm are tentatively assigned to the isomers 4-7a/ 4-7b.

![Scheme 4-3](image)

Scheme 4-3. Reagents: (i) ClSiMe₃; (ii) (a) nBuLi, (b) ClPr₂; (iii) BrMn(CO)₅

To a solution of 4-7a/ 4-7b was added BrMn(CO)₅, and the progress of the reaction was monitored by use of ³¹P NMR techniques; after 2 h, multiple phosphorus-containing species were observed in solution, with no high-frequency resonances that could correspond to η⁵-(2-2e)Mn(CO)₃ (vide infra). However, after a total of 18 h a yellow solid precipitated from the reaction mixture, which in turn was isolated (27 % yield) and subsequently identified as 4-8 on the basis of NMR spectroscopic, X-ray
crystallographic, and other characterization data. The crystallographically determined structure of 4-8 is shown in Figure 4-6, and relevant crystallographic data are listed in Table 4-1. The metrical parameters within the Mn coordination sphere of 4-2 are quite similar to those observed for the silylated analogue, 4-8. Similarly, the elongated Si-C\text{indenyl} distance (1.954(3) Å) relative to the other Si-C distances (ave ~ 1.86 Å) in 4-8 is in keeping with trends observed in crystallographically characterized indenylsilanes.\textsuperscript{18}

Compound 4-8 represents one of two possible geometric isomers, with respect to the relative orientation of the SiMe\textsubscript{3} fragment and the Br atom. While the other isomer may be present in the crude reaction mixture, it is plausible that the syn-geometry exhibited by 4-8 is in fact the preferable one, with the trans-disposition of the silyl fragment, the NC(15)H\textsubscript{3} group, and the bromide minimizing unfavorable steric interactions.

\textbf{Figure 4-6.} The crystallographically determined structure of 4-8, shown with 50% displacement ellipsoids. The minor component of the disordered isopropyl carbon atom and selected hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) for 4-8: Mn-Br 2.5216(4); Mn-P 2.3516(7); Mn-N 2.211(2); Mn-C8 1.834(3); Mn-C9 1.792(3); Mn-C10 1.791(3); Si-C1 1.954(3); C1-C2 1.495(3); C2-C3 1.354(3); N1-C2 1.468(3); P-C3 1.801(2).

Given the preference of Mn to coordinate to the P-donor fragment in 2-2 and related ligands, alternative synthetic routes to η\textsuperscript{5}-(2-2e)Mn(CO)\textsubscript{3} were pursued, involving
incorporation of the η⁵-Mn(CO)₃ fragment into the 2-dimethylaminoindenyl framework, followed by the introduction of the diisopropylphosphino group. Treatment of 2-1b-Li with BrMn(CO)₅ provided 4-9 (Scheme 4-4) in 41% isolated yield. The apparent C₅ symmetry observed in the crystallographically determined structure of 4-9 (Figure 4-7, Table 4-1) is in agreement with the solution ¹H and ¹³C NMR spectral data obtained for this complex.

**Scheme 4-4.** Reagents: (i) BrMn(CO)₅; (ii) (a) nBuLi, (b) CIP'Pr₂; (iii) (a) nBuLi, (b) BrMn(CO)₅, (c) CIP'Pr₂

As has been observed for other 2-aminobenzocymantrenes,¹ᵇ,¹⁴ bonding between the Mn(CO)₃ fragment and the indenyl group in 4-9 deviates significantly from ideal η⁵-coordination, with the Mn-C2 distance being significantly longer than the other four Mn-Cᵢ₆ndenyl distances. Associated with this structural distortion is the fact that the carbon atoms within the C₅ portion of the indenyl ring are not co-planar; the ‘hinge angle’ (i.e. the difference between the planes defined by {C1, C3, C7a, C3a} and {C1, C2, C3}) in 4-9 is 10.0(2)°, whereas the ‘fold angle’ (i.e. the difference between the planes defined by the C₅ and C₆ rings) is 3.8(1)°.¹⁵ As well, despite the fact that the NMe₂ in 4-9 is

138
pyramidal ($\Sigma$angle at N ~ 351°), the rather short N-C$_{indeny}$ distance (1.368(2) Å) indicates partial conjugation between the nitrogen lone pair and the indeny system.

**Figure 4-7.** The crystallographically determined structure of 4-9, shown with 50% displacement ellipsoids. Selected hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) for 4-9: Mn-C1 2.148(1); Mn-C2 2.248(1); Mn-C3 2.146(2); Mn-C3a 2.179(1); Mn-C7a 2.183(1); N-C2 1.368(2); N-C8 1.457(2); N-C9 1.457(2).

In an attempt to install the P-donor fragment, 4-9 was treated with nBuLi (at -78 °C) and subsequently ClP'Pr$_2$. Unfortunately, analysis of the crude reaction mixture ($^{31}$P NMR) revealed the formation of 2-2a, 2-2b and numerous other phosphorus-containing products, with no high-field resonances corresponding to the target compound. In a final attempt to prepare $\eta^5$-(2-2e)Mn(CO)$_3$, 4-6b-Li was sequentially treated with BrMn(CO)$_3$ and ClP'Pr$_2$. Once again, the $^1$H and $^{31}$P NMR spectra of the complex product mixture formed showed no sign of the target compound, $\eta^5$-(2-2e)Mn(CO)$_3$. Storage of this reaction mixture at -35 °C resulted in the formation of a minute quantity of crystalline material, whose identity as rac-4-10 was confirmed by a single-crystal X-ray diffraction study (Figure 4-8, Table 4-1). The decomposition of indeny metal complexes to yield 1,1'-biindenones has been observed previously.
On the basis of the numerous unsuccessful attempts to prepare $\eta^5$-(2-2)Mn(CO)$_3$ via ligand 2-2 or through methods attempting to add the P'Pr$_2$ functionality after installing the $\eta^5$-Mn(CO)$_3$ fragment, interest was shifted to examine the utility of the racemic P(S)$_2$N-substituted benzocymantrene $\eta^5$-(4-1b)Mn(CO)$_3$ as a precursor to $\eta^5$-(2-2e)Mn(CO)$_3$. This vein of research, conducted by another student in the Stradiotto group, has proven successful; in this case, quantitative conversion to $\eta^5$-(2-2e)Mn(CO)$_3$ was achieved by heating a toluene solution of $\eta^5$-(4-1b)Mn(CO)$_3$ and Cl$_3$SiSiCl$_3$ at 85 °C for 14 d (eq 4-2). The complexity of the reaction mixtures discussed above for various attempts to prepare $\eta^5$-(2-2e)Mn(CO)$_3$ are in stark contrast to the nearly quantitative yield of $\eta^5$-(4-1b)Mn(CO)$_3$ that is obtained from the reaction of 4-1b-Li with BrMn(CO)$_2$ and subsequent deprotection of the phosphine-sulfide fragment.
4.3 Summary and Conclusions

Although isolable five-coordinate, 16-electron $\kappa^2-(P,N)$Mn(l) cations supported by 2-2 and related ligands remain elusive, successful preparation and structural characterization of the unusual six-coordinate, 18-electron Mn(l) species 4-3a and 4-3b, which feature inner-sphere tetrafluoroborate and triflate ligands, has been achieved. The results described herein also indicate that the coordination chemistry of 2-2 and related ligands with Mn(CO)$_n$ fragments is dominated by the formation of $\kappa^2-(P,N)$ complexes. It appears that the preparation of $\eta^5$-Mn(CO)$_3$ derivatives of 2-dimethylaminoindenes is only viable in the absence of an adjacent P-donor fragment (as in the synthesis of 4-9), or if a neighboring P-donor fragment is rendered unavailable for binding (as in the sequential conversion of 4-1a to $\eta^5$-(4-1b)Mn(CO)$_3$, and then to $\eta^5$-(2-2e)Mn(CO)$_3$).

Ongoing research by other members of the Stradiotto group targets the resolution of the planar chiral $\eta^5$-(2-2e)Mn(CO)$_3$ and related ancillary ligands, as well as the development of heterobimetallic complexes and their use in catalysis.
4.4 Experimental Section

General Considerations. See Section 2.5 and 3.4 for a description of general experimental conditions. Any changes or additions to those procedures are described here: Purification of CH$_3$CN was achieved by refluxing over CaH$_2$ for 4 d under N$_2$. All commercial reagents were obtained from Aldrich and were used as received, with the exception that BrMn(CO)$_5$, AgSO$_3$CF$_3$, and AgBF$_4$ were dried in vacuo for 12 h prior to use, and Li(EOF)$_2$B(C$_6$F$_5$)$_3$ was obtained from Boulder Scientific. Compound 2-1$^{22}$ and $\eta^5$-(4-1b)Mn(CO)$_3$$_{1b}$ were prepared employing literature procedures. Compounds 2-2 and 2-2e-Li were prepared as described in Chapter 2. All $^1$H, $^{11}$B, $^{13}$C, $^{19}$F, and $^{31}$P NMR data were collected at 300 K on a Bruker AV-500 spectrometer operating at 500.1, 160.5, 125.8, 470.6, and 202.5 MHz (respectively) with chemical shifts reported in parts per million downfield of SiMe$_4$ (for $^1$H and $^{13}$C), 85% H$_3$PO$_4$ in water (for $^{31}$P), CFCl$_3$ (for $^{19}$F), or BF$_3$ in diethyl ether (for $^{11}$B, with peak width at half height following the reported chemical shift). IR spectra were collected on a Bruker VECTOR 22 FT-IR instrument, employing Nujol mulls.

Synthesis of $\kappa^2$-(P,N-2-2b)Mn(CO)$_3$Br (4-2): To a magnetically stirred solution of 2-2a (0.17 g, 0.62 mmol) in THF (1.5 mL) was added a slurry of BrMn(CO)$_5$ (0.17 g, 0.62 mmol) in THF (2 mL) via pipette. The reaction mixture was left to stir for 24 h during which the mixture became mostly homogeneous. Analysis of the crude reaction mixture ($^{31}$P NMR) confirmed both the consumption of 2-2a, and the quantitative formation of a single phosphorus-containing species at 59.8 ppm. The reaction mixture was then filtered through Celite and the resulting dark orange solution was evaporated, leaving 4-2 as an analytically pure orange powder (0.22 g, 0.45 mmol, 73%). Crystals of
4-2·0.5C7H8 suitable for single-crystal X-ray diffraction analysis were grown from toluene at -35 °C. Anal. Calcd. for C26H26O3PNNMnBr (%): C: 48.60, H: 5.30, N: 2.83; Found: 48.44, H: 4.94, N: 2.67. 1H NMR (C6D6): δ 7.15-6.99 (m, 4H, Ar-Hs), 2.72 (s, 3H, NMea), 2.62-2.55 (m, 1H, P(CHMeaMeb)), 2.46 (s, 2H, CH2), 2.42 (s, 3H, NMeb), 2.35 (m, 1H, P(CHMeaMeb)), 1.67 (d of d, 3JPH = 17.3 Hz, 3JHH = 6.8 Hz, 3H, P(CHMeaMeb)), 1.45 (d of d, 3JPH = 14.0 Hz, 3JHH = 7.0 Hz, 3H, P(CHMeaMeb)), 1.30 (d of d, 3JPH = 16.3 Hz, 3JHH = 6.8 Hz, 3H, P(CHMeaMeb)), 0.92 (d of d, 3JPH = 14.7 Hz, 3JHH = 7.1 Hz, 3H, P(CHMeaMeb)); 13C{1H} NMR (C6D6): δ 174.4 (d, 2JPC = 19.8 Hz, C2), 143.0 (C7a), 140.5 (C3a), 133.1 (d, 1JPC = 21.7 Hz, C3), 127.0, 125.9, 124.7, 122.3 (C4, C5, C6, C7), 58.5 (NMeb), 54.3 (NMea), 31.8 (d, 1JPC = 22.0 Hz, P(CHMeaMeb)), 30.8 (d, 3JPC = 9.0 Hz, C1), 30.4 (d, 1JPC = 24.0 Hz, P(CHMeaMeb)), 22.4 (P(CHMeaMeb)), 20.9 (P(CHMeaMeb)), 19.9 (d, 2JPC = 6.0 Hz, P(CHMeaMeb)), 19.5 (P(CHMeaMeb)); 31P{1H} NMR (C6D6): δ 59.8; FTIR (cm⁻¹) ν(CO): 2013, 1926, 1895.

Synthesis of κ²-(P₂N-2-2b)Mn(CO)₃BF₃ (4-3a): To a magnetically stirred solution of 4-2 (0.025 g, 0.050 mmol) in toluene (3 mL), was added a slurry of AgBF₄ (0.010 g, 0.051 mmol) in toluene (1 mL) via pipette. A clear yellow solution resulted, followed by immediate development of a white precipitate. The mixture was stirred for 5 min and then was filtered through Celite to remove the precipitated material. A 31P NMR spectrum of the filtered solution revealed formation of a single new phosphorus-containing product at 63.5 ppm. Solvent and other volatile materials were then removed in vacuo to yield 4-3a as an analytically pure yellow powder (0.015 g, 0.031 mmol, 62%). Crystals of 4-3a suitable for single crystal X-ray diffraction analysis were grown from a concentrated toluene solution at room temperature. Anal. Calcd. For C26H26O3PNNMnBF₄ (%): C 47.93;
H 5.23; N 2.79. Found: C 47.91; H 5.41; N 2.95. $^1$H NMR (CD$_2$D$_6$): δ 7.32-6.97 (m, 4H, Ar-H$_8$), 2.48 (s, 2H, C1-H$_2$), 2.44 (s, 3H, NMe$_a$), 2.40 (s, 3H, NMe$_b$), 2.29-2.24 (m, 2H, P(CHMe$_2$)$_2$), 1.49 (d of d, $^3$J$_{PH}$ = 17.6 Hz, $^3$J$_{HH}$ = 6.5 Hz, 3H, P(CHMe$_a$Me$_b$)), 1.20 (d of d, $^3$J$_{PH}$ = 17.1 Hz, $^3$J$_{HH}$ = 6.6 Hz, 3H, P(CHMe$_c$Me$_d$)), 1.04 (d of d, $^3$J$_{PH}$ = 15.2 Hz, $^3$J$_{HH}$ = 6.9 Hz, 3H, P(CHMe$_a$Me$_b$)), 0.80 (d of d, $^3$J$_{PH}$ = 15.3 Hz, $^3$J$_{HH}$ = 6.8 Hz, 3H, P(CHMe$_c$Me$_d$)); $^{13}$C{${^1}$H} NMR (CD$_2$D$_6$): δ 220.7 (CO), 174.9 (d, $^2$J$_{PC}$ = 19.7 Hz, C2), 143.2 (d, $^1$J$_{PC}$ = 4.6 Hz, C3a or C7a), 139.2 (C7a or C3a), 132.2 (d, $^1$J$_{PC}$ = 23.4 Hz, C3), 127.2, 126.5, 124.9, 121.7 (C4, C5, C6, C7), 57.0 (NMe$_a$), 52.7 (NMe$_b$), 30.9 (d, $^3$J$_{PC}$ = 9.1 Hz, C1), 29.8 (d, $^1$J$_{PC}$ = 19.8 Hz, P(CHMe$_c$Me$_d$)), 28.6 (d, $^1$J$_{PC}$ = 27.5 Hz, P(CHMe$_a$Me$_b$)), 20.3 (d, $^2$J$_{PC}$ = 5.0 Hz, P(CHMe$_a$Me$_b$)), 20.0 (d, $^2$J$_{PC}$ = 5.8 Hz, P(CHMe$_c$Me$_d$)), 19.6 (P(CHMe$_a$Me$_b$)), 19.3 (P(CHMe$_c$Me$_d$)); $^{31}$P{${^1}$H} NMR (CD$_2$D$_6$): δ 63.5; $^{19}$F{${^1}$H} NMR (1:1 toluene:THF): δ -152.3 (MnFBF$_3$), -293.5 (MnFBF$_3$); $^{11}$B{${^1}$H} NMR (1:1 toluene:THF): δ 0.31 ($\Delta v_{1/2}$ = 63 Hz); FTIR (cm$^{-1}$) ν(CO): 2038, 1952, 1912.

**Synthesis of κ$^2$-(P,N-2-2b)Mn(CO)$_3$OSO$_2$CF$_3$ (4-3b):** To a magnetically stirred solution of 4-2 (0.23 g, 0.46 mmol) in toluene (7 mL), was added a slurry of AgSO$_3$CF$_3$ (0.12 g, 0.46 mmol) in toluene (6 mL) via pipette. Immediately, a bright yellow solution formed followed by generation of a white precipitate. The reaction mixture was allowed to stir for 4 h, after which the precipitate was removed by filtration through Celite. Further product was extracted from the solid residue of the filtration by use of THF (4 x 3 mL) until the residue was colorless. The THF extractions were combined with the original toluene filtrate and all solvent and other volatile materials were removed in vacuo to yield 4-3b as an analytically pure yellow powder (0.17 g, 0.030 mmol, 65%). Crystals of 4-3b suitable for single crystal X-ray diffraction analysis were grown from the slow
evaporation of toluene at room temperature. Anal. Calcd. For C_{21}H_{26}O_{6}PNMnSF_{3} (%): C 44.77; H 4.65; N 2.49. Found: C 44.41; H 4.93; N 2.33. 1H NMR (CD_{6}D): δ 7.14-7.11 (m, 2H, Ar-Hs), 7.02-6.99 (m, 2H, Ar-Hs), 2.47 (s, 2H, C1-H2), 2.41 (s, 3H, NMe_{a}), 2.39 (s, 3H, NMe_{b}), 2.35-2.25 (m, 2H, P(CHMe_{2})_{2}), 1.41 (d of d, 3J_{PH} = 17.1 Hz, 3J_{HH} = 7.0 Hz, 3H, P(CHMe_{a}Me_{b})), 1.23 (d of d, 3J_{PH} = 17.3 Hz, 3J_{HH} = 7.0 Hz, 3H, P(CHMe_{a}Me_{d})), 0.85 (d of d, 3J_{PH} = 15.2 Hz, 3J_{HH} = 7.2 Hz, 3H, P(CHMe_{a}Me_{d})); 13C{^1H} NMR (CD_{6}D): δ 174.7 (d, 2J_{PC} = 19.5 Hz, C2), 142.5 (d, J_{PC} = 4.6 Hz, C3a or C7a), 139.5 (d, J_{PC} = 3.3 Hz, C7a or C3a), 132.3 (d, 1J_{PC} = 23.1 Hz, C3), 127.2, 126.4, 124.9, 122.0 (C4, C5, C6, C7), 57.1 (NMe_{b}), 53.3 (NMe_{a}), 30.8 (d, 3J_{PC} = 9.2 Hz, C1), 29.3 (d, 1J_{PC} = 19.1 Hz, P(CHMe_{a}Me_{d})), 28.2 (d, 1J_{PC} = 26.6 Hz, P(CHMe_{a}Me_{b})), 20.2 (d, 2J_{PC} = 6.2 Hz, P(CHMe_{a}Me_{b}) or P(CHMe_{c}Me_{d})), 20.1 (d, 2J_{PC} = 2.1 Hz, P(CHMe_{c}Me_{d}) or P(CHMe_{a}Me_{b})), 19.7 (P(CHMe_{a}Me_{b})), 19.4 (P(CHMe_{c}Me_{d})); 31P{^1H} NMR (CD_{6}D): δ 62.6; 19F{^1H} NMR (1:1 toluene:THF): δ - 77.4; FTIR (cm^{-1}) ν(CO): 2036, 1957, 1916.

**Synthesis of [κ²-(P,N-2-2b)Mn(CO)_{4}]^{+}BF_{4}^{-} (4-4):** To a magnetically stirred solution of BrMn(CO)_{5} (0.044 g, 0.16 mmol) in THF (3 mL) was added a slurry of AgBF_{4} (0.034 g, 0.17 mmol) in THF (3 mL) via pipette. Immediately upon addition of AgBF_{4} a dark brown precipitate formed from the yellow solution. After 1.5 h the precipitated solid was separated by filtration through Celite. The clear yellow filtrate was then added to a solution of 2-2a (0.044 g, 0.16 mmol) in THF (3 mL) via pipette. The reaction mixture was monitored periodically (31P NMR) over the following 21 d, after which time all phosphorus-containing intermediates were observed to evolve into a single phosphorus-containing product at 69.8 ppm. The reaction mixture was then filtered through Celite and
concentrated in vacuo to a volume of 5 mL. From this solution the product (4-4) was obtained as analytically pure yellow crystals, which were isolated by decanting the supernatant, and dried in vacuo (0.025 g, 0.047 mmol, 30%). Anal. Calcd. for C_{21}H_{26}O_{4}PNMnBF_{4} (%): C: 47.67, H: 4.95, N: 2.65; Found: 47.42, H: 5.24, N: 2.72. A sample of these crystals proved suitable for single crystal X-ray diffraction analysis. \(^1\)H NMR (CD_{2}D_{6}:CD_{2}Cl_{2}, 3:1): \(\delta\) 7.32 (d, \(^3J_{HH} = 6.0\) Hz, 1H, H4 or H7), 7.20-7.13 (m, 2H, H5 and H6), 7.00 (d, \(^3J_{HH} = 8.0\) Hz, 1H, H7 or H4), 3.99 (s, 2H, CH_{2}), 2.77 (s, 6H, NMe_{2}), 2.49-2.44 (m, 2H, P(CHMe_{3}Me_{b})_{2}), 1.06 (d of d, \(^3J_{PH} = 18.3\) Hz, \(^3J_{HH} = 6.9\) Hz, 6H, P(CHMe_{3}Me_{b})_{2}, 0.80 (d of d, \(^3J_{PH} = 17.3\) Hz, \(^3J_{HH} = 7.1\) Hz, 6H, P(CHMe_{3}Me_{b})_{2}): \(^{13}\)C\(^{1}\)H NMR (CD_{2}Cl_{2}): \(\delta\) 209.7 (CO), 176.3 (d, \(^2J_{PC} = 16.4\) Hz, C2), 143.7 (d, \(^J_{PC} = 6.2\) Hz, C3a or C7a), 137.2 (C7a or C3a), 131.8 (d, \(^1J_{PC} = 32.1\) Hz, C3), 128.4, 125.8, 124.8, 122.0 (C4, C5, C6, C7), 60.9 (NMe_{2}), 32.4 (d, \(^3J_{PC} = 9.1\) Hz, C1), 31.1 (d, \(^1J_{PC} = 26.1\) Hz, P(CHMe_{3}Me_{b})_{2}), 20.5 (P(CHMe_{3}Me_{b})_{2}), 19.6 (P(CHMe_{3}Me_{b})_{2}); \(^{31}\)P\(^{1}\)H NMR (CD_{2}Cl_{2}): \(\delta\) 69.3; \(^{19}\)F\(^{1}\)H NMR (CD_{2}Cl_{2}): \(\delta\) -153.1; \(^{11}\)B\(^{1}\)H NMR (CD_{2}Cl_{2}): \(\delta\) -0.84 (\(\Delta\nu_{1/2} = 29\) Hz); FTIR (cm\(^{-1}\)) \(\nu\)(CO): 2097, 2028, 1993, 1907.

**Reaction of 2-2e-Li with BrMn(CO)_{5}:** To a magnetically stirred slurry of 2-2e-Li (0.15 g, 0.65 mmol) in toluene (3 mL) was added a slurry of BrMn(CO)_{5} (0.18 g, 0.65 mmol) in toluene (2 mL). After 20 h, \(^{31}\)P NMR analysis of the reaction mixture revealed the formation of multiple phosphorus-containing products giving rise to signals at 60 ppm (~20%), 53 ppm (~70%), -2 ppm (~5%), and -6 ppm (~5%). Storage of this reaction mixture at -35 °C for 20 h yielded a brown, microcrystalline precipitate which displayed \(^{31}\)P NMR signals at 60 ppm (~10%) and 53 ppm (~90%). This solid was isolated, dried in vacuo, re-dissolved in toluene (2 mL), and the resulting solution stored at room
temperature. Although no crystalline material was obtained from this solution initially, storage for a prolonged period of time (> 10 months) resulted in the formation of a minute quantity of crystalline material, which gave rise to $^{31}$P NMR resonances at 217 and 69 ppm (1:1 ratio). The identity of this complex as 4-5 was determined on the basis of data obtained from a single-crystal X-ray diffraction experiment.

**Synthesis of 1-SiMe$_2$-2-NMe$_2$-indenene (4-6):** Although the synthesis of 4-6 has been alluded to in a previous report, $^{15}$ complete synthetic details and structural characterization data were not provided. Compound 2-1b-Li (0.31 g, 1.9 mmol) was dissolved in THF (10 mL) and cooled to -80 °C. To this cold, magnetically stirred solution was added freshly distilled ClSiMe$_3$ (0.25 mL, 2.0 mmol) via syringe. The reaction mixture warmed to room temperature over 2 h and the THF and other volatile materials were removed in vacuo over 16 h. The product was extracted into toluene (12 mL) and isolated from insoluble by-products by filtration through Celite. The solvent and other volatile materials were removed in vacuo to yield 4-6 as an analytically pure pale brown solid (0.41 g, 1.8 mmol, 93%). Anal. Caled. For C$_{14}$H$_{21}$NSi (%): C 72.66; H 9.15; N 6.05. Found: C 72.64; H 9.02; N 5.93. $^1$H NMR (C$_6$D$_6$): δ 7.32-7.24 (m, 3H, C4-H, C5-H or C6-H, C7-H), 7.07 (t of d, $^3$J$_{HH}$ = 7.5 Hz, $^4$J$_{HH}$ = 1.5 Hz, C6-H or C5-H), 5.62 (s, 1H, C3-H), 3.27 (s, 1H, C1-H), 2.35 (s, 6H, NMe$_2$), 0.04 (s, 9H, SiMe$_3$); $^{13}$C{$^1$H} NMR (C$_6$D$_6$): δ 161.2 (C2), 145.9 (C7a), 139.9 (C3a), 125.4, 122.4, 118.1 (C4, C6, C7), 120.3 (C5), 97.9 (C3), 42.8 (C1), 41.8 (NMe$_2$), -3.2 (SiMe$_3$).

**Synthesis of $\kappa^2$-P,N-(1-SiMe$_3$-2-NMe$_2$-3-$^3$PPr$_2$-indenyl)Mn(CO)$_3$Br (4-8):** To a magnetically stirred solution of 4-6 (0.04 g, 0.17 mmol) in THF (2 mL) at 0 °C was added nBuLi (0.11 mL of 1.6 M hexanes solution, 0.17 mmol) via syringe. The reaction
mixture immediately turned bright yellow. After stirring for 1 h at room temperature, the reaction mixture was cooled to -35 °C and a solution of ClPPr₂ (0.26 g, 0.17 mmol) in THF (1.5 mL) was added. After 2 h of stirring at room temperature, the THF was removed in vacuo and the residue was extracted into C₆D₆. ¹H and ³¹P NMR spectral data revealed consumption of the starting materials and formation of two new phosphorus-containing products at +11.8 ppm and -3.2 ppm, tentatively assigned as 4-7a and 4-7b, respectively. The C₆D₆ solution was then filtered through Celite, and additional product was recovered by washing the Celite filter with 1 mL of C₆H₆. In a separate vial, a slurry of BrMn(CO)₅ (0.047 g, 0.17 mmol) in THF (2 mL) was prepared and added via pipette to the magnetically stirred benzene reaction mixture. All of the solid material dissolved in solution and the color darkened to orange. The mixture stirred for 18 h, during which a bright yellow precipitate formed in the dark brown solution. The supernatant was decanted and the yellow solid was dried in vacuo to remove any solvent and other volatile materials, yielding 4-8 as a yellow powder (0.026 g, 0.046 mmol, 27%). Crystals suitable for single crystal X-ray diffraction analysis were grown by vapor diffusion of Et₂O into a CDCl₃ solution of 4-8 at room temperature. Anal. Calcd. For C₂₃H₃₄O₅SiPNNMnBr (%): C 48.77; H 6.05; N 2.47. Found: C 48.14; H 5.78; N 2.65. Repeat analysis on this complex consistently led to marginally low %C values. ¹H NMR (CDCl₃): δ 7.45 (d, ³JHH = 7.5 Hz, 1H, C4-H), 7.28 (d, ³JHH = 7.3 Hz, 1H, C7-H), 7.25-7.22 (m, 1H, C6-H), 7.15 (t, ³JHH = 7.4 Hz, 1H, C5-H), 3.73 (s, 1H, C1-H), 3.28 (s, 3H, NMe₃), 3.21-3.05 (m, 2H, P(CHMe₃Me₃), 2.97 (s, 3H, NMe₃), 1.63 (d of d, ³JPH = 14.8 Hz, ³JHH = 7.0 Hz, P(CHMe₃Me₃), 1.54-1.47 (m, 6H, P(CHMe₃Me₃)Me₃), 1.11 (d of d, ³JPH = 15.2 Hz, ³JHH = 7.2 Hz, P(CHMe₃Me₃)), 0.00 (s, 9H, SiMe₃); ¹³C{¹H} NMR (CDCl₃): δ
180.3 (d, $^2J_{PC} = 19.3$ Hz, C2), 146.2 (d, $^2J_{PC} = 4.7$ Hz, C3a), 139.8 (C7a), 127.3 (d, $^1J_{PC} = 24.9$ Hz, C3), 125.3 (C6), 123.8, 123.7 (C5 and C7), 122.0 (C4), 62.3 (NMe$_2$), 53.1 (NMe$_3$), 42.5 (d, $^3J_{PC} = 8.2$ Hz, C1), 30.5 (d, $^1J_{PC} = 23.8$ Hz, P(CHMe$_3$NMe$_3$), 26.1 (d, $^1J_{PC} = 24.2$ Hz, P(CHMe$_3$NMe$_3$)), 21.7 (P(CHMe$_3$NMe$_3$)), 21.0 (P(CHMe$_3$NMe$_3$)), 19.9 (d, $^2J_{PC} = 7.0$ Hz, P(CHMe$_3$NMe$_3$)), 19.5 (P(CHMe$_3$NMe$_3$)), 0.0 (SiMe$_3$); $^{31}$P{$^1$H} NMR (CDCl$_3$): $\delta$ 60.2; FTIR (cm$^{-1}$) v(CO): 2012, 1926, 1895.

**Synthesis of $\eta^5$-(2-1b)Mn(CO)$_3$ (4-9):** To a magnetically stirred slurry of 2-1b-Li (0.48 g, 0.29 mmol) in Et$_2$O (30 mL), was added a slurry of BrMn(CO)$_5$ (0.80 g, 0.29 mmol) in Et$_2$O (10 mL) via pipette. A ruby red, cloudy mixture formed immediately. After stirring for 16 h, the reaction mixture lightened in color to yellow, with a fine white precipitate apparent. The mixture was then filtered through Celite and the solvent was removed in vacuo. The product was extracted from the residue by repeated benzene extractions to a total volume of 30 mL. The benzene solvent was removed in vacuo and the residual solid was washed with pentane (3 x 5 mL). The remaining solid was dried in vacuo, yielding 4-9 as an analytically pure yellow powder (0.35 g, 0.12 mmol, 41%). Crystals suitable for single crystal X-ray diffraction analysis were grown from a concentrated pentane solution of the solid at room temperature. Anal. Calcd. For C$_{14}$H$_{12}$O$_3$NMn (%): C 56.58; H 4.07; N 4.71. Found: C 56.77; H 3.82; N 4.87. $^1$H NMR (C$_6$D$_6$): $\delta$ 7.17-6.76 (m, 4H, Ar-Hs), 4.08 (s, 2H, C1-H and C3-H), 2.11 (s, 6H, NMe$_2$); $^{13}$C{$^1$H} NMR (C$_6$D$_6$): $\delta$ 225.5 (CO), 135.3 (C3a and C7a), 125.3 (C4 and C7 or C5 and C6), 125.1 (C5 and C6 or C4 and C7), 99.7 (C2), 53.7 (C1 and C3), 39.4 (NMe$_2$); FTIR (cm$^{-1}$) v(CO): 2013, 1935, 1919.

**Crystallographic Solution and Refinement Details.** Crystallographic data were obtained at 193(±2) K on a Bruker PLATFORM/SMART 1000 CCD diffractometer,
using samples that were mounted in inert oil and transferred to a cold gas stream of the
diffractometer. Programs for diffractometer operation, data collection, data reduction and
absorption correction were supplied by Bruker. Crystal structure diagrams were generated
by use of the ORTEP-3 program. The structures were solved by use of direct methods
and refined by use of full-matrix least-squares procedures (on $F^2$) with $R_1$ on the basis of
$F_o^2 \geq 2\sigma(F_o^2)$ and $wR_2$ on the basis of $F_o^2 \geq -3\sigma(F_o^2)$. Anisotropic displacement
parameters were employed throughout for the non-hydrogen atoms, and all hydrogen
atoms were added at calculated positions and refined by use of a riding model employing
isotropic displacement parameters on the basis of the isotropic displacement parameter of
the attached atom. During the refinement of the $P2_1$ polymorph of 4-2•0.5C$_7$H$_8$, the
behavior of the Flack absolute structure parameter (0.217(17)) indicated a degree of
racemic twinning in the crystal; the SHELXL-93 TWIN instruction was employed to
accommodate this twinning. Complete experimental details for these compounds are
available through the Cambridge Crystallographic Database. Tabulated crystallographic
data is presented in Table 4-1.
Table 4-1. Crystallographic Data for 4-2, 4-3a, 4-3b, and 4-4

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### Table 4-1 Continued. Crystallographic Data for 4-5, 4-8, 4-9, and 4-10

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4.5 References and Endnotes


10. A recently reported PCN-based Rh(III) pincer complex features a coordinated (and fluxional) tetrafluoroborate anion that is displaced by THF at reduced temperatures:


15. For a thorough discussion of structure and bonding phenomena in amino-substituted η⁵-indenyl complexes, see: Greidanus, G.; McDonald, R.; Stryker, J. M. Organometallics 2001, 20, 2492, and references therein.


17. For a report in which a similar synthetic methodology is successfully employed in the synthesis of η⁵-indenyl complexes, see: Starzewski, K. A. O.; Kelly, W. M.; Stumpf, A.; Freitag, D. Angew. Chem. Int. Ed. 1999, 38, 2439.


Chapter 5: Preparation of Neutral Rh(I) and Ir(I) \( \kappa^2-(P,O)MCOD \) Catalyst Complexes and Exploration of Their Utility in Alkene Hydrogenation and Hydrosilylation

5.1 Introduction

The study of transition metal complexes supported by mixed donor chelating ligands is an active and fruitful area of chemical research.\(^1\)\(^-\)\(^3\) One reason for the interest in such complexes is that the incorporation of a non-symmetric chelate binding environment around the transition metal can facilitate substrate activation, and can provide selectivity in subsequent transformations occurring within the metal coordination sphere.\(^1\)\(^-\)\(^3\) The synthetic utility of Rh and Ir catalyst complexes stabilized by mixed donor ligands has been demonstrated for many transformations involving the activation of E-H bonds (E = main group element) in small molecule substrates, including (but not limited to) hydrogenation, hydrosilylation, hydroboration, and hydroformylation reactions.\(^2\)

In this context, the development of new classes of reactive group 9 transition metal coordination complexes supported by donor-functionalized indene ligands, including 1-P\(^{\prime}\)Pr\(_2\)-2-NMe\(_2\)-indene (2-2a), 2-NMe\(_2\)-3-P\(^{\prime}\)Pr\(_2\)-indene (2-2b), and related derivatives was outlined in Chapters 2 and 3. These ligands have proven capable of supporting both neutral and cationic Rh and Ir metal fragments in a \( \kappa^2-P,N \) fashion, and upon deprotonation of the indene backbone and introduction of a cationic metal fragment, zwitterionic \( \kappa^2-P,N \) complexes. The ligand class represented by 2-2 has also found utility in supporting related platinum group metals.\(^4\)\(^-\)\(^5\) As has been discussed in previous chapters, the driving force behind continuing to develop charge-neutral zwitterionic group 9 metal complexes of this type arises from the desire to identify new neutral group
9 catalyst complexes that possess the advantageous reactivity traits of more conventional cationic systems, while circumventing the low solubility, thermal instability, and other limitations that can be associated with Rh(I) and Ir(I) salts. Reactivity studies have revealed that the zwitterion ($\kappa^2$-$P,N$-$2,2e$)Rh(COD), 2-7, is an effective catalyst for C-H/Si-H dehydrogenative cross-coupling, while the Ir analogue 3-3 exhibits modest catalytic activity for alkene hydrogenation (Chapter 3).

It is extremely rare for neutral Ir(I) species to function as alkene hydrogenation catalysts; for example, while Wilkinson’s complex, 1-1, is effective in mediating the reduction of some classes of olefins, it the Ir analogue is completely inactive. Since these early investigations conducted by Wilkinson that demonstrate this dichotomy between the Rh and Ir congeners, progress towards preparing other neutral Ir(I) catalyst complexes for E-H bond activations remains limited.

In light of the superior catalytic properties commonly exhibited by late transition metal complexes featuring $\kappa^2$-heterobidentate ligation strategies, especially with hard (such as N) and soft (such as P) ligand pairings, an alternative anionic ligand featuring contrasting donor atoms structurally similar to 2-2 was sought. One other class of mixed donor ligands that has found widespread use are phosphorus-oxygen ligands, which bind in a $\kappa^2$-$P,O$ fashion to the metal. Nickel catalysts of this type, including $\kappa^2$-[Ph$_2$PCH$_2$C(=O)O]NiCOD, are employed in the Shell Higher Olefin Process (SHOP), which represents a multi-billion dollar a year industry globally for the production of ethene oligomers. The established utility of $P,O$-ligands in tuning the reactivity properties of metal complexes made this variant an attractive alternative to $P,N$-ligands, and thus the catalytically active $\kappa^2$-$P,O$ phosphinoenolate complexes were targeted.
Within the few reports that feature $\kappa^2$-P,O-Rh(I) complexes of this type as alkene hydrogenation catalysts, the feasibility of employing an aliphatic hydrocarbon reaction medium was not evaluated,\textsuperscript{10} and the hydrogenation of alkenes mediated by analogous Ir(I) complexes has yet to be documented.

This chapter discusses the preparation and characterization of the new phosphinoenolate complexes ($M = \text{Rh, 5-1; Ir, 5-2}$) in addition to examination of their catalytic abilities in mediating alkene hydrogenation and hydrosilylation. These catalytic results are placed in the context of analogous reactions catalyzed by Wilkinson’s catalyst (1-1) and Crabtree’s catalyst (1-10).

\section*{5.2 Results and Discussion}

\subsection*{5.2.1 Preparation of Neutral $\kappa^2$-(P,O)-Rh(COD) and $\kappa^2$-(P,O)-Ir(COD) Complexes}

In the course of surveying the reactivity properties of $\kappa^2$-(P,N-2-2b)M(COD) ($M = \text{Rh, Ir}$), it was noted that heating in a THF/H$_2$O mixture (5:1, 60 °C, 48 h) resulted in the clean conversion to the neutral $\kappa^2$-P,O species 5-1 and 5-2 (Scheme 5-1). These new complexes were isolated and characterized spectroscopically, and also by use of X-ray diffraction methods; an ORTEP\textsuperscript{11} diagram is provided in Figure 5-1, while selected metrical parameters and relevant X-ray experimental data and are collected in Tables 5-1 and 5-2, respectively. Table 5-2 appears in the experimental section after description of the crystallographic solution details. The structural features of 5-1 are consistent with those of 5-2, and the overall geometric features in these $\kappa^2$-(P,O)-M(COD) complexes mirror those observed in related complexes.\textsuperscript{12} Notably, the C2-C3 distances in 5-1 and 5-2 (1.367(3) Å and 1.380(7) Å, respectively) are in keeping with a $\text{C=C}$ double bond, and
the O-C2 distances (1.304(2) Å and 1.302(6) Å, respectively) are elongated relative to the C=O bond typically found in ketones (∼1.23 Å); both of these observations are consistent with a phosphinoenolate structural formulation for 5-1 and 5-2.

\[
\begin{align*}
\text{[2-6a]}^+\text{BF}_4^- : \text{M} &= \text{Rh} \\
\text{[3-2b]}^+\text{PF}_6^- : \text{M} &= \text{Ir}
\end{align*}
\]

**Scheme 5-1.** Synthesis of the Neutral Phosphinoenolate Rh(I) and Ir(I) Complexes (5-1, 5-2) from P,N-Cationic Metal Precursors ([2-6a]}^+\text{BF}_4^-, [3-2b]}^+\text{PF}_6^-)

In addition, the structure of 5-1 is comparable to other crystallographically characterized neutral Rh-phosphinoenolate complexes, with the structural features of 5-1 deviating significantly from the alternative β-ketophosphine formulation. One interesting feature of these complexes is that the M-alkene distances *trans* to P (average distance of the Rh-C15 and Rh-C16 bonds is ∼2.2 Å) are elongated relative to the Rh-alkene distances *trans* to O (average bond distance of the Rh-C11 and Rh-C12 bonds is ∼2.11 Å), in keeping with the greater *trans*-influence predicted for a phosphine fragment relative to an alkoxy donor on the metal fragment.

Upon examination of the solubility and relative thermal stability of the complexes 5-1 and 5-2, it was found that no decomposition was observed for complex 5-2 upon heating in toluene over two weeks at 100 °C (by $^{31}$P NMR), in contrast to the temperature-sensitive nature of Crabtree’s catalyst 1-10. The Rh(I) complex 5-1 did not prove as robust as the Ir(I) analogue; upon heating at 100 °C in toluene for 2 weeks, a
mixture (40:60) of an unidentified singlet accompanied the starting complex 5-1, indicative of some thermal decomposition process underway.

![Structures 5-1 and 5-2](image)

**Figure 5-1.** The crystallographically determined structure of 5-1·0.25CH₂Cl₂ and 5-2, shown with 50% displacement ellipsoids and with the atomic numbering scheme depicted; selected hydrogen atoms and the dichloromethane solvate in the case of 5-1 have been omitted for clarity. Only one of the two crystallographically independent molecules of 5-2 is shown.

**Table 5-1.** Interatomic Distances (Å) and Angles (°) for 5-1·0.25CH₂Cl₂ and 5-2

<table>
<thead>
<tr>
<th></th>
<th>5-1·0.25CH₂Cl₂</th>
<th>5-2</th>
</tr>
</thead>
<tbody>
<tr>
<td>M-P</td>
<td>2.3181(5)</td>
<td>2.320(1)</td>
</tr>
<tr>
<td>M-O</td>
<td>2.076(1)</td>
<td>2.058(3)</td>
</tr>
<tr>
<td>M-C&lt;sub&gt;alkene&lt;/sub&gt;&lt;sup&gt;a&lt;/sup&gt;</td>
<td>2.207(2)</td>
<td>2.181(5)</td>
</tr>
<tr>
<td>M-C&lt;sub&gt;alkene&lt;/sub&gt;&lt;sup&gt;b&lt;/sup&gt;</td>
<td>2.214(2)</td>
<td>2.164(5)</td>
</tr>
<tr>
<td>M-C&lt;sub&gt;alkene&lt;/sub&gt;&lt;sup&gt;c&lt;/sup&gt;</td>
<td>2.113(2)</td>
<td>2.117(5)</td>
</tr>
<tr>
<td>M-C&lt;sub&gt;alkene&lt;/sub&gt;&lt;sup&gt;d&lt;/sup&gt;</td>
<td>2.112(2)</td>
<td>2.099(6)</td>
</tr>
<tr>
<td>P-C3</td>
<td>1.787(2)</td>
<td>1.779(5)</td>
</tr>
<tr>
<td>O-C2</td>
<td>1.304(2)</td>
<td>1.302(6)</td>
</tr>
<tr>
<td>C1-C2</td>
<td>1.515(3)</td>
<td>1.514(7)</td>
</tr>
<tr>
<td>C2-C3</td>
<td>1.367(3)</td>
<td>1.380(7)</td>
</tr>
<tr>
<td>C3-C3a</td>
<td>1.476(3)</td>
<td>1.467(7)</td>
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<tr>
<td>C1-C7a</td>
<td>1.500(3)</td>
<td>1.499(7)</td>
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<td>C3a-C7a</td>
<td>1.413(3)</td>
<td>1.415(7)</td>
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<tr>
<td>P-M-O</td>
<td>84.29(4)</td>
<td>84.3(1)</td>
</tr>
<tr>
<td>M-O-C2</td>
<td>115.2(1)</td>
<td>115.8(3)</td>
</tr>
<tr>
<td>O-C2-C3</td>
<td>127.8(2)</td>
<td>127.4(5)</td>
</tr>
<tr>
<td>C2-C3-P</td>
<td>113.9(2)</td>
<td>113.7(4)</td>
</tr>
<tr>
<td>C3-P-M</td>
<td>98.6(7)</td>
<td>98.6(2)</td>
</tr>
</tbody>
</table>

<sup>a</sup>The metal-cyclooctadiene distances <em>trans</em> to phosphorus. <sup>b</sup>The metal-cyclooctadiene distances <em>trans</em> to oxygen.
5.2.2 Attempted Syntheses of 1-Pr2-2-indanone

Having only obtained the neutral $\kappa^2-P,O$ coordination complexes 5-1 and 5-2 indirectly via hydrolysis of the related $\kappa^2-P,N$ cations [2-6a]$^+\text{BF}_4^-$ and [3-2b]$^+\text{PF}_6^-$, preparing directly the parent ligand 1-Pr2-2-indanone was of considerable interest. Attempted syntheses to this ligand are outlined in Scheme 5-2; to date, the successful preparation of this ligand has not been achieved. Although related $\beta$-ketophosphine ligands have been prepared similarly by Braunstein,\textsuperscript{16} lithiation of 2-indanone followed by introduction of chlorodiisopropylphosphine produced rather complex reaction mixtures ($^1\text{H}$ and $^{31}\text{P}$ NMR), from which no pure materials could be isolated. Similar results were obtained upon addition of the chlorophosphine to a mixture of triethylamine and 2-indanone. As well, the enamine 1-Pr2-2-NMe2-indene is not hydrolyzed, either upon treatment with water or under aqueous acidic conditions.\textsuperscript{17} In light of this latter observation, it is evident that the formally cationic group 9 metal fragments in [2-6a]$^+\text{BF}_4^-$ and [3-2b]$^+\text{PF}_6^-$ play an important role in mediating what can be described as a traditional enamine hydrolysis involving 3-Pr2-2-NMe2-indene (2-2b). One possibility is that these metal fragments act as Lewis acids upon coordination to nitrogen in 2-2b, thereby preventing conjugation of the NMe2 group with the adjacent indene fragment,\textsuperscript{18} weakening the C_{indene}–N bond, and rendering the NMe2 group more susceptible to substitution relative to the uncoordinated amine in 1-Pr2-2-NMe2-indene. The mechanism of this hydrolysis reaction that transforms the cationic [$\kappa^2-(P,N\text{-2-2b})\text{M(COD)}]^+X^-$ complexes into the neutral $\kappa^2-(P,O\text{-indene})\text{M(COD)}$ complexes is currently unknown, but represents a potential target for future investigations, as well as probing alternative synthetic routes to the proposed parent ligand 1-Pr2-2-indanone.
Scheme 5-2. Attempted Synthetic Routes to 1-PPr₂-2-indanone

5.2.3 Catalytic Hydrogenation of Styrene Mediated by 5-1 and 5-2

In an initial reactivity study to compare the catalytic abilities of the neutral Rh(I) and Ir(I) \( \kappa^2\)-P, O bound complexes, the metal-mediated hydrogenation of alkenes was examined. As discussed in Chapter 3, cationic square-planar Ir(I) complexes including 3-1 and related species have a demonstrated track-record as effective homogeneous alkene hydrogenation catalysts,\(^8\) while effective neutral Ir(I) analogues remain rare. Preliminary reactivity studies employing the neutral Ir(I) complex 5-2 revealed that it is a competent catalyst for styrene hydrogenation in a range of solvents and under mild conditions (22 \( ^\circ\)C, \( \sim 1 \) atm H\(_2\), 1.0 mol%; Table 5-3). While incomplete conversion was observed in CH\(_2\)Cl\(_2\) (68 %; entry 5-3.1), clean reductions were achieved after 4 h in both THF (entry 5-3.2) and benzene (entry 5-3.3). Remarkably, in hexanes 5-2 proved capable of quantitatively reducing styrene after only 0.25 h (entry 5-3.4) and at double the initial rate observed in CH\(_2\)Cl\(_2\), THF, or benzene; this catalytic performance rivals that of the
benchmark complex 1-10 in CH₂Cl₂.¹⁵ Whereas 1-10¹⁵c and other cationic Ir(I) species, as well as the Ir(I) zwitterion 3-5 (Chapter 3), are catalytically inactive in the presence of CH₃CN, the reduction of styrene mediated by 5-2 proceeded to a limited extent in a mixture of C₆H₆ and CH₃CN (entry 5-3.5).

### Table 5-3. Alkene Hydrogenation Mediated by κ²-\((P,O)\)M(COD) Complexes

<table>
<thead>
<tr>
<th>Entry</th>
<th>Loading [mol%]</th>
<th>Catalyst</th>
<th>Substrate</th>
<th>Solvent</th>
<th>Yield [%]</th>
<th>TOF[^b]</th>
</tr>
</thead>
<tbody>
<tr>
<td>5-3.1</td>
<td>1.0</td>
<td>5-2</td>
<td>Styrene</td>
<td>CH₂Cl₂</td>
<td>68</td>
<td>125</td>
</tr>
<tr>
<td>5-3.2</td>
<td>1.0</td>
<td>5-2</td>
<td>Styrene</td>
<td>THF</td>
<td>&gt;99</td>
<td>170</td>
</tr>
<tr>
<td>5-3.3</td>
<td>1.0</td>
<td>5-2</td>
<td>Styrene</td>
<td>C₆H₆</td>
<td>&gt;99</td>
<td>185</td>
</tr>
<tr>
<td>5-3.4</td>
<td>1.0</td>
<td>5-2</td>
<td>Styrene</td>
<td>Hexanes</td>
<td>&gt;99</td>
<td>400</td>
</tr>
<tr>
<td>5-3.5</td>
<td>1.0</td>
<td>5-2</td>
<td>Styrene</td>
<td>~4:3 C₆H₆ and CH₃CN</td>
<td>29</td>
<td>30</td>
</tr>
<tr>
<td>5-3.6</td>
<td>0.5</td>
<td>5-2</td>
<td>Styrene</td>
<td>Hexanes</td>
<td>&gt;99</td>
<td>590</td>
</tr>
<tr>
<td>5-3.7</td>
<td>0.5</td>
<td>5-2</td>
<td>Styrene (open air setup)[^c,d]</td>
<td>Hexanes</td>
<td>&gt;99</td>
<td>480</td>
</tr>
<tr>
<td>5-3.8</td>
<td>0.1</td>
<td>5-2</td>
<td>Styrene</td>
<td>Hexanes</td>
<td>35</td>
<td>645</td>
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<tr>
<td>5-3.9</td>
<td>5.0</td>
<td>5-1</td>
<td>Styrene</td>
<td>CH₂Cl₂</td>
<td>7</td>
<td>0</td>
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<tr>
<td>5-3.10</td>
<td>5.0</td>
<td>5-1</td>
<td>Styrene</td>
<td>Hexanes</td>
<td>3</td>
<td>0</td>
</tr>
<tr>
<td>5-3.11</td>
<td>0.5</td>
<td>5-2</td>
<td>Cyclohexene</td>
<td>Hexanes</td>
<td>57</td>
<td>260</td>
</tr>
<tr>
<td>5-3.12</td>
<td>0.5</td>
<td>5-2</td>
<td>1-methyl-cyclohexene</td>
<td>Hexanes</td>
<td>7</td>
<td>35</td>
</tr>
</tbody>
</table>

[^a]: Conditions: 22 °C, ~1 atm H₂, 4 h (except for entry 5-3.4, 0.25 h).[^b]: Calculated at 0.25 h; TOF = (moles product/moles catalyst)/0.25 h. The reagents, catalyst, and solvent were handled in the open air and no efforts were made to purify the hexanes prior to use.[^c]: Solutions of 5-2 in C₆D₆ stored under air are stable for a minimum of 4 h ([³¹P NMR).

The clean reduction of styrene was also achieved by lowering the loading of 5-2 to 0.5 mol% (entry 5-3.6), and no significant loss of catalytic activity occurred when the hydrogenation was conducted on the bench-top without the rigorous exclusion of oxygen and using hexanes that had not been dried (entry 5-3.7). Modest catalytic productivity (35%) was also detected at the 0.1 mol% 5-2 loading level (entry 5-3.8). By comparison, the Rh(I) complex 5-1 proved vastly inferior to 5-2, with less than 10% styrene...
conversion observed after 4 h employing 5.0 mol% 5-1 in either CH₂Cl₂ or hexanes. Substituted alkenes were more of a challenge; while complex 5-2 proved capable of reducing cyclohexene to a significant extent (57%, entry 5-3.11), minimal conversion was achieved for the hydrogenation of 1-methyl-cyclohexene (7%, entry 5-3.12). However, in light of the very mild reaction conditions (~1atm, 22°C) employed in this initial survey, the fact that 5-2 can achieve these levels of conversion with more hindered alkenes suggests that it may be an effective hydrogenation catalyst for a wider range of substrates under optimized reaction conditions.

5.2.4 Catalytic Addition of Triethylsilane to Styrene Mediated by 5-1 and 5-2

The hydrosilylation of unsaturated substrates mediated by a transition metal catalyst complex has been the focus of active research for several decades, owing to the utility of the resulting organosilanes in applications ranging from the preparation of silicon-containing polymers to the synthesis of bioactive compounds.¹⁹-²² In particular, the addition of silanes to unsaturated alkenes can result in complex product distributions including both saturated silane and vinylsilane products, and thus can serve as prototypes for E-H addition reactions where selectivity towards one product can be a challenge, as discussed in Chapter 3. In the interest of evaluating the utility of 5-1 and 5-2 as selective catalysts for either the hydrosilylation or dehydrogenative silylation in comparison with Wilkinson's catalyst 1-1, as well as the prototypical Ir(I) catalyst 1-10, the catalytic addition of triethylsilane to styrene employing these complexes at the 5.0 mol% loading level was examined. The anticipated products of this reaction are given in Equation 5-1 (reproduced from Chapter 3 for ease of discussion in this chapter).
Initially, the dehydrogenative silylation of styrene in benzene at 22 °C using a 5 mol% catalyst loading was examined so as to benchmark the catalytic performance of 5-1 and 5-2 against that of 1-1. Generally, the reaction of styrene with triethylsilane (1:1 or 5:1 ratio) in the presence of a catalytic amount of 5-1 in benzene gave predominantly the dehydrogenative silylation product \( E-1 \)-triethylsilyl-2-phenylethene (3-10b), as is noted in Table 5-4 (entries 5-4.1 and 5-4.2). The linear hydrosilylation product 1-triethylsilyl-2-phenylethene (3-10a), the branched hydrosilylation product 1-triethylsilyl-1-phenylethane (3-10c), as well as trace amounts in some cases of \( Z-1 \)-triethylsilyl-2-phenylethene (3-10d) were also observed. Similar to catalyst 5-1, the silane 3-10b was the major product formed in the reaction employing 5 mol% of the prototypical catalyst 1-1, with a 5:1 ratio of styrene to triethylsilane at 22 °C in benzene (entry 5-4.7); however, 1-1 exhibits superior selectivity and activity relative to 5-1 under these conditions (entries 5-4.2 and 5-4.7). In using 5-2 under similar reaction conditions, very little consumption of triethylsilane was noted (entries 5-4.5 and 5-4.6), although trace amounts of the branched dehydrogenative silylation product 3-10e were observed in those product distributions. In all instances, an equimolar amount of ethylbenzene compared to 3-10b and 3-10d was detected, indicating that the excess styrene acts as a hydrogen acceptor.
Table 5-4. Addition of Triethylsilane to Styrene, Employing 5 mol% Catalyst

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Solvent</th>
<th>styrene: Et₃SiH</th>
<th>Temp. [°C]</th>
<th>Yield [%]b</th>
<th>3-10b</th>
<th>3-10a</th>
<th>3-10c</th>
</tr>
</thead>
<tbody>
<tr>
<td>5-4.1</td>
<td>5-1</td>
<td>benzene</td>
<td>1:1</td>
<td>22</td>
<td>38</td>
<td>27</td>
<td>11</td>
<td>&lt;1</td>
</tr>
<tr>
<td>5-4.2</td>
<td>5-1</td>
<td>benzene</td>
<td>5:1</td>
<td>22</td>
<td>66</td>
<td>58</td>
<td>8</td>
<td>&lt;1</td>
</tr>
<tr>
<td>5-4.3</td>
<td>5-1</td>
<td>hexanes</td>
<td>5:1</td>
<td>22</td>
<td>84</td>
<td>74</td>
<td>10</td>
<td>&lt;1</td>
</tr>
<tr>
<td>5-4.4</td>
<td>5-1</td>
<td>THF</td>
<td>5:1</td>
<td>22</td>
<td>86</td>
<td>72</td>
<td>14</td>
<td>&lt;1</td>
</tr>
<tr>
<td>5-4.5</td>
<td>5-2</td>
<td>benzene</td>
<td>1:1</td>
<td>22</td>
<td>&lt;1</td>
<td>1</td>
<td>&lt;1</td>
<td>1</td>
</tr>
<tr>
<td>5-4.6</td>
<td>5-2</td>
<td>benzene</td>
<td>5:1</td>
<td>22</td>
<td>&lt;1</td>
<td>1</td>
<td>&lt;1</td>
<td>1</td>
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<td>5-4.7</td>
<td>1-1</td>
<td>benzene</td>
<td>5:1</td>
<td>22</td>
<td>94</td>
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<td>6</td>
<td>4</td>
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<tr>
<td>5-4.8</td>
<td>1-10</td>
<td>DCEc</td>
<td>5:1</td>
<td>22</td>
<td>3</td>
<td>2</td>
<td>1</td>
<td>&lt;1</td>
</tr>
<tr>
<td>5-4.9</td>
<td>5-1</td>
<td>benzene</td>
<td>1:1</td>
<td>60</td>
<td>95</td>
<td>74</td>
<td>21</td>
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<td>5-4.10</td>
<td>5-1</td>
<td>benzene</td>
<td>5:1</td>
<td>60</td>
<td>&gt;99</td>
<td>93</td>
<td>7</td>
<td>&lt;1</td>
</tr>
<tr>
<td>5-4.11</td>
<td>5-1</td>
<td>THF</td>
<td>5:1</td>
<td>60</td>
<td>&gt;99</td>
<td>90</td>
<td>10</td>
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<td>DCEc</td>
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<td>72</td>
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<td>7</td>
<td>4</td>
<td>1</td>
<td>2</td>
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<td>benzene</td>
<td>5:1</td>
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<td>5-2</td>
<td>THF</td>
<td>5:1</td>
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<td>12</td>
<td>6</td>
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<td>3</td>
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<td>DCEc</td>
<td>5:1</td>
<td>60</td>
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<td>5</td>
<td>2</td>
<td>&lt;1</td>
</tr>
<tr>
<td>5-4.17</td>
<td>1-1</td>
<td>benzene</td>
<td>5:1</td>
<td>60</td>
<td>&gt;99</td>
<td>94</td>
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<td>4</td>
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<td>5:1</td>
<td>60</td>
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<td>84</td>
<td>3</td>
<td>12</td>
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<td>1-10</td>
<td>DCEc</td>
<td>5:1</td>
<td>60</td>
<td>&gt;99</td>
<td>40</td>
<td>7</td>
<td>51</td>
</tr>
</tbody>
</table>

*a* based on consumption of triethylsilane at 24 h, except for entries 5-4.17 and 5-4.18, where complete consumption was observed after 4 h. *b* product distribution based on GC-MS and GC-FID data, rounded to the nearest whole number; in all cases, other silicon-containing products including 3-10d and 3-10e each totalled less than 1% of the yield. *c* DCE = 1,2-dichloroethane.

Noting that 3-10b was the dominant product for experiments conducted at room temperature in benzene, evaluation of how altering the solvent, temperature, and ratio of substrates impacts the course of catalytic reactions mediated by 5-1 and 5-2 was conducted. Initially, the effect of reaction temperature on the yield and product distribution was examined; as expected, the overall conversion was increased by raising the reaction temperature from 22 °C to 60 °C: for reactions employing 5-1 in benzene, the yield increased by over 30% to give >99% conversion on going from entry 5-4.2 to 5-4.10, and an improvement in yield was also achieved for analogous reactions conducted.
in THF (entries 5-4.4 and 5-4.11). As well, improved yields were obtained for elevated-temperature reactions mediated either by 1-1 in benzene (entries 5-4.7 and 5-4.17) or by Crabtree’s catalyst (1-10) in 1,2-dichloroethane (entries 5-4.8 and 5-4.19). In contrast, 5-2 performed rather poorly at 60 °C in a range of solvents (entries 5-4.13 to 5-4.16), despite the fact that hydrosilylation reactions mediated by other neutral Ir(I) complexes have been reported.24,25 The selectivity of catalyst 5-1 towards the formation of 3-10b also improved by increasing the reaction temperature; whereas 3-10b is favored by 7:1 over 3-10a at 22 °C in benzene (entry 5-4.2), this ratio increases to 13:1 at 60 °C (entry 5-4.10), a trend that has been observed previously.26 As well, the yield and selectivity of the reactions mediated by 5-1 were enhanced by increasing the ratio of styrene to triethylsilane from equimolar to a four fold excess of styrene (entries 5-4.9 and 5-4.10).26

The reaction solvent also had a strong influence on the conversion and selectivity of the catalysts; whereas 5-1 behaved similarly in THF and benzene at 60 °C (entries 5-4.10 and 5-4.11), in 1,2-dichloroethane at this temperature both the yield and selectivity diminished (entry 5-4.12). Similar results were observed with 1-1 (entries 5-4.17 and 5-4.18). Alternatively, employing hexanes in place of benzene at 22 °C with 5-1 provided increased selectivity and nearly a 20% increase in overall yield (entries 5-4.2 and 5-4.3). As mentioned previously, poor conversions were achieved using 5-2, regardless of the solvent employed (entries 5-4.14, 5-4.15, and 5-4.16). Given that 1-10 has an established affinity for the hydrogenation of alkenes in chlorocarbon solvents,7 it is reasonable that 1,2-dichloroethane is a suitable medium for the hydrosilylation of styrene mediated by this complex; complete conversion of triethylsilane was achieved at 60 °C (entry 5-4.19).
Notably, complex 1-10 proved unusual in comparison to 5-1, 5-2, and 1-1 in favoring the branched hydrosilylation product 3-10c over 3-10b (entry 5-4.19).

5.2.5 Reactivity of Triethylsilane with 5-1 and 5-2

It was noted during the catalytic survey that reactions employing 5-2 turned from pale yellow to cherry red within a few hours of the start of a catalytic experiment, whereas reactions featuring 5-1 did not exhibit this color change. In light of these observations, and given the divergent catalytic abilities of 5-1 and 5-2 for the addition of triethylsilane to styrene, a separate set of experiments were undertaken in which a four-fold excess of triethylsilane was added to a solution of 5-2 in benzene and the mixture was heated at 60 °C. The cherry red color observed previously developed within a few hours, and data obtained from a $^{31}$P NMR spectroscopic study revealed quantitative conversion to new phosphorus-containing products over the course of five days. In contrast, a similar experiment conducted with 5-1 yielded no observable net reaction between triethylsilane and the metal complex under similar conditions. Although definitive conclusions based on these observations can not be made, the detection of a reaction between 5-2 and triethylsilane indicated that the poor performance of 5-2 is not related directly to the inability of this complex to activate the silane substrate; it is possible to envisage the formation of a stable Ir(III) silyl complex that is resistant to insertion of styrene for 5-2, whereas in the case of 5-1, this reversibly formed intermediate is sufficiently reactive so as to enable catalytic turnover.
5.3 Summary and Conclusions

The synthetic utility of Rh and Ir catalyst complexes that feature mixed donor ligands has been demonstrated for many E-H bond activations (E = main group element) in small molecule substrates.\textsuperscript{2} To complement the development of new Rh(I) and Ir(I) coordination complexes supported by donor-functionalize indene ligands, including 1-P\textsuperscript{3}Pr\textsubscript{2}-2-NMe\textsubscript{2}-indene (2-2\textbf{a}), 2-NMe\textsubscript{2}-3-P\textsuperscript{3}Pr\textsubscript{2}-indene (2-2\textbf{b}), in this chapter the development of a new class of neutral Rh(I) and Ir(I) coordination complexes featuring a $\kappa^2$-bound 2-\textit{O}-3-P\textsuperscript{3}Pr\textsubscript{2}-indene ligand was presented.

In contrast to the preponderance of evidence suggesting that Ir(I) complexes must be formally cationic in order to function effectively as homogeneous alkene hydrogenation catalysts, an unusual example of a neutral, square-planar Ir(I) complex (5-2) that mediates the hydrogenation of alkenes under mild conditions (~1 atm H\textsubscript{2}, 22 °C) and without the need for rigorous inert-atmosphere conditions has been observed. The solubility and stability profiles of this neutral complex provide practical advantages over traditional cationic Ir(I) complexes; while 1-10 is temperature-sensitive, functions almost exclusively in chlorocarbons, and is intolerant to coordinating solvents, the neutral complex 5-2 is thermally robust and exhibits optimal catalytic performance in aliphatic hydrocarbons while remaining active in a range of other polar and non-polar media.

Having established the efficacy of $\kappa^2$-P,\textit{O} phosphinoenolate ligation in supporting neutral, alkane-soluble Ir(I) alkene hydrogenation catalysts, derivatives of 5-2 that mediate the reduction of tri- and tetra-substituted alkenes are currently being pursued by other members of the Stradiotto research group. As part of this effort, chiral variants of 5-2 are also being developed, in anticipation that enhanced rates and
enantioselectivities may be achieved for asymmetric alkene hydrogenations mediated by such chiral catalysts in aliphatic hydrocarbons.

The ability of the neutral Rh and Ir phosphinoenolate complexes 5-1 and 5-2 to mediate the addition of triethylsilane to styrene was also explored. Complex 5-1 proved to be an effective catalyst for dehydrogenative silylation in a range of solvents, exhibiting selectivity for E-1-triethylsilyl-2-phenylethene comparable to that of 1-1 in benzene at 60 °C, as well as good catalytic performance in hexanes – a solvent in which 1-1 is not soluble. For reactions mediated by 5-1, the conversion and selectivity both improved upon increasing the reaction temperature and/or the styrene to silane ratio. Conversely, the Ir analogue 5-2 displayed rather poor catalytic productivity under all conditions surveyed. These results are opposite to those noted for catalytic alkene hydrogenation, in which 5-2 vastly out-performs 5-1. Building on these results, future work will include assessing the catalytic abilities of 5-1, 5-2, and related coordination complexes derived from 1-P2Pr2-2-indanone, with respect to the addition of other E-H containing substrates to multiple bonds.

5.4 Experimental

General Considerations. See Sections 2.5, 3.4, and 4.4 for a description of general experimental conditions. Any changes or additions to those procedures are described here: 1,2-Dichloroethane, styrene, cyclohexene, 1-methylocyclohexene, and triethylsilane (Aldrich) were degassed by using three repeated freeze-pump-thaw cycles and dried over activated 3 Å molecular sieves for 7 d prior to use. Wilkinson’s catalyst ((PPh3)3RhCl; 1-
was prepared employing published methods. Compounds [2-6a]**BF₄**⁻ and [3-2b]**PF₆**⁻ were prepared by employing procedures described in Chapter 3.

**Synthesis of (κ²-P, O-indene)Rh(COD), 5-1.** The complex [2-6a]**BF₄**⁻ (0.065 g, 0.12 mmol) was dissolved in THF (5 mL). The resulting orange solution was transferred to a re-sealable reaction flask that was sealed under nitrogen with a PTFE valve. The reaction flask was transferred to the Schlenk line and distilled water (pre-sparged 30 minutes with nitrogen) was added to the mixture (1 mL) via syringe. The headspace of the reaction flask was partially evacuated and the vessel sealed and placed into a 60 °C oil bath. After 2 days of heating, the flask was removed from the oil bath and cooled to room temperature, at which time all solvent and other volatile materials were removed in vacuo. The flask was transferred to the glovebox and the solid yellow residue was extracted with pentane (3 x 5 mL). Subsequently, the pentane fractions were combined and filtered through a Celite column to remove any insoluble material. Removal of the pentane solvent and other volatile materials in vacuo yielded 5-1 as an analytically pure yellow solid (0.045 g, 0.098 mmol, 80 %). Anal. Calcd for C₃₃H₃₂PORh (%): C 60.27; H 7.04. Found: C 59.98; H 6.98. **¹H NMR** (C₆D₆): δ 7.20 (m, 1H, Ar-H), 7.01 (m, 1H, Ar-H), 6.95-6.90 (m, 2H, Ar-Hs), 5.37-5.36 (m, 2H, COD), 3.76-3.73 (m, 2H, COD), 3.39 (s, 2H, C1-H₂), 2.25-2.15 (m, 4H, P(CHMe₂)₂ and COD), 2.14-2.05 (m, 2H, COD), 1.82-1.75 (m, 2H, COD), 1.67-1.59 (m, 2H, COD), 1.21-1.15 (m, 12H, P(CHMe₃Me₅)₂ and P(CHMe₃Me₇)₂); **¹³C{¹H} NMR** (C₆D₆): δ 202.7 (d, **²JPC** = 24.2 Hz, C2), 145.8 (s, C7a), 140.1 (d, **²JPC** = 7.8 Hz, C3a), 126.4, 124.3, 120.1, 116.5 (C4, C5, C6, and C7), 101.1 (COD), 94.3 (d, **¹JPC** = 44.6 Hz, C3), 66.5 (d, **¹JPC** = 13.1 Hz, COD), 38.4 (d, **³JPC** = 12.1 Hz, C1), 33.5 (COD), 28.1 (COD), 23.9 (d, **¹JPC** = 24.4 Hz, P(CHMe₂)₂), 19.2
(P(CHMe₄Me₅)₂), 18.6 (P(CHMe₄Me₅)₂); ³¹P{¹H} NMR (C₆D₆): δ 38.1 (d, Jₚₚₚ = 153.0 Hz). Single crystals of 5-1·0.25CH₂Cl₂ were grown from a concentrated pentane/CH₂Cl₂ solution stored at -35 °C for 16 h.

**Synthesis of (κ²-P₂O-indene)Ir(COD), 5-2.** A procedure analogous to that described for the synthesis of 5-1 was employed, using the complex [3-2b]⁺PF₆⁻ (0.067 mg, 0.093 mmol) in place of [2-6a]⁺BF₄⁻ and a larger amount of pentane (3 x 10 mL) for the extraction step. Complex 5-2 was isolated as an analytically pure yellow solid (0.038 mg, 0.067 mmol, 74 %). Anal. Calcd for C₂₃H₂₃POIr (%): C 50.44; H 5.89. Found: C 50.22; H 6.11. ¹H NMR (C₆D₆): δ 7.19 (m, 1H, Ar-H), 7.00-6.97 (m, 2H, Ar-Hs), 6.93 (m, 1H, Ar-H), 5.09-5.04 (m, 2H, COD), 3.75-3.52 (m, 2H, COD), 3.42 (s, 2H, C1-H₂), 2.36 (m, 2H, P(CHMe₂)₂), 2.20-2.11 (m, 2H, COD), 2.05-1.95 (m, 2H, COD), 1.70-1.64 (m, 2H, COD), 1.51-1.47 (m, 2H, COD), 1.16-1.11 (m, 12H, P(CHMe₄Me₅)₂ and

P(CHMe₄Me₅)₂); ¹³C{¹H} NMR (C₆D₆): δ 205.4 (d, JₚC = 22.0 Hz, C2), 144.9 (s, C7a), 141.2 (d, JₚC = 8.2 Hz, C3a), 127.2 (C4 or C7), 125.6 (C5 or C6), 121.3 (C7 or C4), 117.7 (C6 or C5), 97.9 (d, JₚC = 51.7 Hz, C3), 89.6 (d, JₚC = 12.3 Hz, COD), 50.8 (COD), 38.5 (d, JₚC = 10.2 Hz, C1), 35.2 (COD), 29.4 (COD), 25.0 (d, JₚC = 30.3 Hz, P(CHMe₂)₂), 19.9 (P(CHMe₄Me₅)₂), 18.9 (P(CHMe₄Me₅)₂); ³¹P{¹H} NMR (C₆D₆): δ 31.7. Crystals of 5-2 suitable for single crystal X-ray diffraction analysis were obtained from a concentrated pentane solution of 5-2 stored at -35 °C.

**General Protocol for Hydrogenation Experiments.** The protocol used for hydrogenation reactions employing 0.5 mol% catalyst loading in hexanes under inert-atmosphere conditions is provided as a representative procedure. A solution of catalyst compound in hexanes (0.002 M, 0.014 mmol, total 7 mL of solution) was allowed to
equilibrate for 5 min, at which point the alkene (0.4 M, 2.8 mmol) was added by use of an Eppendorf pipette. The vial was then sealed and shaken vigorously. Subsequently, 1 mL aliquots of the mixture were placed in glass reactor cells, which were each equipped with a magnetic stir bar and sealed under nitrogen with a PTFE valve. The cells were transferred immediately to a Schlenk line and degassed by use of three freeze-pump-thaw cycles employing liquid nitrogen. Magnetic stirring of the solutions was initiated and the evacuated cells were backfilled with hydrogen gas (~ 1 atm, UHP grade). Clear yellow homogeneous solutions were observed throughout. At the desired sampling time, the reactor cell was opened to air and 2 mL of pentane was added via Pasteur pipette. The resultant mixtures were then filtered through a short Al$_2$O$_3$ column (2 cm) from which clear, colorless solutions eluted. These solutions were transferred to GC vials and sealed. Products of each reaction were identified by use of GC-MS and quantitative data were obtained from GC-FID analysis; tabulated data represent the average of two runs.

**General Protocol for Hydrosilylation Experiments.** The protocol used for these reactions employing 5.0 mol% catalyst loading (relative to Et$_3$SiH) in benzene with a styrene to silane ratio of 5:1 run at 60 °C is provided as a representative procedure. A solution of the catalyst compound in benzene (0.005 M, 0.023 mmol, total 4.5 mL solution) was allowed to equilibrate for 5 min, at which point the alkene (0.5 M, 2.3 mmol) was added by use of an Eppendorf pipette. The vial was then sealed and shaken vigorously for 15 seconds. Subsequently, Et$_3$SiH (0.1 M, 0.45 mmol) was added to the reaction mixture by use of an Eppendorf pipette, and the vial was then sealed and shaken as before. Aliquots (1 mL) of the mixture were placed in glass reactor cells, which were each equipped with a magnetic stir bar and sealed under nitrogen with a PTFE valve. The
cells were transferred immediately to a Schlenk line, submerged in a temperature-controlled oil bath (60 °C), and magnetic stirring of the solutions was initiated. In the case of 5-1, clear yellow homogeneous solutions were observed throughout; for 5-2, clear red solutions developed during the course of the catalytic reactions. At the desired sampling time, the reactor cell was opened to air and ~1 mL of pentane was added via Pasteur pipette. The resultant mixtures were then filtered through a short Al₂O₃ column (2 cm) from which clear, colorless solutions eluted. These solutions were transferred to GC vials and sealed. Products of each reaction were identified by use of GC-MS,²₈,²⁹ while quantitative data were obtained from GC-FID analysis; tabulated data represent the average of at least two runs.

Crystallographic Solution and Refinement Details for 5-1 and 5-2. Crystallographic data for 5-1·0.25CH₂Cl₂ and 5-2 were obtained at 193(±2) K on a Bruker PLATFORM/SMART 1000 CCD diffractometer using a graphite-monochromated Mo Kα (λ = 0.71073 Å) radiation, employing a sample that was mounted in inert oil and transferred to a cold gas stream on the diffractometer. Crystal structure diagrams were generated by use of the ORTEP program.¹¹ The structure of 5-1 was solved by use of direct methods and refined by use of full-matrix least-squares procedures (on F²) with R₁ based on \( F_o^2 \geq 2\sigma(F_o^2) \) and \( wR_2 \) based on \( F_o^2 \geq -3\sigma(F_o^2) \). In the course of the solution and refinement process, a positional disorder involving one carbon atom of the 1,5-cyclooctadiene ligand was identified and subsequently modeled in a satisfactory manner over two half-occupied positions (C17a and C17b). As well, attempts to refine peaks of residual electron density as chlorine and carbon atoms of an inversion-disordered dichloromethane molecule were unsuccessful. As such, the data were corrected for
disordered electron density through the use of the SQUEEZE procedure as implemented in PLATON (PLATON - a multipurpose crystallographic tool; Utrecht University, Utrecht, the Netherlands). A total solvent-accessible void volume of 178 Å³ with a total electron count of 49 (consistent with one molecule of solvent dichloromethane) was found in the unit cell. The structure of 5-2 was solved by use of the Patterson search/structure expansion and refined by use of full-matrix least-squares procedures (on $F^2$) with $R_1$ based on $F_o^2 \ (2\sigma(F_o^2))$ and $wR_2$ based on $F_o^2 \geq -3\sigma(F_o^2)$. In the course of the solution and refinement process, two crystallographically independent molecules of 5-2 were identified; the interatomic distances and angles associated with these two independent molecules are indistinguishable. Anisotropic displacement parameters were employed throughout for the non-hydrogen atoms, and all hydrogen-atoms were added at calculated positions and refined by use of a riding model employing isotropic displacement parameters based on the isotropic displacement parameter of the attached atom.
Table 5.2. Crystallographic Data for 5-1·0.25CH₂Cl₂ and 5-2

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5.5 References and Endnotes


5. Wile, B. M.; Burford, R. J.; McDonald, R.; Ferguson, M. J.; Stradiotto, M. Organometallics 2006, 25, 1028.


17. The enamine 1-PtPr₂-2-NMe₂-indene is not hydrolyzed under similar conditions. For a discussion of enamine hydrolysis, see: Sollenberger, P. Y.; Martin, R. B. *J. Am. Chem. Soc.* 1970, 92, 4261.


Chapter 6: Discussion

6.1 Conclusions and Significance of the Research

Over the last 40 years, homogeneous transition metal catalysts have been developed into useful and versatile tools for the synthesis of fine and bulk chemicals that we use in our everyday lives.¹ In the area of group 9 transition metal chemistry, the synthetic utility of cationic Rh and Ir catalyst complexes stabilized by mixed donor bidentate P,N ancillary ligands has been demonstrated for many transformations involving the activation of E-H bonds (E = main group element) in small molecule substrates. However, the range of reaction conditions under which these cationic complexes may be used is limited in part by their poor solubility properties. In addition, the systematic design of cationic complexes is complicated by the somewhat unpredictable influence of the outersphere counteranion on catalytic performance. More recently, various research groups have focused on the development of charge-neutral formally zwitterionic alternatives to traditional cationic systems since zwitterionic catalysts can possess certain reactivity advantages over cationic catalysts, as described in Chapter 1.

The scope of anionic ligands that effectively sequester the anionic charge in zwitterionic Rh and Ir complexes remains limited, with no examples of heterobidentate chelating anionic ligands known previous to the work presented in this thesis. In addition, there has been no systematic examination of the catalytic properties of formally zwitterionic Ir(I) complexes, despite the well established utility of Ir(I) cations. In the research presented in this thesis, a fundamentally new heterobidentate P,N ligand has
been developed: 1-P'Pr₂-2-NMe₂-indene (2-2) can be prepared via a two-step modular synthetic pathway from readily available starting materials. While this ligand can support neutral and cationic Rh(I) and Ir(I) fragments, more interestingly it can be deprotonated to generate a 10π-indenide unit which serves as an anionic charge reservoir. Upon complexation of a cationic Rh or Ir fragment by this substituted indenide ligand (2-2e), an unusual and entirely new class of formally zwitterionic Rh and Ir complexes are generated; these represent the first heterobidentate zwitterionic group 9 metal catalysts.

A comparison of the catalytic properties of these group 9 zwitterions with their structurally analogous cationic relatives has provided the opportunity to assess the impact of altering only the electronic characteristics of a formally cationic metal fragment, without significantly altering the steric profile of the metal coordination sphere. Notably, the results of catalytic hydrogenation and hydrosilylation studies confirm that the zwitterionic group 9 complexes bound by the P,N-indenide ligand (2-2e) constitute an effective class of neutral catalyst complexes for these types of E-H additions to unsaturated substrates, and whose solubility and reactivity properties are in some instances divergent from and superior to those of more traditional Rh and Ir [(κ²-P,N)M(COD)]⁺X⁻ salts. These cationic and zwitterionic group 9 complexes represent a complementary family of catalysts for the addition of E-H bonds to alkenes, when issues of catalytic activity/selectivity and solvent compatibility are considered.

A second significant area of research in this thesis constitutes the discovery of late metal complexes supported by an alternative ‘hard-soft’ 2-phosphinoenolate ligand, 1-P'Pr₂-2-O-indene. In contrast to the preponderance of evidence that suggests Ir(I) complexes must be cationic in order to function effectively as alkene hydrogenation
catalysts, the neutral Ir complex 5-2 that features this ligand is able to reduce alkenes under very mild reaction conditions (~1 atm H₂, 22 °C) in a range of solvents including hexanes, benzene, THF, CH₂Cl₂, and MeCN. In fact, this (κ²-P,O)Ir(COD) complex represents the most active neutral Ir(I) alkene hydrogenation catalyst known.

6.2 Future Directions

Currently, the origin of the reactivity differences observed between structurally related group 9 cationic and zwitterionic complexes presented in this thesis are not known; however, the observation that the Rh cation [2-6a]+BF₄⁻ cleanly reacts with PMePh₂ to generate [Rh(PMePh₂)₄]+BF₄⁺, while under similar conditions only the COD ligand in the Rh zwitterionic 2-7 was displaced suggests that the more tightly bound anionic indenide ligand in the zwitterionic complexes may represent a potential source of such divergent reactivity. In the zwitterionic complexes, it is possible that charge separation may not be absolute; if this is the case, the electrophilicity of the metal center would likely be somewhat reduced relative to their cationic relatives, [2-6a]+X⁻ and [3-2b]+X⁻, which in turn could also influence the catalytic behavior displayed by these species. In addition, the backbone indenide unit in the formally zwitterionic species may participate in some unknown way during the course of catalytic transformations. In this regard, synthetic and mechanistic experiments directed towards addressing these questions are future targets.

The utility of the zwitterionic Rh and Ir complexes presented in this document has been demonstrated for two well-established catalytic reactions: the hydrogenation and the hydrosilylation of alkenes. In addition, the reactivity of these new complexes is comparable to, and in some cases superior to, the benchmark systems developed by
Wilkinson (Rh) and Crabtree (Ir). Ensuing reactivity studies involving the catalytic application of the zwitterionic complexes 2-7 and 3-3 and the cationic analogues [2-6a]+X− and [3-2b]+ X in reactions where there exists no general class of catalyst complexes represents an important target. Examples of such reactions might include hydroamination and hydrophosphination, in which an N-H or P-H bond would be added to an unsaturated substrate.

Cationic group 9 coordination chemistry has been dominated to date by various forms of P and N ancillary ligands and thus it is somewhat surprising that the neutral Ir(I) complex bound by an anionic P,O-indenyl ligand is such an active hydrogenation catalyst. Given that anionic P,O ligands have received relatively little attention in platinum-group metal catalyst design, exploring the catalytic abilities of such species featuring a diverse array of phosphinoenolate and related anionic ‘hard-soft’ ligands represents a wealth of potential research. In addition, the catalytic preference for, and solubility of the neutral Ir(I) phosphinoenolate complex in hexanes, suggests that these types of neutral group 9 catalysts may be excellent candidates as catalysts for reactions conducted in supercritical media.⁵

Finally, as has been alluded to in Chapter 1, ancillary ligands can serve as effective tools for chirality transfer in a catalytic application. In particular, the asymmetric hydrogenation of unsaturated substrates mediated by cationic Ir(I) complexes featuring chiral P,N-bidentate ligands has received much attention.³ However, the development of chiral anionic ligand variants capable of supporting cationic late transition metal fragments to generate formally zwitterionic chiral complexes remains largely unaddressed. To this end, exploring alternative forms of the P,N-indene ligand 2-2

182
which incorporate chiral fragments represents an important future target, especially in light of the promising catalytic abilities of the achiral cationic and zwitterionic Rh and Ir complexes presented in this thesis.

6.3 References


Bibliography


Dickson, R. S. Homogeneous Catalysis with Compounds of Rhodium and Iridium; Reidel: Dordrecht, 1985.


Rankin, M. A.; McDonald, R.; Ferguson, M. J.; Stradiotto, M. Organometallics 2005, 24, 4981.


Weast, R. C. (Ed.) *CRC Handbook of Chemistry and Physics, 56th ed.*, CRC Press, Ohio, **1975**, F 211.


