THE SYNTHESIS AND CHARACTERIZATION OF NEW PLATINUM, GOLD
AND SILVER COMPLEXES, AND THEIR APPLICATION AS
HYDROSILYLATION CATALYSTS

by

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Abstract

Late transition metal complexes are traditionally employed as catalysts for a variety of organic transformations. The hydrosilylation reaction represents the formal addition of a Si-H bond to an unsaturated organic substrate, and is one such transformation that has received much attention in the scientific literature. The recent development of a series of P,N- and P-substituted indene ligands by the Stradiotto group prompted a study of group 10 and 11 complexes derived from these complexes. Synthesis and structural characterization of Pd(II), Pt(II), Au(III) and Au(I) species is reported, followed by stability and reactivity studies for these complexes. Selected complexes, as well as several M(I)/phosphine (M = Ag, Au) mixtures were evaluated as catalysts for the hydrosilylation reaction. Comparison of a neutral Pt(II) complex and a closely related neutral, charge-separated Au(III) zwitterion reveals significant differences in stability and reactivity, as well as in catalytic competence for the hydrosilylation of alkenes. Key Pt(II) complexes also display interesting reactivity that points to the potential for related species to accomplish intermolecular C-H bond activation. The Ag(I) and Au(I) catalyst systems described represent the first examples of Ag-mediated and room temperature Au-mediated hydrosilylation reactions, and as such, represent a significant contribution to scientific development. Future directions and proposed modifications to substituted indene ligands are discussed.

List of Abbreviations and Symbols Used

δ	chemical shift
η	hapticity (contiguous donor atoms)
κ	hapticity (non-contiguous donor atoms)
μ	bridging ligand
Å	Angstrom (10^{-10} meters)
atm	atmospheres
BN	aminoborate
BP	phosphinoborate
^{n}Bu	*n*-butyl
^{t}Bu	*tert*-butyl
cat	catalyst
COD	1,5-cyclooctadiene
Cp*	pentamethylcyclopentadienyl
Cy	cyclohexyl
d	doublet
DCE	1,2-dichloroethane
dd	doublet of doublets
DEPE	1,2-bis(diethylphosphino)ethane
DMAP	4-(dimethylamino)pyridine
DMSO	dimethylsulfoxide
DPPP	1,2-bis(diphenylphosphino)propane
dt	doublet of triplets
E	main group donor fragment
ESI	electrospray ionization
Et	ethyl
FID	flame-ionization detector
GC	gas chromatography
h	hour(s)
Hz	Hertz
IR	infrared
m	multiplet

Me	methyl
mol	mole
MS	mass spectrometry
m/z	mass-to-charge ratio
NBD	norbornadiene (bicyclo[2.2.1]hepta-2,5-diene)
NMR	nuclear magnetic resonance
OA	oxidative addition
ORTEP	Oak Ridge thermal ellipsoid plot
OTf	triflate (trifluoromethane sulfonate)
p	*para*
Ph	phenyl
^{i}Pr	*iso*-propyl
PTFE	poly(tetrafluoroethylene)
RE	reductive elimination
s	singlet
t	triplet
THF	tetrahydrofuran
TOF	turnover frequency ([moles product/moles catalyst]/time)
TON	turnover number (moles product/moles catalyst)
Tp	tris(pryazolyl)borate

Author's Statement Regarding Conventions, Nomenclature and Publication

Chemical structures in this thesis are drawn following conventions commonly employed in organometallic literature. Formal charges, as employed in conventional Lewis diagrams have been omitted to clarify the bonding at the metal center. As such, a dative interaction is inferred when a two-electron donor (an "L" donor, such as a phosphine or an amine) interacts with a metal center, and the bond is drawn as a straight-line, rather than an arrow (except in cases where inclusion of such arrows clarifies the bonding model). Covalent bonds between one-electron donors (an "X" donor, such as halogen atoms or alkyl groups) and a metal center are also represented using a straight-line. Charges on the metal center refer to the oxidation state of the metal minus the number of X ligands.

Nomenclature also follows that in the published literature. Where appropriate, IUPAC guidelines have been followed, though this is not exclusively the case. Compounds are numbered sequentially by chapter, and are referred to in the text by this identifier. Referencing is also chapter specific, with a collected bibliography, sorted alphabetically by first author following the text as Chapter 8.

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(1)   Wile, B. M.; McDonald, R.; Ferguson, M. J.; Stradiotto, M. *Organometallics*, **2005**, *24*, 1959-1965.

(2)   Wile, B. M.; Burford, R. J.; McDonald, R.; Ferguson, M. J.; Stradiotto, M. *Organometallics*, **2006**, *25*, 1028-1035.

(3)   Wile, B. M.; Stradiotto, M. *Chem. Commun.*, **2006**, 4104-4106.

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"There is a single light of science, and to brighten it anywhere
is to brighten it everywhere"

- Isaac Asimov

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Chapter 1 – Introduction

1.1   Late Transition Metals in Homogeneous Catalysis

Metals have been shown to catalyze a number of chemical transformations in an efficient manner. In particular, the elements of the transition series (groups 3 through 10) have figured prominently in the traditional application of metal catalysis to organic chemistry. A distinction is often made between homogeneous catalysis, in which smaller, soluble coordination adducts of metal centers are in intimate contact with reactants in the solution phase, and heterogeneous catalysis, in which larger groups of metal atoms (often polymeric or bulk metal aggregations) interact with reactants in another phase. This thesis will focus on the synthesis, characterization and evaluation of complexes that may be viewed as homogeneous catalysts.

The "platinum group metals" (i.e. Ru, Os, Rh, Ir, Pd and Pt) are of particular importance to the field of homogeneous catalysis, due to the large number of organic transformations they catalyze. The relatively mild conditions required by reactions employing platinum group metals, as well as the higher selectivity observed when compared to other transition and alkali metals, leads to their high synthetic utility and varied application.[1] Platinum group metals typically exhibit a high degree of stability in multiple oxidation states, allowing access to a number of catalytic pathways. Moreover, these metal complexes have been observed to engender reactivity in electron-rich organic substrates such as olefins and arenes, thereby allowing for greater activity or selectivity in the activation of inert bonds. This assembly and disassembly of E-H and E-C bonds, where E may be any main group donor fragment, is of fundamental importance to synthetic chemistry.

Molecules or ions are commonly bound to transition metals as ligands in either a covalent or dative fashion. By altering the ligand used, one may correspondingly vary both the steric and electronic environments of the metal center. Thus, a judiciously chosen ligand may prove as important to the performance of a catalyst as the identity of the metal itself. Tailoring both the metal and the ligand (or ligands') architecture to yield rationally designed coordination complexes figures prominently in current organometallic research, and promises to increase the scope and specificity of organo-transition metal catalyzed reactions.

1.2   Mixed-Donor Ligands

Chelating ligands bearing equivalent donors are ubiquitous in transition metal chemistry. While the success of these ligands in engendering useful reactivity properties to assorted metal fragments is without question, increasing attention has been paid to the emerging class of mixed-donor ligands, of which those bearing P and N donor atoms have garnered considerable interest.[2,3] This is particularly evident in the case of (κ^2-P,N)Pd complexes, which have demonstrated catalytic superiority to related complexes featuring P,P and N,N ligands.[2-4] Examples include the oligomerization of olefins as studied by Brookhart and co-workers,[5-9] as well as any number of chiral transformations accomplished using asymmetric P,N ligands.[4,10-16] These studies reveal the success of P,N ligands, in particular those featuring a rigid backbone (i.e. substituted arenes), and demonstrate that the activity and/or selectivity of the resulting catalyst is highly dependant on the substitution at both P and N sites.

While chelating ligands bearing equivalent donors bind to a metal in a symmetric fashion, this is not the case when a P,N ligand is employed. The overlap between the relatively soft phosphine and an electron-rich late transition metal is stabilized by the

involvement of the π-accepting orbitals on P, relative to the harder N-donor, for which

such acceptor orbitals are not accessible. The result is an inequivalent bonding

environment in the resultant metal complexes, as illustrated in Figure 1.1 (see the

discussion of M-X bond lengths trans to P and N in the square planar $(\kappa^2\text{-}P,N)MX_2$

complexes **2.1**, **2.3b**, **2.4** and **3.1** in Chapters 2 and 3). Consequently, the phosphine is

thought to provide a stable, non-labile bond to the metal center, while the harder N-arm

has the potential to decoordinate. Thus, P,N ligands are poised to exhibit such

"hemilabile" behavior, generating an open coordination site at the metal as required,

while maintaining stability of the metal complex by virtue of the proximity of a stabilizing

donor.
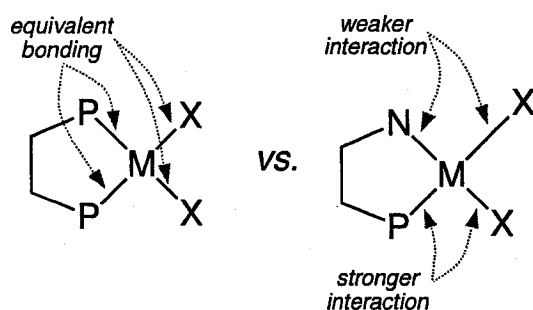
Figure 1.1   Bonding in generic $\kappa^2\text{-}P,P$ and $\kappa^2\text{-}P,N$ metal complexes.

While the P,N effect has been explored extensively for Pd complexes over the

last two decades, comparatively little is known about the effect of a P,N ligand set on Pt

or Au complexes. In the case of Pt(II), investigations by Jones and co-workers,[17,18]

Milstein and co-workers,[19-21] and Schubert and co-workers[22-27] represent the majority of

research into P,N-type ligands. The requirement for chelate opening prior to oxidative

addition or reductive elimination in a Pt(II)/Pt(IV) cycle has been well documented;[28-32] it

is thought that a hemilabile P,N ligand might assist in this process, leading to superior

catalyst performance. Homogeneous catalysis by Au is dominated by metal-containing

salts, and as such, few studies involving rationally prepared metal/ligand complexes have been conducted.[33-36]

1.3 The Hydrosilylation Reaction

The addition of a Si-H bond to an unsaturated organic fragment is known as the hydrosilylation reaction. Alkenes and alkynes are the most common substrates for this reaction, though the hydrosilylation of carbonyl and C-N multiple bonds is becoming increasingly important.[37-39] While numerous transition metal complexes are known to catalyze hydrosilylation reactions,[37,38,40] the most commonly employed and effective catalysts are $H_2PtCl_6 \cdot H_2O$ (hexachloroplatinic acid, or "Speier's catalyst" in ^iPrOH solution)[41] and "Karstedt's catalyst" (1.1).[42,43] These pre-catalysts have remarkable activity, proving effective at loadings of 10^{-3} mol% and lower.[44] While the active species derived from these pre-catalysts was originally proposed to be homogeneous,[45-47] arguments for a heterogeneous mechanism were made based on light scattering data, and the observance of Pt colloids upon evaporation of catalytically active solutions.[48-50] More recent studies by Lewis and co-workers employing extended X-ray absorption fine structure (EXAFS) spectroscopy, small angle X-ray scattering (SAXS) and X-ray photoelectron spectroscopy (XPS) during catalysis have revealed that the most catalytically competent Pt species in the solution are in fact monomeric, rather than colloidal.[51] This implies that a homogeneous mechanism may be used as a reasonable descriptor for the behavior of such hydrosilylation catalysts.

1.1
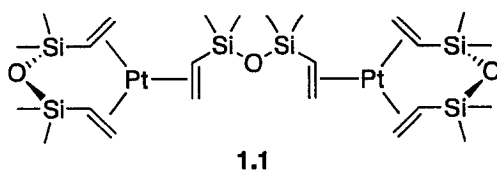
Figure 1.2   Karstedt's catalyst.

5

The accepted mechanisms for transition metal catalyzed hydrosilylation are the

Chalk-Harrod and modified Chalk-Harrod (or Lewis) mechanisms, shown below (Figure

1.3). While both mechanisms invoke oxidative addition (OA) and coordination of the

alkene (the order of these steps may be reversed in some cases),[52] they diverge when

coming to the alkene insertion step. While insertion into the metal hydride bond can only

result in reductive elimination (RE) to yield a saturated product (the Chalk-Harrod

mechanism),[46,47] insertion into the metal silane bond offers two possibilities (the modified

Chalk-Harrod mechanism).[53-57] Here, reductive elimination again generates a saturated

alkyl silane, in contrast to β-H elimination, which generates a vinyl silane and an

equivalent of dihydrogen gas. While these two mechanisms can account for the

observed products of the hydrosilylation reaction, a recent report by Glaser and Tilley

suggests that an alternative pathway involving a metal silylene intermediate may operate

in some cases.[58]
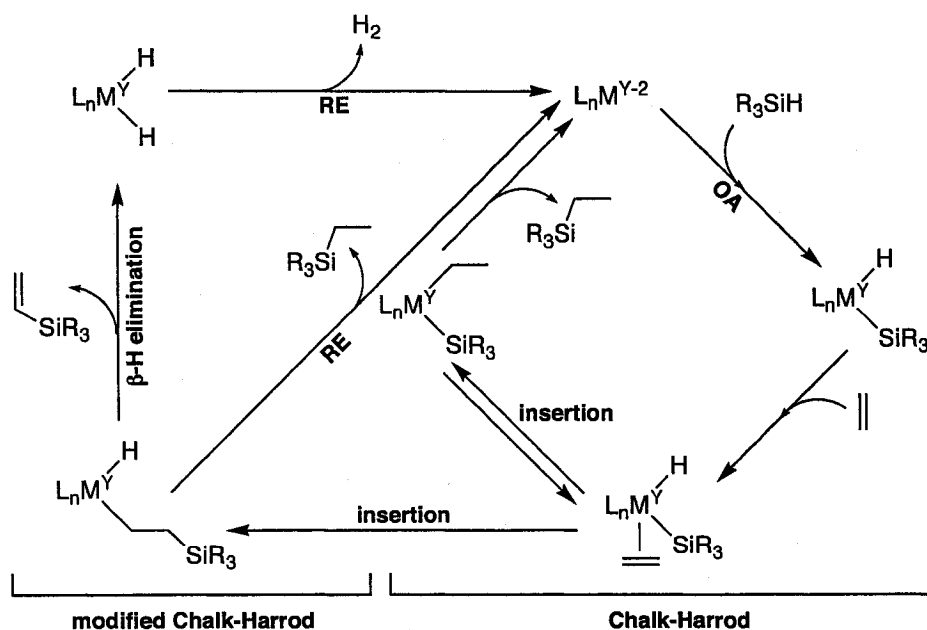
Figure 1.3   The Chalk-Harrod and modified Chalk-Harrod mechanisms for the
hydrosilylation of alkenes (adapted from Crabtree).[40]

1.4   Cationic and Zwitterionic Transition Metal Complexes

1.4.1   Cationic Transition Metal Complexes

The transformation of neutral metal complexes into cationic species exhibiting coordinative unsaturation has been employed as a means of enhancing the reactivity of metal complexes. Notably, early examples of cationic group 9 metal complexes by Schrock and Osborn,[59] and Crabtree,[60] displayed increased efficacy for the catalytic hydrogenation of unsaturated substrates, relative to neutral catalysts. More recently, cationic group 9 complexes have displayed interesting reactivity or catalytic activity not observed in related neutral species, as exemplified by C-H activation studies and related work by Bergman and co-workers.[61-65] Another well-known example of the advantageous use of cationic metal catalysts is Zeigler-Natta type olefin polymerization, for which Zeigler and Natta received the Nobel Prize in Chemistry in 1963. While severe conditions are required for the thermal polymerization of propylene (200 °C, >1000 atm),[40] the use of a neutral early transition metal pre-catalyst (usually a metal halide or metallocene) in combination with a strong Lewis acid co-catalyst (such as methylalumoxane or $B(C_6F_5)_3$),[66-71] produces a highly ordered polymer under milder conditions (often 25 °C, 1 atm).

Group 10 metal complexes have featured prominently in the study of cationic catalysts. Brookhart and co-workers,[5-9] and others,[72,73] have demonstrated the advantages of cationic (κ^2-P,N)Pd systems over neutral analogues for a multitude of reactions. Recently, chiral P,N ligands coordinated to a cationic Pd center have been used as competent catalysts for the asymmetric allylic alkylation reaction.[11-14] Pt complexes featuring cationic centers have been examined extensively as catalysts for the selective functionalization of methane (the so-called "Shilov system"),[74-82] due to the

difficulty associated with activating the relatively inert C-H bonds of methane (for further discussion, please see section 1.5). The enhanced reactivity of cationic complexes is typically rationalized by invoking an increase in electrophilicity of the metal center. It is often the case that the most difficult step in a given catalytic transformation is the selective activation of a relatively inert bond.[32,75-77] Coordination of such an electron-rich σ bond is thus rendered favorable by a more electrophilic metal center.

Though numerous advantages to cationic systems relative to their neutral congeners are apparent, there also exist several drawbacks. The fact that such cationic complexes are by nature ionic typically dictates their low solubility in low-polarity media, such as alkanes. Thus, reactions must be carried out in polar solvents that may be unsuitable for sensitive reactants and/or that may attenuate the activity of the catalyst through competitive binding for the metal active site. Furthermore, the use of a cationic metal species requires a balance of charge, often through the use of a low-coordinating anion such as BF_4^-, PF_6^-, OTf⁻ or $B(C_6F_5)_4^-$. When counterbalancing anions with closer proximity to the metal center (i.e. less outer-sphere character) are employed, ion-pairing is often observed, resulting in reduced or inconsistent catalyst activity.[66,83]

1.4.2 Zwitterionic Transition Metal Complexes

Some of the challenges associated with the use of cationic transition metal catalysts can be rectified using a zwitterionic approach. In the context of organometallic chemistry, a zwitterionic metal complex features a charged metal center and an oppositely charged ligand, for which reasonable resonance structures cannot be drawn such that these opposite charges are placed adjacent to one another. In practice, this often means that a formally cationic metal center is ligated by an organic framework bearing an overall negative charge, though formally anionic metal centers supported by

a cationic ligand are also known.[84-86] In principle, zwitterionic complexes should provide

increased solubility in low-polarity solvents relative to cationic complexes due to a

moderately less electrophilic metal center, and the formal neutrality of the complex

(relative to ionic salts, which bear charge). As such, issues of anion and solvent

coordination to the cationic metal center are obviated or reduced.

One popular class of anionic ligands are the poly(pyrazolyl)borate (or Tp) ligands

originally reported by Trofimenko.[87-89] In a recent review, Trofimenko notes that about

2000 papers have been published dealing with poly(pyrazolyl)borates, and complexes of

70 elements have been reported.[90] The success of this ligand motif is likely due to the

large variability of both steric and electronic factors accomplished by substituting the 3, 4

and 5 positions (see Figure 1.4). Though these ligands are formally anionic by virtue of

the negative charge formally assigned to boron (**1.2a**), resonance contributors in which

the negative charge is moved to a pyrazole ring (**1.2b**) or negated altogether (**1.2c**) are

possible. As such, complexes derived from poly(pyrazolyl)borate ligands are not formally

zwitterionic. Recent reports have highlighted the success of late transition metal

complexes featuring Tp ligands in mediating the activation of C-H bonds.[32,91-94]
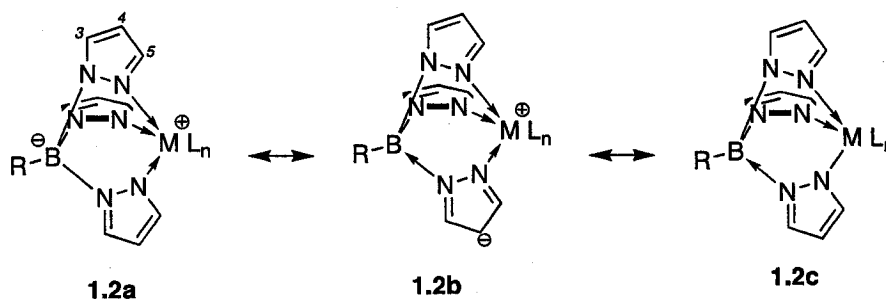
Figure 1.4   Resonance contributors to a generic tris(pyrazolyl)borate/metal complex.

Zwitterionic metal complexes have played an important role in the evolution of

olefin polymerization catalysts over the last two decades. As discussed in section 1.4.1,

the use of cationic early transition metal complexes led to catalysts of exceptional activity,[67-71] though coordination of the counterion was later revealed to be a deactivating process.[66,69,83] With the first report of a zwitterionic "pre-activated" metallocene by Hlatky and Turner (1.3) in 1989,[95] precedent was set for a new class of highly active group 4 olefin polymerization catalysts. Subsequent reports from a number of researchers showed the incorporation of perfluoroborate moieties in the ligand to be a general and successful strategy for the preparation of formally zwitterionic metallocenes, as seen in compounds 1.4[96] and 1.5.[97] Moving the anionic borate moiety from the catalyst "active site" to the backbone of the ligand provided a less sterically hindered metal center, as demonstrated by 1.6[98] and 1.7,[99] though the length of the tether was found to be crucial to the stability of the zwitterion.
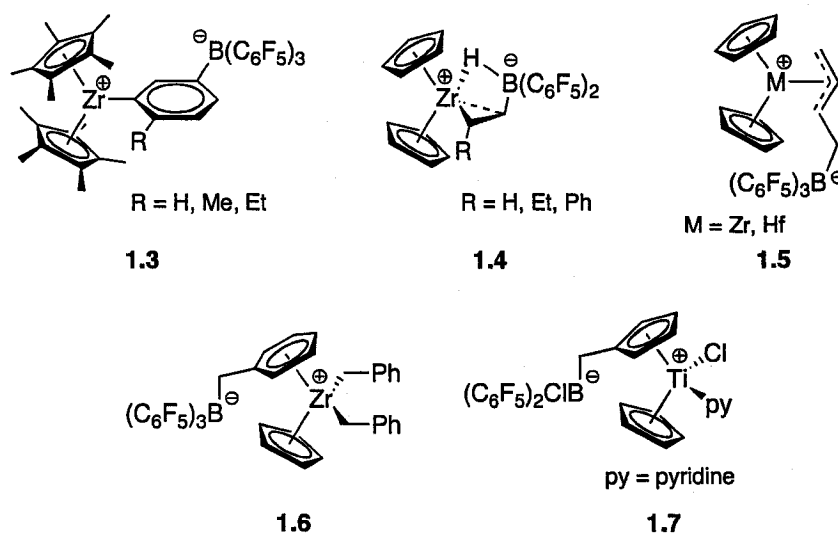
Figure 1.5   Selected zwitterionic group 4 catalysts for olefin polymerization.

Rh complexes featuring an anionic borato moiety vastly dominate the field of late transition metal catalysis using zwitterionic species. Though extensive study of these systems has led to an increased understanding of their properties and utility, comparatively little scrutiny of metals from other groups, or complexes featuring a non-

borato, anionic ligand set has been undertaken. Nevertheless, a brief survey of these Rh/borate complexes allows for some conjecture as to the general properties of late transition metal zwitterions.

The development of compound **1.8** by Schrock and Osborn,[100] which was later scrutinized by Alper and co-workers,[101-103] initiated research into the utility of late transition metal zwitterions as catalysts for a number of reactions. Alper and co-workers found that **1.8** catalyzed the regioselective hydroformylation of unsaturated organic molecules in an efficient fashion, under mild conditions.[101] It was also demonstrated that the zwitterionic Rh complex **1.8** served as a catalyst for a number of transformations, including the regioselective hydroformylation of p-isobutylstyrene (to produce the ibuprofen precursor 2-(4-isobutylphenyl)propanal),[101] the silylformylation of olefins,[102] and the hydrogenation of imines.[103] This pioneering work demonstrated the utility of late transition metal zwitterions as catalysts for reactions in which the utility of cationic metal complexes was established previously.

1.8   **1.9**
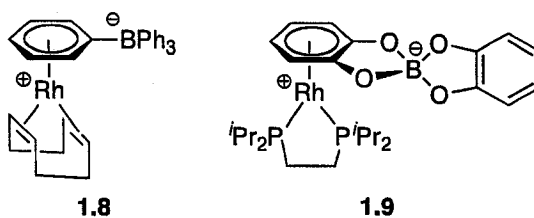
Figure 1.6   Zwitterionic Rh species featuring π-bound arene units.

The discussion of Rh zwitterions in the literature continued when Marder, Baker and co-workers later implicated complex **1.9** as a resting state of the catalytic cycle for the hydroboration of unsaturated species.[104] This claim was later bolstered by the rational preparation of **1.9**, followed by its use as an effective catalyst for the diboration of olefins.[105] As predicted, the zwitterionic species **1.8** and **1.9** exhibited increased solubility in non-polar media relative to their cationic relatives, and may be more

successful due to the attenuated electrophilicity of the Rh center. While **1.8** and **1.9** both

feature a π-bound arene ring, more recent reports of zwitterionic complexes have

focused on main group donors bridged by a borato moiety, as in the chiral "boratabox"

ligands of Pfaltz and co-workers,[106] and the phosphinoborate (BP) and aminoborate (BN)

ligands of Peters and co-workers.

First reported by Tilley and Peters in 1999,[107] (and coincidently also reported later

that same year by Nocera and co-workers)[108] the BP ligands (Figure 1.7) at first glance

bear a striking resemblance to the Tp ligands popularized by Trofimenko. While both

incorporate donor-arms pendant upon a central borato unit, direct comparison has

shown the BP and Tp ligands to be "...electronically, as well as sterically, quite

distinct..."[109] Notably, the anionic borate appears to be insulated from the metal center to

a greater extent in the BP ligands than in the Tp ligands, both spatially and

electronically.[110] This latter point may be rationalized on the basis of resonance

arguments, namely the absence of simple resonance contributors that effectively

delocalize charge onto one of the donor atoms (Figure 1.8).

1.10 **1.11** **1.12** **1.13**
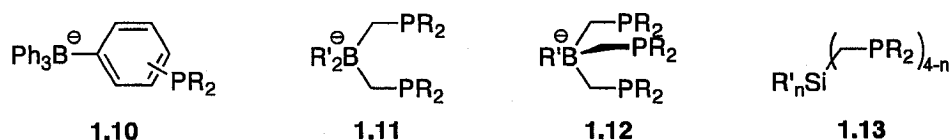
Figure 1.7 Generic examples of the BP ligands studied by Peters and co-workers, and a related neutral analogue featuring a central silane.

1.14a **1.14b** *(unconventional)* **1.14c**
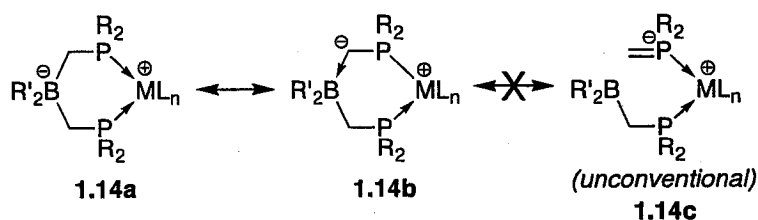
Figure 1.8 Resonance contributors to a generic bis(phosphino)borate complex.

The use of bis-chelating ligands of the type **1.11** for late transition metal complexes has demonstrated the merits of a zwitterionic approach. In a recent report,[111] Peters and Betley compared a zwitterionic Rh complex featuring **1.11** (R = R' = Ph) to a cationic species supported by the related neutral ligand **1.13** (R = R' = Ph, n = 2), as measured by their effectiveness as catalysts for the hydrogenation, hydroboration and hydrosilylation of styrene. While the catalytic results indicated that the two types of complexes behaved similarly, the zwitterions demonstrated activity in highly coordinating solvent (MeCN) as well as preserving solubility over a wide range of solvents. In contrast, cationic systems were deactivated in polar reaction media, and proved to be insoluble in non-polar solvents. Despite the steric differences in **1.11** and **1.13** related to the substitution of Si for B⁻, it is clear that the related cationic and zwitterionic Rh complexes described by Peters and co-workers display divergent reactivity in a number of reaction media.

Peters and co-workers also explored the use of (phosphino)tetraphenylborate ligands **1.10** as coordinating, monoanionic ligands that would be both sterically demanding and electron releasing.[112] It was found that Pd complexes generated in situ from **1.10** served as effective catalysts for the Suzuki coupling of phenylboronic acid and aryl chlorides, supporting such claims. Similarly, studies conducted to compare the rationally prepared zwitterionic complex **1.15a** to related cationic species **1.16a** and **1.17a** showed all complexes to display similar activities in THF solution.[113] Though less polar solvents were not explored in this report, the observation that the anionic ligand did not appreciably attenuate the activity of the cationic Pd center is encouraging; this points to the potential interchangeability of cationic and zwitterionic metal complexes.

Ph_2B ... Ph_2 ... P ... M ... Me ... THF ... Ph_2

1.15a M = Pd
1.15b M = Pt

Ph_2Si ... Ph_2 ... P ... M ... Me ... THF ... Ph_2 ... $^\ominus B(C_6F_5)_4$

1.16a M = Pd
1.16b M = Pt

Ph_2 ... P ... M ... Me ... THF ... Ph_2 ... $^\ominus B(C_6F_5)_4$

1.17a M = Pd
1.17b M = Pt
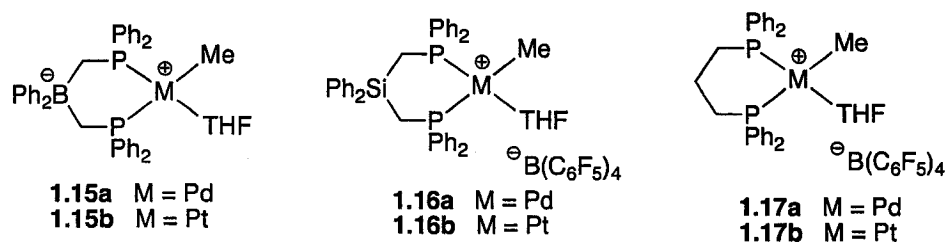
Figure 1.9   Group 10 complexes featuring bis(phosphino)borate and related neutral ligands.

Peters and co-workers have also prepared a zwitterionic Pt species, **1.15b** and examined its reactivity in comparison to related cationic systems, **1.16b** and **1.17b**.[114,115] Their findings indicate that **1.15b** activates Ph-H bonds under mild conditions (50 °C, 4 h), generating a complex in which Me has been replaced by Ph. IR studies of CO adducts of **1.15b**-**1.17b** (in which the THF ligand was displaced by CO) revealed the BP fragment in **1.15b** to be the most electron-releasing ligand. It was also found that under prolonged thermolysis in C_6D_6, **1.15b** showed significant D-atom incorporation, while neither **1.16b** nor **1.17b** exhibited similar scrambling. This and other reactivity studies led Peters and co-workers to surmise that while the bis(phosphino)silane in **1.16b** and DPPP in **1.17b** acted as relatively innocent ligands, the BP ligand in **1.15b** was observed to take on a κ^3 binding mode as a result of interaction of one of the Ph rings from the BPh_2 portion of the ligand.

1.5   Platinum in Homogeneous Catalysis

While Pt has found use as a catalyst for a variety of transformations,[116] a primary focus has remained the selective activation and oxidation of inert C-H bonds. A prime example is the oxidation of alkanes to furnish alcohols, aldehydes or carboxylic acids; so called "Shilov chemistry".[74,117,118] Early studies by Shilov and co-workers demonstrated that a Pt(II) system was capable of methane oxidation at relatively mild temperatures

(100-120 °C) in water to produce MeOH and MeCl, though a stoichiometric equivalent of

Pt(IV) (as $[PtCl_6]^{2-}$) was required as an oxidant.[119] Subsequent work by Periana and co-

workers described the use of a (κ^2-N,N)Pt(II) system in the presence of SO_3/H_2SO_4 for

the oxidation of methane to methylbisulfate (MeOSO$_3$H, see Figure 1.10).[82]
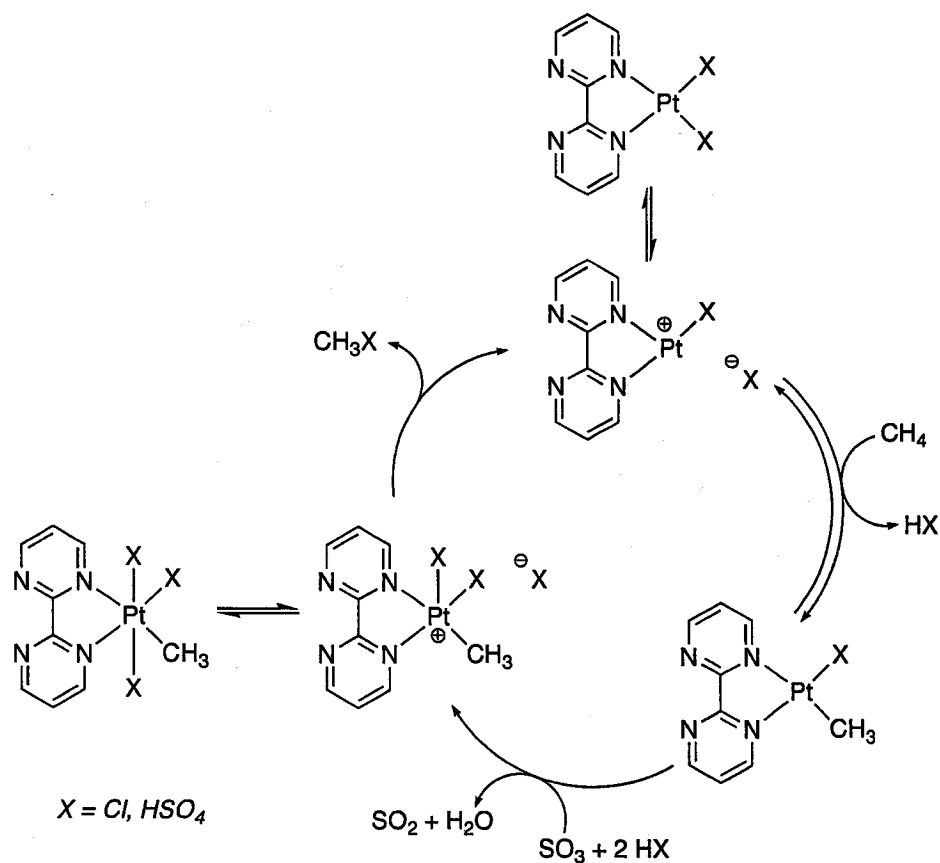
Figure 1.10 The Catalytica system for the oxidation of methane to methylbisulfate.

Continued investigation by Periana and co-workers has demonstrated the

success of cationic Pt(II) complexes (often ligated by κ^2-N,N ligands) in achieving C-H

bond activation with a focus on the applications of such a process to the catalytic

functionalization of alkanes.[81,120,121] Also of recent importance to the field of Pt-mediated

bond activation chemistry are the detailed mechanistic studies reported by Goldberg and

co-workers.[28-32,93,122] Through a combination of theoretical calculations and experimental

work, Goldberg and co-workers have clearly demonstrated that reductive elimination from Pt(IV) occurs through a 5-coordinate intermediate, rather than a 6-coordinate complex as one might expect. By microscopic reversibility, one would expect oxidative addition to Pt(II) to involve a 3-coordinate intermediate, as has also been shown. These studies have proved pivotal to the understanding of the behavior of Pt complexes in C-H and other bond activation chemistry. The significant impact of work on (κ^2-N,N)Pt-mediated C-H bond activation by Bercaw, Labinger and co-workers cannot be overstated, but is too voluminous to be addressed in detail in this document. Interested readers are advised to consult a recent paper,[123] as well as the following reviews.[75,76,124]

The advantages of P,N ligation in Pt chemistry have been demonstrated by Schubert and coworkers in a series of reports concerning the activation of a variety of E-H bonds. The use of simple κ^2-P,N ligands and a neutral Pt center are sufficient to provide a general increase in efficiency of the reaction with organosilanes, relative to analogous (κ^2-P,P)Pt complexes.[125] Also observed is efficient C-Cl and Si-Cl bond activation,[25,126] which is notably not accomplished with the corresponding (κ^2-P,P)Pt complex. Further studies by Schubert and co-workers involving the formation of disiloxanes from tertiary silanes,[22,23] and C-Cl/Si-H metathesis to form chlorosilanes,[27] have also demonstrated an advantage to P,N ligation relative to related P,P fragments when complexed to Pt.

1.6   Gold in Homogeneous Catalysis

Gold is known to serve as a soft, carbophilic Lewis acid catalyst for a variety of transformations.[33-36] The propensity for Au(I) or Au(III) to coordinate an unsaturated organic fragment such as an alkene or alkyne and in doing so, render it prone to

nucleophilic attack has been well documented in recent years. However, though interesting and important reactions have been observed, relatively few studies have been carried out that conclusively establish mechanism. Indeed, this is highlighted by the work of Toste and co-workers, who have to date published 12 communications over the past 3 years. While these reports describe new transformations catalyzed by Au salts (for recent examples please see),[127-129] neither full papers nor mechanistic studies have been forthcoming.

The observation that Au(I) and Au(III) salts both serve as effective catalysts in many transformations has left unanswered questions about the oxidation state of the active catalyst in many cases. The ease of reduction from Au(III) to Au(I) and the relatively high oxidation potential of Au suggest that formation of a Au(I) active catalyst may be a reasonable assumption in many cases.[130] However, recent calculations show that Au(I) and Au(III) systems are similar in energy, and as such, are both viable oxidation states for a variety of reactions.[131,132]

Recent reports by He and co-workers have highlighted the formation of carbon-heteroatom bonds from unactivated alkenes and weak nucleophiles (phenols, carboxylic acids, and amines) catalyzed by Au(I).[133-135] These transformations are thought to proceed via coordination of a Lewis acidic phosphine-gold cation to the alkene, followed by attack of the nucleophile. Notably, while yields were similar to those observed using other late transition metals, the products did not contain related unsaturated species, as are often observed when Pd is employed.[136] This may be attributed to the observed low tendency for Au to effect β-hydride elimination; a step presumably required in the formation of such unsaturated products.

He and Shi have also reported on the functionalization of aromatic C-H bonds,[137,138] which they believe to occur via direct C-H activation, rather than Lewis acidic

activation or Freidel-Crafts chemistry. This statement is supported by the disappearance

of aromatic signals in the ^{1}H NMR spectrum when the Au catalyst and arene are mixed.

While this is not conclusive proof of Au-mediated C-H activation, Li and co-workers also

propose activation of a C-H bond in reports describing the coupling of 1,3-diketones with

alkenes or imines, catalyzed by Au.[139-141]

Interest in Au species as catalysts for a variety of reactions has grown

tremendously over in recent years. Despite this fact, very little insight into the

mechanism by which these transformations occur has been gained. While many of these

catalysts are presumed to act as Lewis acids, the possibility that some of these systems

are in fact operating in a more "transition metal" fashion exists. Just as the prevailing

view that Au is a catalytically inactive metal has faded in recent years, so too may the

notion that Au catalysis ends at Lewis acid chemistry. A large part of elucidating the

behavior of homogeneous gold species will be probative studies of reactivity and ligand

effects, especially in comparison to transition metals.

1.7   Silver in Homogeneous Catalysis

Despite the use of heterogeneous silver catalysts for ethylene epoxidation on an

industrial scale,[142] the exploration of processes mediated by homogeneous Ag

compounds only began in earnest in the previous two decades. In the majority of cases,

Ag is employed as (or is assumed to serve as) a Lewis acid. For example, Yamamoto

and co-workers,[143-146] as well as others,[147-150] have successfully employed Ag(I)/BINAP

systems for a variety of addition and aldol-type reactions. Dias and co-workers have

reported that **1.18** catalyzes the insertion of carbenes into both C-X[151] and C-H bonds.[152]

In both cases, it is thought that Ag is acting as a Lewis acid, via formation of a silver

carbenoid intermediate. Other reports of Ag-catalyzed transformations include

aziridination,[153] silacyclopropanation,[154] and cyclopropanation reactions.[155] Though few

probative mechanistic studies have been conducted, it is presumed that Ag is serving as

a Lewis acid in these cases as well.
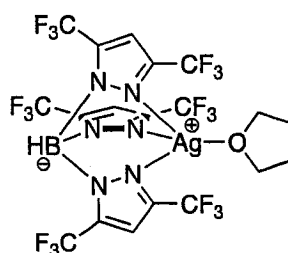
1.18

Figure 1.11   Ag complex employed by Dias and co-workers.

A recent report by He and co-workers highlighting the AgOTf-catalyzed

intramolecular addition of alcohols and carboxylic acids to alkenes proposes olefin

coordination to a Ag cation, which in turn promotes attack by a nucleophilic oxygen

atom.[156] While the activation of unsaturated organic fragments by Ag cations is known, in

this case, mechanistic proposals are made solely on the basis of a shift in the olefinic

signals in the ^1H NMR spectrum on addition of AgOTf, and as such are still tentative in
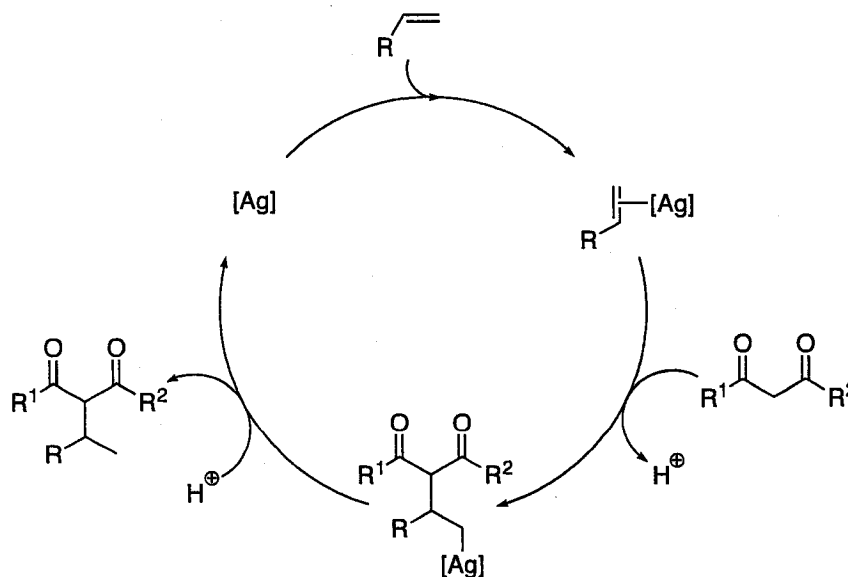
Figure 1.12   Catalytic cycle proposed by Li and co-workers involving Lewis acidic Ag.

nature. Similarly, Li and Yao suggest that Ag may serve as a Lewis acid, rendering a coordinated alkene susceptible to attack (Figure 1.12).[157] Other studies by Li and co-workers invoke Ag as both a Lewis acid and a "transition metal",[158-160] though there is little evidence for anything other than Lewis acid behavior.

1.8   This Work: Motivation and Goals

At the outset of this project, a new ligand had been developed in the Stradiotto group based on an indene framework (Figure 1.13), that incorporated a number of strategic design features. Firstly, a proton may be abstracted from the indene framework to generate an anionic ligand featuring a stable 10-π electron indenide unit. Complexation of this anionic ligand to a cationic metal center would thus result in the formation of a formally zwitterionic (charge-separated) neutral species. Similarly, the use of the same cationic metal center in conjunction with the parent neutral ligand would generate a related cationic complex. This is distinct from the approach taken by other researchers studying zwitterionic metal species (see section 1.4.2) in that the close relationship between indene and indenide allow for the evaluation of the zwitterionic effect in the absence of complicating steric factors. Secondly, the incorporation of both P and N donors allows for the possibility of a hemilabile ligand (see section 1.2). The success of P,N ligation in Pd catalysis serves as a sufficient motivating factor for studies of related ligands in Pt and Au chemistry. In addition, the modularity of this design ensures that the ligand properties may be readily altered in subsequent generations by varying the phosphino or amino fragment or donor employed.

can deprotonate
to give stable
10-π anion

easily tuned κ^2-P,N
binding site

PR$_2$

—NR'$_2$

potentially hemilabile
donor
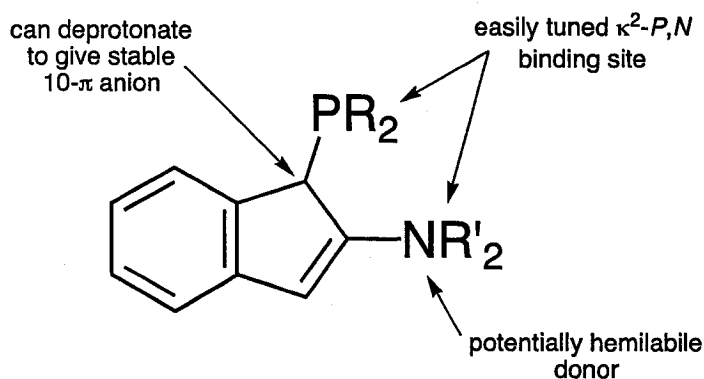
Figure 1.13   Design aspects of the class of indene ligands employed in this work.

Initial studies in the group were conducted on Rh complexes of this class of

ligands,[161,162] and continued throughout the course of this research. Subsequent research

into Mn,[163] Ru,[164,165] Ir,[166] and other related chemistry[167-170] involving this general ligand

set continued to establish the viability of the ligand design. Near the outset of this

research in the Stradiotto group, it became of interest to examine the behavior of such

ligands in conjunction with group 10 and 11 metals. It was expected that the success of

P,N ligation strategies in Pd, and to some extent in Pt chemistry (see section 1.5) would

be reflected in this work, as signaled by the presence of a defined P,N effect, or the

observation of interesting or unprecedented bond activation involving κ^2-P,N complexes.

Similarly, it was hoped that the presence of such a P,N ligand would be manifested as a

clear distinction between Au or Ag complexes featuring P,N and either P,P or N,N or

monodentate ligation. Moreover, a thorough study of well-defined Pt and Au complexes

and their solution behavior would constitute a significant contribution to the scientific

literature.

Also of interest was the study of a set of related zwitterionic and neutral species.

The isovalent relationship between Pt(II) and Au(III) has been remarked upon for some

time.[116,171,172] While studies comparing related zwitterionic and cationic complexes

derived from neutral and anionic ligands bound to the same cationic center have been

reported (see Figure 1.9),[114,161] no such related studies of a late transition metal and its

isovalent, right-side neighbor have been initiated. Thus, the study of neutral Pt(II) and

zwitterionic (charge-separated, neutral) Au(III) complexes was deemed to be of

importance due to the potential for direct comparison of electronic effects independent of

ligand steric factors and counterion effects.

In attempting to address these goals, a number of variations on the general

ligand described in Figure 1.13 were employed (Figure 1.14). These ligands were

prepared as described in previous reports from the Stradiotto group,[161,162] or other

literature sources (see Chapter 7 for details).[173] Notably, the structurally related isomers

1.19a/1.19b and **1.20a/1.20b** exhibited distinct spectral features, and often divergent

behavior when complexed to a metal center.

1.19a R = ^{i}Pr   **1.19b** R = ^{i}Pr   **1.21** R = ^{i}Pr   **1.23**
1.20a R = Ph   **1.20b** R = Ph   **1.22** R = Ph
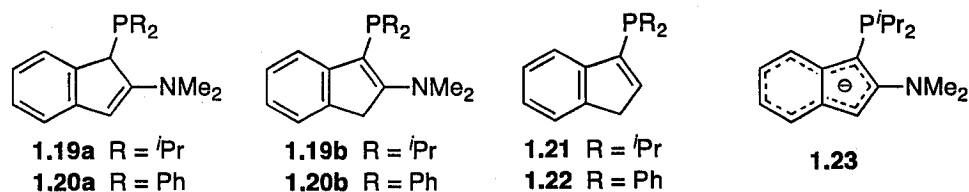
Figure 1.14   P,N ligands employed in this work.

1.9   References

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Chapter 2 – Synthesis and Reactivity of Neutral Platinum(II) Complexes

2.1 Introduction

The preparation of neutral Pt(II) complexes featuring **1.19** was a natural extension of concurrent research in the Stradiotto group with other late transition metals (see section 1.8), especially due to the well-established propensity for E-H bond activation by Pt(II) under homogenous reaction conditions.[1,2] A survey of the recent literature reveals that most of the Pt(II) complexes that are able to effect intermolecular C-H bond activation are cationic, and feature a bidentate N,N ancillary support,[3-13] though examples of neutral $(N)_n$Pt(II) complexes,[14-20] as well as those featuring κ^2-P,P ligands (both neutral and cationic) are known.[2,19-21]

While the success of cationic Pt(II) complexes in mediating organic transformations is not in question, it has been suggested that the ability of such 16-electron $[(\kappa^2$-$N,N)$Pt(R)(L)]^+ X^-$ species to activate C-H bonds may be attributed more to their capacity to generate unsaturated, 14-electron, three-coordinate $[(\kappa^2$-$N,N)$Pt(R)]^+ X^-$ intermediates upon loss of a neutral, two-electron donor (L), rather than to the formally cationic nature of the Pt(II) center.[2] Moreover, $[L_2$Pt(R)]^+ X^-$ species are also prone to attack by polar solvent molecules, or to attenuated activity due to close contact between the cationic metal center and the X^- anion (see section 1.4.1). As such, the development of a system that would provide access to *neutral*, unsaturated $LPtR_2$ reactive intermediates in low-polarity solvents (e.g. hydrocarbons) is highly desirable. Chelating, mixed-donor P,N-ligands are poised to exhibit hemilabile behavior when coordinated to Pt(II),[22,23] potentially generating such an environment. NMR evidence for hemilabile behavior in a $(\kappa^2$-$P,N)$Pt(II) complex has been presented by Komiya and co-workers.[24]

For (κ^2-P,N-**1.19**)PtX$_2$ systems in particular, the formation of unsaturated (κ^1-P,N-**1.19**)PtX$_2$ intermediates becomes increasingly favorable since the uncoordinated dimethylamino group is stabilized by entering into conjugation with the π-system of the indene backbone.[25-27] As oxidative addition to Pt(II) is known to occur through a 3-coordinate, 14-electron intermediate, and similarly reductive elimination from Pt(IV) through a 5-coordinate, 16-electron species,[28] a hemilabile P,N ligand offers a facile means of generating such low-coordinate environments, while stabilizing both low- and high-oxidation state platinum species formed in the course of E-H bond activation processes. Though the reactivity of Si-H and Sn-H bonds with (κ^2-P,N)Pt(II) complexes has been explored by Schubert and co-workers,[29-34] relatively few examples of C-H and/or C-C activation effected by such platinum species have been communicated.[35-39] Following is a report on the synthesis and characterization of new Pt(II) complexes featuring **1.19**, including a preliminary survey of the E-H bond activation capabilities and other reactivity properties of (κ^2-P,N-**1.19**)PtMe$_2$ and related compounds.

2.2   Results and Discussion

2.2.1   Synthesis of Neutral Pt Complexes

Target complexes of the type (κ^2-P,N-**1.19**)PtX$_2$ were prepared as outlined in Scheme 2.1. Treatment of **1.19a** with either *cis/trans*-(Me$_2$S)$_2$PtCl$_2$ or PtCl$_2$ affords (κ^2-P,N-**1.19b**)PtCl$_2$ (**2.1**) in 84% and 55% yield, respectively. Similarly, the reaction of **1.19a** with (η^4-COD)PtClMe provides (κ^2-P,N-**1.19b**)PtClMe (**2.2**) in 91% yield. In the formation of both **2.1** and **2.2**, the ligand precursor **1.19a** undergoes a structural rearrangement that places the P^{i}Pr$_2$ fragment at the vinylic (C3) position on the indene backbone, resulting in the exclusive formation of (κ^2-P,N-**1.19b**)PtX$_2$ species. In contrast,

preparation of a complex of the type (κ^2-P,N-1.19)PtMe$_2$ proved to be a greater synthetic

challenge. The ligand 1.19 did not cleanly displace the bis-alkene donor from either

(COD)PtMe$_2$ or (NBD)PtMe$_2$, resulting in the formation of multiple products, and

decomposition to yield platinum metal. Attempts to generate the desired metal complex

via methylation of the related dichloride, 2.1 also proved unsuccessful. Use of MeLi,

MeMgBr, Me$_2$Zn[40] or Me$_4$Sn[41,42] produced a number of phosphorus-containing products,

including the "mono-methylated" complex 2.2 and other, unidentified compounds. While

it is likely that undesired reactivity involving the ligand framework is occurring when more
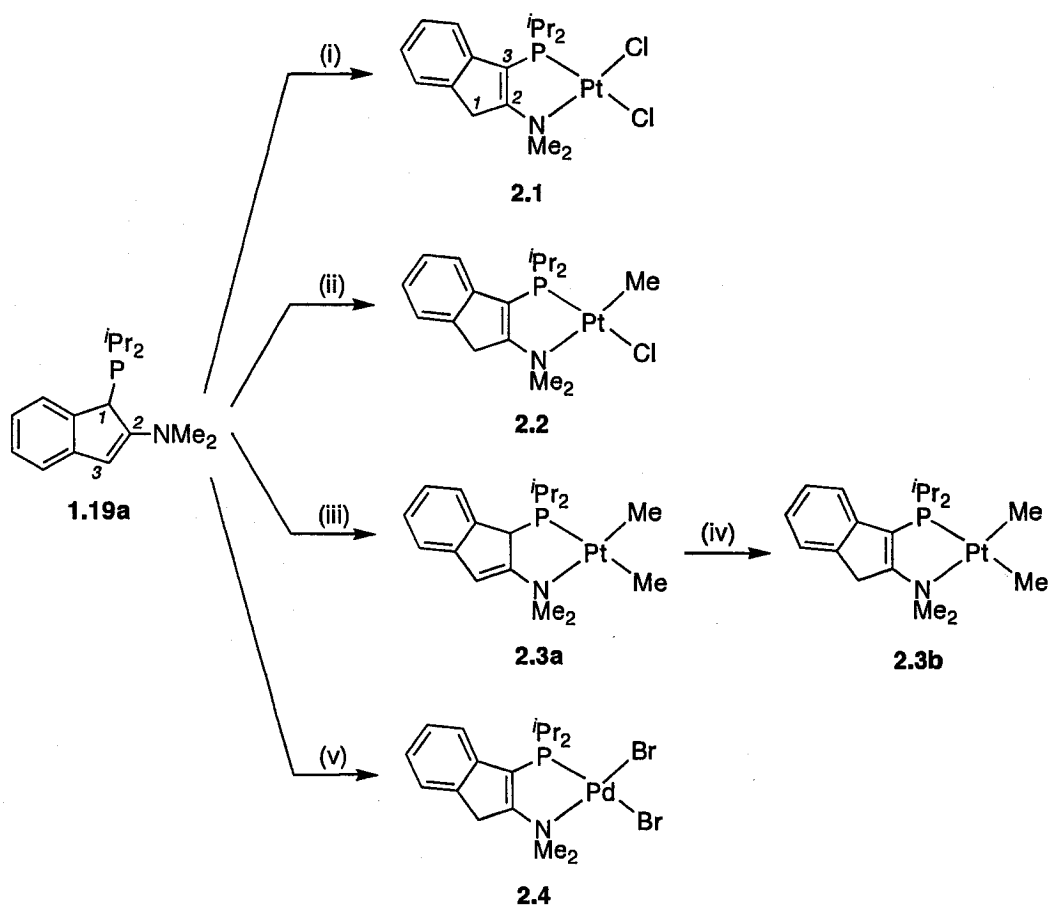
Scheme 2.1 Preparation of neutral group 10 complexes derived from 1.19. Reagents
and conditions: (i) cis/trans-(SMe$_2$)$_2$PtCl$_2$ or PtCl$_2$; (ii) (η^4-COD)PtClMe; (iii)
0.5 [(μ-SMe$_2$)PtMe$_2$]$_2$; (iv) a) 22 °C, 15 d; b) 50 °C, 45 h; c) Et$_3$N, 22 °C, 7
d; or d) ^{i}PrOH, 22 °C, 10 min; (v) PdBr$_2$.

aggressive reagents such as MeLi are used, the possibility of forming Pt-Sn bonds when Me_4Sn was employed led to a subsequent investigation into related chemistry (see section 2.2.4).

Ultimately, **1.19a** was found to react cleanly with 0.5 equiv of $[(\mu\text{-}SMe_2)PtMe_2]_2$ at 22 °C over 3 h to give pure $(\kappa^2\text{-}P,N\text{-}\textbf{1.19a})PtMe_2$ (**2.3a**), which was isolated in 97% yield. Notably, the allylic (C1) isomer **2.3a** was the isolated product of the above reaction, in contrast to the vinylic isomer observed for **2.1** and **2.2**. The isomerization of the allylic isomer **2.3a** to $(\kappa^2\text{-}P,N\text{-}\textbf{1.19b})PtMe_2$ (**2.3b**) does proceed slowly in the solid and in solution; after 15 d at 22 °C in toluene, over 95% conversion to **2.3b** is observed (based on ^1H and ^{31}P NMR data). Similar results are obtained either by heating toluene solutions of **2.3a** (50 °C, 45 h) or by the addition of 10 equiv of NEt_3 (22 °C, 7 d). The solvent-dependent interconversion of allylic and vinylic indenylphosphine isomers is an established phenomenon.[27] Notably, the clean rearrangement of **2.3a** to **2.3b** in a THF/^{i}PrOH mixture is rapid (22 °C, 10 min), allowing for the isolation of pure **2.3b** in nearly quantitative yield. It is likely that the observed increase in the rate of isomerization is due to stabilization of a charged intermediate by the polar, protic solvent.

The structures of **2.1**, **2.2**, **2.3a**, and **2.3b** depicted in Scheme 2.1 are supported by 1D- and 2D-NMR spectroscopic data. The $^{31}P\{^1H\}$ NMR spectrum for each complex is comprised of a singlet with accompanying Pt satellites. In the case of **2.2**, the magnitude of this coupling constant ($^1J_{PtP}$ = 4487 Hz) confirms the *cis*-disposition of the phosphine and methyl fragments. In the case of **2.2**, a $^{195}Pt\{^1H\}$ NMR spectrum was acquired, and it exhibited a doublet centered at δ = -2558 ($^1J_{PtP}$ = 4497 Hz) as expected. The alternative isomer featuring a methyl group *trans* to phosphorus would be expected to give rise to a much lower $^1J_{PtP}$ value, given the stronger *trans*-influence of the methyl substituent,

relative to chloride;[30] indeed, the $^1J_{PtP}$ in **2.3b** (2039 Hz) is diminished relative to **2.2**. The

C_S symmetry of **2.1**, **2.2**, and **2.3b** is evident in the ^1H and ^{13}C NMR data for these

complexes. Conversely, the ^1H and ^{13}C NMR spectra of **2.3a** clearly indicate a lack of

mirror-plane symmetry, with both vinylic and allylic C-H units on the indene backbone, as

well as pairs of non-equivalent ^iPr and Me fragments, being clearly discernible. The

structures of **2.1** and **2.3b** were also confirmed based on data obtained from single-

crystal X-ray diffraction studies.
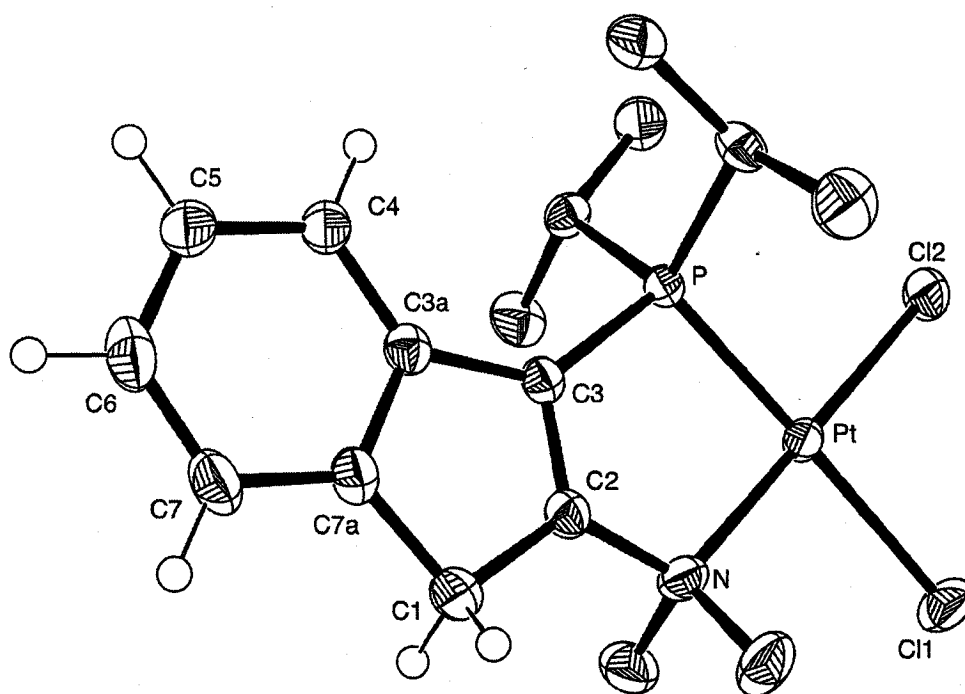
Figure 2.1   ORTEP diagram for **2.1**, showing the atomic numbering scheme for
selected atoms, with 50% displacement ellipsoids. Selected hydrogen
atoms have been omitted for clarity.

The crystal structure of **2.1** is presented in Figure 2.1, and relevant

crystallographic parameters are collected in Chapter 7. The platinum center in **2.1**

deviates only modestly from ideal square-planar geometry ($\Sigma_{\text{angles at Pt}} \sim 360°$), with the Pt-

Cl1 distance *trans* to the P-donor (2.3753(8) Å) being significantly longer than the

corresponding Pt-Cl2 distance *trans* to N (2.2978(8) Å), in keeping with the greater *trans*-

influence of the P-donor fragment. Although data from crystallographically characterized

(κ^2-*P*,*N*)PtCl$_2$ complexes were not found in the literature, the interatomic distances in **2.1**

can be compared with those found in other Pt(II) complexes.[24,33,39,43,44]
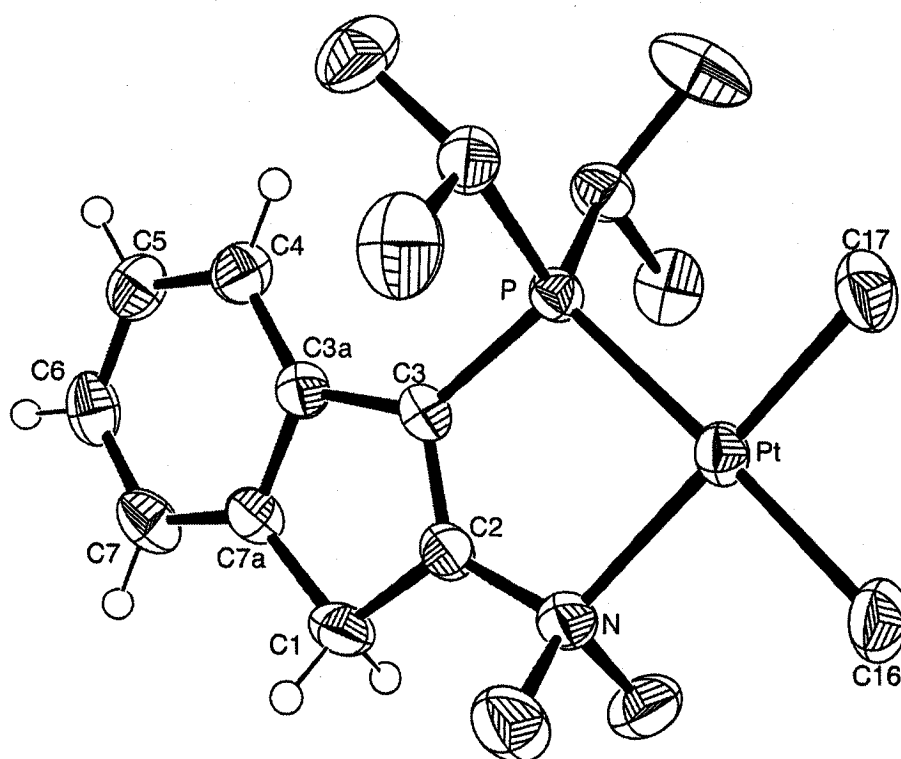
Figure 2.2   ORTEP diagram for **2.3b**, showing the atomic numbering scheme for selected atoms, with 50% displacement ellipsoids. Selected hydrogen atoms have been omitted for clarity.

The crystal structure of **2.3b** is presented in Figure 2.2, and relevant

crystallographic parameters are collected in Chapter 7. Compound **2.3b** also exhibits

only slight deviations from an ideal square planar geometry ($\Sigma_{\text{angles at Pt}} \sim 360°$). While the

Pt-C bond lengths are significantly different from one another (2.095(4) Å *trans* to P, and

2.043(4) Å *trans* to N) due to the greater *trans*-influence of the phosphine donor relative

to the amine, this difference is less pronounced than in the case of **2.1**. The structural

details of **2.3b** are in keeping with those observed for other $(\kappa^2\text{-}P,N)\text{PtMe}_2$

complexes.[30,33,45]

As a side note, **1.19** was also successfully complexed to palladium by stirring

with a suspension of PdBr_2 in toluene for 20 h, to yield $(\kappa^2\text{-}P,N\text{-}\textbf{1.19})\text{PdBr}_2$ (**2.4**) in 73%

yield. The complex is stable in chlorinated solvents, and exhibits similar spectral features

to those observed for **2.1**, with the exception of platinum coupling. Single crystals

suitable for X-ray diffraction were grown from a concentrated solution of **2.4** in toluene.

The crystal structure of **2.4** is presented in Figure 2.3, and relevant crystallographic

parameters are collected in Chapter 7. The palladium center deviates only modestly from

Figure 2.3   ORTEP diagram for **2.4**, showing the atomic numbering scheme for
selected atoms, with 50% displacement ellipsoids. Selected hydrogen
atoms have been omitted for clarity.

square planar ($\Sigma_{angles\ at\ Pd}$ ~360°), and the Pd-Br bond lengths (2.5158(6) and 2.4200(6) Å)

are significantly different from one another, owing to the greater *trans*-influence of the P-

donor fragment. The difference in bond lengths is approximately of the same magnitude

as the variation observed for **2.1**, and the structural features are comparable to similar

compounds in the literature.[40,45] Although **2.4** itself is not chiral, this complex crystallized

in a chiral space group ($P2_1$); the final refined value for the absolute structure (Flack)

parameter (0.025(8)) indicated that the correct absolute configuration had been

determined.[46,47]

Having established viable synthetic routes to (κ^2-P,N-**1.19**)PtX$_2$ complexes, a

preliminary reactivity survey involving **2.3a** was undertaken. The (κ^2-P,N-**1.19**)PtMe$_2$

complex (**2.3a**) was selected for these initial studies in light of the established propensity

of Pt-CH$_3$ linkages to react with E-H bonds to yield Pt-E and CH$_4$.[2-9,14-21,29-39]

2.2.2 Stability of Neutral Pt Complexes

Complex **2.3a** is stable in benzene, toluene, or THF at 22 °C, with the exception of the

aforementioned slow conversion to **2.3b**. However, thermolysis (70 °C) of **2.3a** in each of

these solvents generated a complex mixture of phosphorus-containing complexes,

including **2.3a** (δ [31]P = 27.6), **2.3b** (δ [31]P = 39.2), and a new Pt-containing species (δ [31]P

= 19.0, $^1J_{PtP}$ ~ 3000 Hz). This new complex represents the major product after 48 h, and

is stable in solution for greater than 5 days, though efforts to isolate this thermolysis

product have thus far proved unsuccessful. However, the observation that the same

thermolysis product appears to form in benzene, toluene, and THF suggests that this

product might arise due to an intramolecular bond activation process (vide infra), rather

than as a result of an intermolecular reaction involving the solvent. Although **2.3a** is

stable in CH_2Cl_2 at 22 °C, heating in this solvent at 50 °C for 18 h cleanly produces (κ^2-P,N-1.19b)PtClMe, **2.2** (Scheme 2.2). In keeping with established reactivity trends observed for (κ^2-P,N)PtMe$_2$ species,[31] $CHCl_3$ proved more reactive than CH_2Cl_2 towards **2.3a**, producing a complex mixture of products including **2.2**. Dissolution of **2.3a** in CH_3CN (or treatment of this complex with one equivalent of CH_3CN in toluene) either at 22 °C or with heating (75 °C for 72 h) resulted in the slow consumption of **2.3a** (based on ^{31}P NMR data) without the formation of detectable phosphorus-containing product(s) or precipitated solids. Given the complexity of the ^{1}H NMR spectrum of the crude reaction mixture, and the fact that pure materials have not to date been isolated from this mixture, the Pt-containing product(s) of this reaction could not be conclusively identified.

2.5
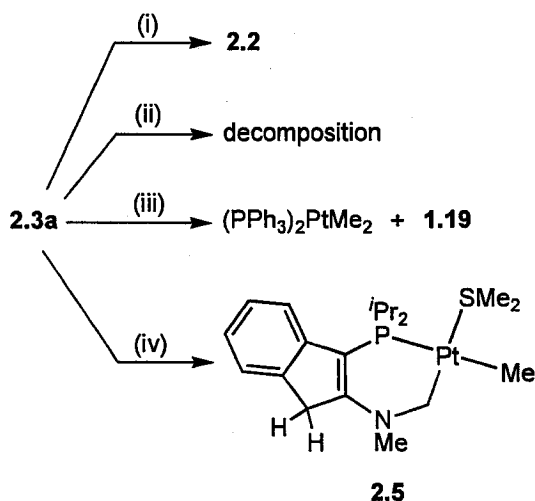
Scheme 2.2 Stability and reactivity of **2.3a**. Reagents and conditions: (i) CH_2Cl_2, 50 °C, 18 h; (ii) (a) $CHCl_3$; (b) DMAP, 75 °C, 72 h; or (c) CH_3CN, 75 °C, 72 h; (iii) 10 equivalents of Ph_3P; (iv) SMe_2, 70 °C, 20 h.

2.2.3 Reactivity of Neutral Pt Complexes with L-donors

In an attempt to assess the binding strength of the P,N-chelate in **2.3a** and to perhaps gain direct evidence for hemilability of the P,N ligand, this complex was

exposed to a variety of two-electron donors (L) in toluene, and the progress of the

reaction was monitored by use of ^{31}P NMR spectroscopic techniques. While no reaction

was observed between **2.3a** and one equiv of 4-dimethylaminopyridine (DMAP) at 22 °C

over 24 h, heating of this mixture at 75 °C resulted in the generation of multiple

phosphorus-containing products. Conversely, treatment of **2.3a** with one equiv of Ph$_3$P at

22 °C generated a mixture containing only (Ph$_3$P)$_2$PtMe$_2$,[48] **1.19**, and unreacted **2.3a**;

upon addition of 10 equivalents of Ph$_3$P, only (Ph$_3$P)$_2$PtMe$_2$, **1.19**, and Ph$_3$P were

detected. These observations suggest that putative (κ^1-*P*,N-**1.19**)Pt(PPh$_3$)Me$_2$

intermediates are more reactive than **2.3a** towards ligand substitution by Ph$_3$P, a

situation that may be attributed to steric crowding in such intermediates. Alternatively, a

toluene solution of **2.3a** was treated with 2.5 equivalents of dimethylsulfide at 22 °C. The

usual slow transformation of **2.3a** into **2.3b** was observed after several days,

accompanied by the appearance of a single new platinum-containing product (δ ^{31}P =

16.8 ppm, $^1J_{PtP}$ = 2006 Hz); after 15 d, this new complex (**2.5**) represented the major

species present in solution. When the reaction was instead conducted at 70 °C,

complete conversion was achieved after 20 h, allowing for the isolation of analytically

pure **2.5** as a brown solid in 61% yield. Indeed, this reaction proved to be viable as a

"one pot" synthesis starting from **1.19a** and one half an equivalent of [(μ-Me$_2$S)PtMe$_2$]$_2$.

Although ^{1}H and ^{13}C NMR spectroscopic data confirmed the presence of a

dimethylsulfide ligand in **2.5**, the other spectral features observed clearly indicated that

this complex was not a simple adduct of the type (κ^1-*P*,N-**1.19**)Pt(SMe$_2$)Me$_2$.

The connectivity in **2.5** was ultimately elucidated based on data obtained from a

single-crystal X-ray diffraction experiment; the structure of **2.5** is presented in Figure 2.4,

and relevant crystallographic parameters are collected in Chapter 7. The platinum center

in **2.5** exhibits typical square-planar geometry (Σ_{angles} at Pt ~ 360°), and is ligated by N-CH$_2$ and CH$_3$ fragments, as well as *cis*-disposed P- and S-donors. The planarity at nitrogen (Σ_{angles} at N ~ 360°) and the contracted N-C2 distance (1.326(5) Å), relative both to the other N-C distances in **2.5** (1.461(5) Å, 1.453(5) Å) as well as the N-C2 distance in **2.1** (1.472(4) Å), indicate that the nitrogen fragment in **2.5** is in conjugation with the indenyl framework.
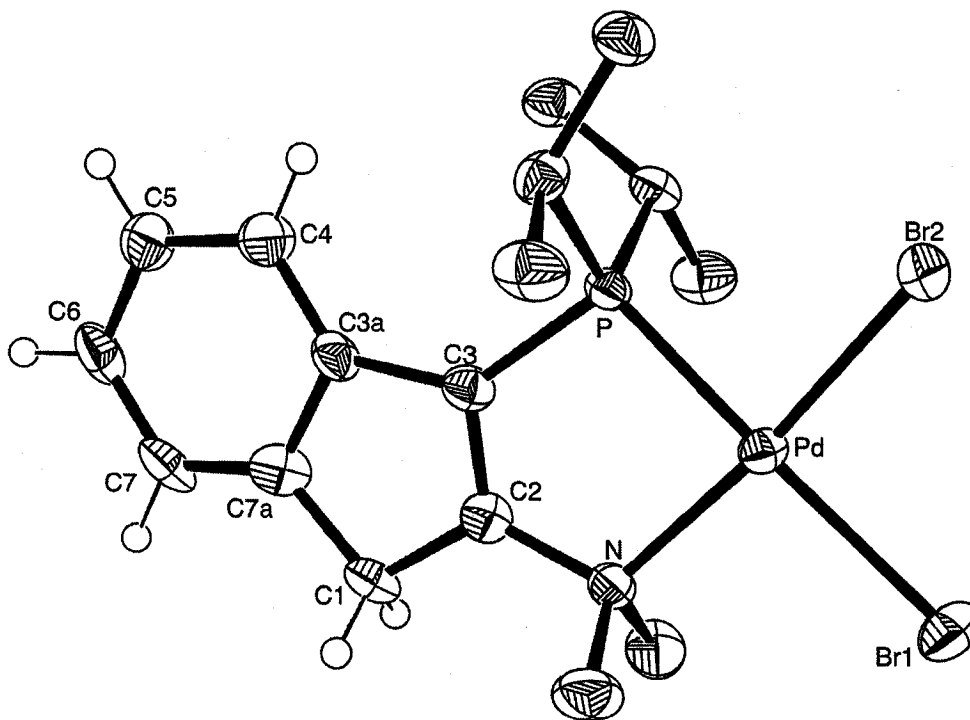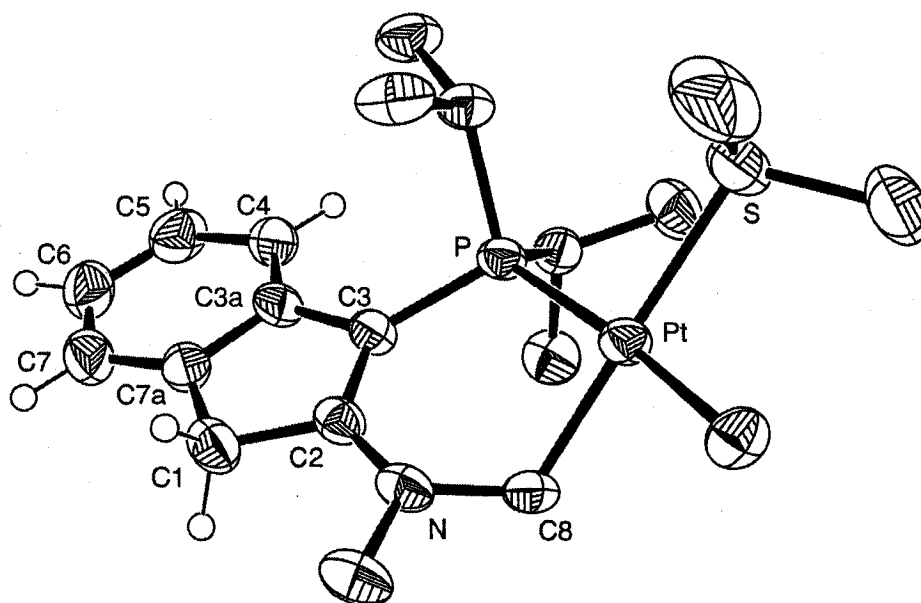

Figure 2.4   ORTEP diagram for **2.5**, showing the atomic numbering scheme for selected atoms, with 50% displacement ellipsoids. Selected hydrogen atoms have been omitted for clarity.

Although details of the mechanistic pathway leading to **2.5** are unknown, this complex may be viewed as arising from an intramolecular C-H activation process involving one of the N(CH$_3$) groups in a three-coordinate intermediate of the type (κ^1-*P*,N-**1.19**)PtMe$_2$, with the loss of CH$_4$ and coordination of dimethylsulfide yielding the observed product (Scheme 2.3). The activation of N-Me C-H bonds has been observed

for a range of transition metal fragments;[49-53] the structural features found in **2.5** are

comparable to those observed in a related cyclometallated platinum complex.[49]
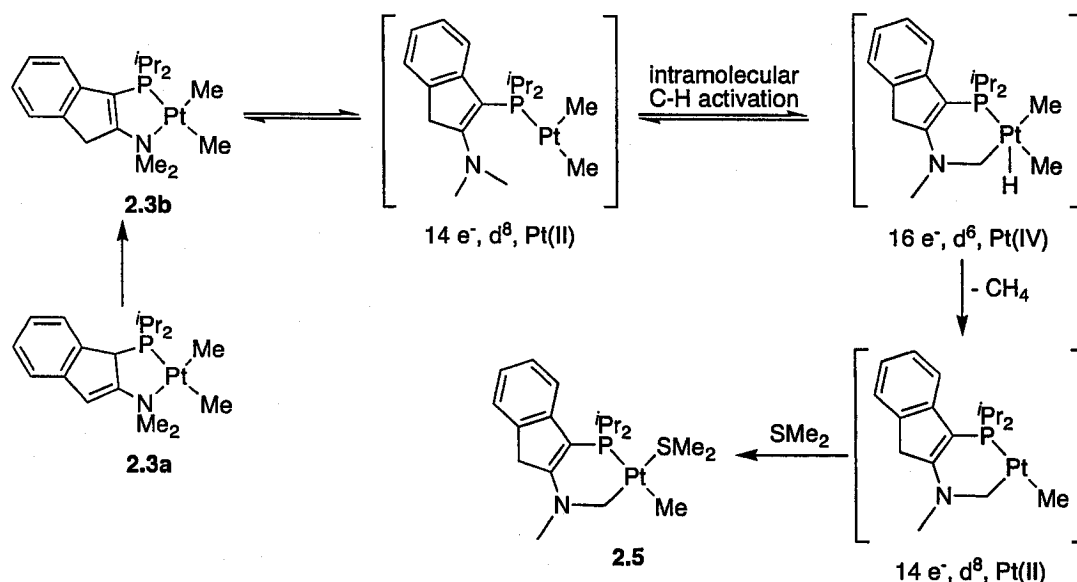
Scheme 2.3 Proposed pathway for intramolecular activation of an $N(CH_3)_2$ C-H bond in **2.3a/2.3b** in the presence of Me_2S to yield **2.5**.

2.2.4 Reactivity of Neutral Pt Complexes with E-H Bonds

In an attempt to survey the intermolecular E-H bond activation capabilities of

2.3a, the reactivity of this complex with a variety of main group substrates (in C_6D_6 or

toluene) was examined. Treatment of **2.3a** with either dihydrogen (1 atm) or

pinacolborane (one equiv) resulted in no observable reaction (^1H and ^{31}P NMR), even

after heating for 3 d at 50 °C. In contrast, PhC≡CH, Ph_3SiH, Ph_2SiH_2, $PhSiH_3$, and Et_3SiH

were each observed to react with **2.3a** to some extent at 22 °C. However, multiple

phosphorus-containing products were generated in each case, regardless of the

subtrate:**2.3a** ratio (1:1, 2:1, or 10:1) or the reaction temperature (22 °C to 75 °C)

employed; the products from these reaction mixtures have thus far not been

unequivocally characterized. In monitoring the reaction of **2.3a** with the aforementioned

silanes by use of ^{1}H NMR techniques, no Pt-H species were detected, and Pt-Me resonances persisted throughout the course of each reaction. These observations led to the assumption that Si-H oxidative addition to the metal center is either not occurring, or results in formation of species with short lifetimes. Complex reactivity between (κ^2-P,N)PtMe$_2$ complexes and organosilanes has been observed previously.[33]

Braunstein,[54-56] Schubert,[34] and others[56] have demonstrated that complexes of the heavier group 10 metals are capable of mediating the dehydrogenative dimerization of Ph$_3$SnH to yield Ph$_6$Sn$_2$. In this context, the reaction of **2.3a** with Ph$_3$SnH (C$_6$D$_6$, 22 °C) was examined. Given the known light-sensitivity of Sn-H bonds,[57-59] the photostability of C$_6$D$_6$ solutions of Ph$_3$SnH in the absence of **2.3a** was evaluated (^{1}H and ^{119}Sn NMR). Solutions stored in the dark for 20 days exhibited NMR signals attributable only to Ph$_3$SnH with no observable H/D exchange involving the Sn-H fragment, and upon exposure to ambient light for 3.5 h only a trace of Ph$_6$Sn$_2$ was detected (^{119}Sn NMR).[34]

The reaction of **2.3a** with Ph$_3$SnH (1:1 ratio) generated a mixture of phosphorus-containing products that gave rise to ^{31}P NMR resonances at 43.6 (~ 5%), 41.0 (~ 5%), and 27.6 (**2.3a**, ~ 90%) ppm; the intensity ratio of these signals did not change significantly over 24 h. In contrast, reactions employing 10 equiv of Ph$_3$SnH resulted in the consumption of **2.3a** after 2 min, accompanied by the clean formation of a single phosphorus-containing product (**2.6**) at 43.6 ppm (singlet with Pt satellites, $^1J_{PtP}$ = 2601 Hz). While signals for unreacted Ph$_3$SnH and dihydrogen (4.46 ppm) were evident in the ^{1}H NMR spectrum of the reaction mixture after 5 min, neither well-resolved Pt-Me signals nor low-frequency resonances associated with Pt-H fragments were observed. Analysis of the reaction mixture after 20 min by use of ^{119}Sn{^{1}H} NMR techniques indicated the presence of Ph$_3$SnH (-163.2 ppm, ~ 45%), Ph$_3$SnMe (-90.2 ppm, ~ 20%), Ph$_6$Sn$_2$ (-141.6 ppm, ~ 20%), and an unidentified complex (-125.9 ppm, ~ 15%, possibly Ph$_4$Sn).[34,60,61]

The Ph_3SnH was ultimately consumed after 4 h, and the product mixture exhibited $^{119}Sn\{^1H\}$ NMR signals at -228.9 (~ 15%), -141.6 (Ph_6Sn_2, ~ 40%), -125.8 (~ 30%), and -90.2 (Ph_3SnMe, ~ 15%) ppm. Although the complex that gives rise to the ^{119}Sn resonance at -228.9 ppm has not been identified, it has been observed, along with Ph_6Sn_2 as an impurity (up to 20%) in samples of Ph_3SnH obtained from commercial sources. Notably, no Pt-coupled $^{119}Sn\{^1H\}$ NMR resonances were observed throughout the course of this reaction. The ^{31}P NMR spectrum of the product mixture after 4 h revealed the presence of one dominant phosphorus-containing species at 18.9 ppm (s, with satellites $J = 133$ Hz), accompanied by low-intensity resonances at 60.2 and 43.6 ppm. Collectively, these spectroscopic observations are consistent with the reaction pathway tentatively proposed in Scheme 2.4, in which **2.3a** initially reacts with Ph_3SnH to give an unobserved (κ^2-P,N-**1.19a**)Pt(H)(Me) intermediate and Ph_3SnMe. Rapid Sn-H oxidative addition of a second molecule of Ph_3SnH, followed by reductive elimination of dihydrogen yields **2.6**; this complex can also be generated directly from the Sn-H oxidative addition of Ph_3SnH to **2.3a**, followed by reductive elimination of methane. Complex **2.6** could then react with the remaining Ph_3SnH over 4 h to yield a mixture of tin products, possibly including **2.7**. While the tentative assignment of **2.7** as a stannylated derivative of **1.19** is based on the lack of discernible Pt-P coupling and the relative magnitude of the observed J_{PSn} coupling,[62,63] an accompanying ^{31}P-coupled signal in the $^{119}Sn\{^1H\}$ NMR spectrum that could be assigned to **2.7** could not be unambiguously identified. Purified samples of **2.7** for further characterization have not, to date, been isolated. The proposed generation of **2.7** underscores the possibility that the observed conversion of Ph_3SnH is mediated by ill-defined Pt species (possibly metallic or colloidal), rather than a discrete complex featuring **1.19**.
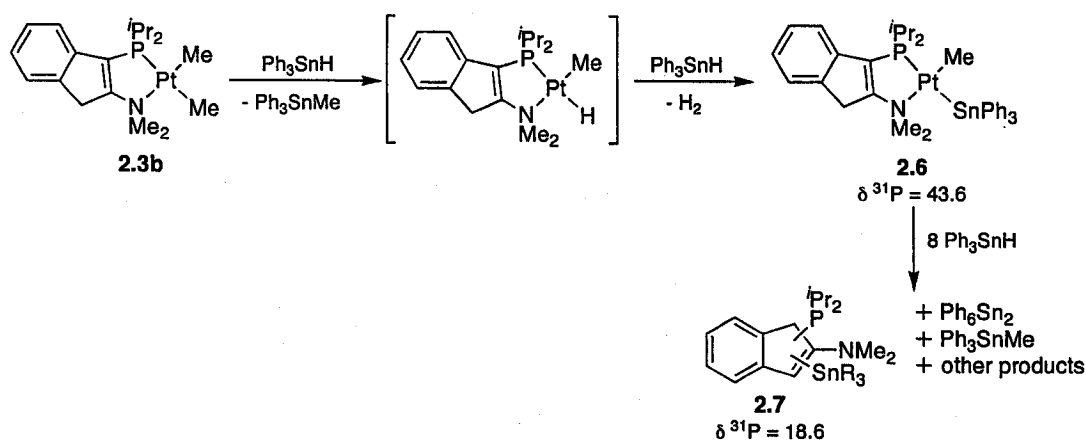
Scheme 2.4 Proposed pathway for the reaction of **2.3a** with excess Ph₃SnH.

Subsequently, the ability of either **2.3** to catalyze the dehydrogenative

dimerization of Ph₃SnH to Ph₆Sn₂ (1 mol% in C₆D₆) was examined. Unfortunately, under

these conditions the consumption of Ph₃SnH was negligible (^{119}Sn{^{1}H} NMR) for

reactions conducted either in the presence or absence of ambient light after 3.5 h.

Braunstein and co-workers[55] have reported that the palladium-catalyzed

dehydrogenative dimerization of Ph₃SnH can be conducted in a variety of solvents

(including CH_2Cl_2) without the exclusion of ambient light, and that no modification of the

kinetic parameters or TON values for various catalysts is observed when reactions are

carried out in the presence of radical scavengers and/or in the dark. Based on this

report, and in preparing to survey the catalytic abilities of **2.3a** in CH_2Cl_2, control

experiments were carried out in which CD_2Cl_2 solutions of Ph₃SnH were monitored (^{1}H

and ^{119}Sn NMR). In the absence of light, no reaction was noted after 4 days; in contrast,

upon exposure to ambient light for 1 h, greater than 50% conversion to Ph₃SnCl (δ ^{119}Sn

= -48)[60,61] was observed, along with a small amount of Ph₆Sn₂. The reduction of alkyl

chlorides by R₃SnH promoted by exposure to UV light is well-established.[64] While no

reaction was observed for Ph₃SnH in CD_2Cl_2 in the presence of 1 mol% **2.3a** in the dark

after 3.5 h, exposure to ambient light under analogous conditions resulted in the

conversion of Ph_3SnH to a mixture of Ph_3SnCl (~ 80%) and Ph_6Sn_2 (~ 20%).

Compound **2.5** was seen as a species of interest due to its potential to activate

E-H bonds. One possible mechanism for the reaction may include oxidative addition of

an E-H fragment to generate a Pt(IV) hydride, followed by reductive elimination of $N-CH_3$

and re-coordination of the $N(CH_3)_2$ donor (see Scheme 2.5). As such, the Pt metal center

would be in close proximity to the second L donor required to provide stability at higher

temperatures. For these reasons, a survey of the reactivity of **2.5** with a variety of E-H

bonds was undertaken.

2.8a E = $SiPh_3$
2.8b E = $SiEt_3$
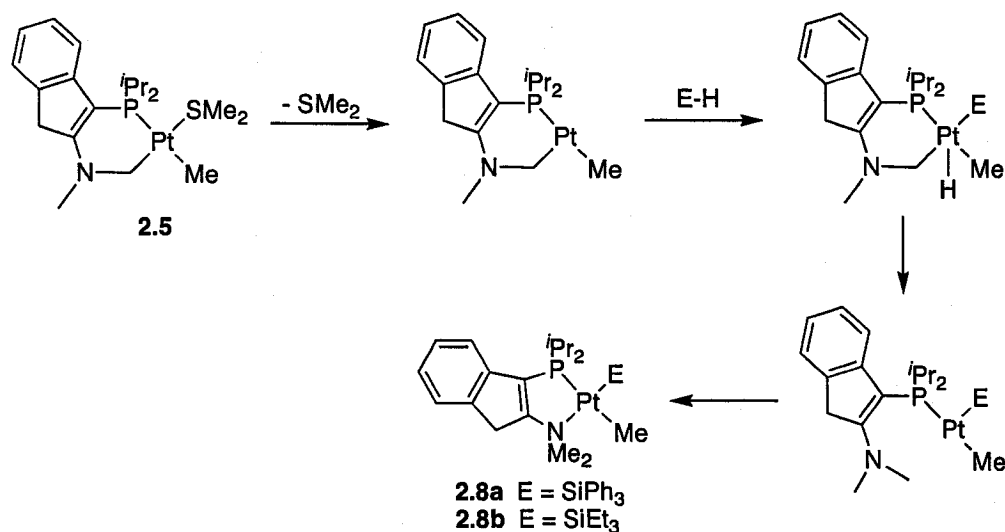
Scheme 2.5 Proposed route for addition of E-H to compound **2.5** to yield (κ^2-*P,N*-**1.19b**)Pt(E)(Me) (**2.8**).

While **2.5** was found to be stable in C_6D_6 solution at room temperature or 70 °C

for at least 48h, when one equivalent of pinacolborane was added, both ^{31}P and ^1H NMR

spectra immediately became broad and featureless. When one equivalent Ph_2PH was

added to **2.5** in C_6D_6, two sets of doublets with Pt satellites centered at $\delta = 19.8$ ($^1J_{PtP} =$

1972 Hz, $^2J_{PP} = 14$ Hz) and -5.4 ($^1J_{PtP} = 1755$ Hz, $^2J_{PP} = 14$ Hz) were observed in the

$^{31}P\{^1H\}$ NMR after 0.5 h. These data, along with the persistence of a P-H resonance in the ^1H NMR spectrum, suggest that Ph_2PH displaced Me_2S as a two-electron donor, leaving the $N-CH_2$ fragment intact.

To increase the likelihood of achieving P-H bond activation, $Ph_2PH\cdot BH_3$ was employed as a reagent. Since the phosphine lone pair is datively coordinated to the borane unit, the appearance of a set of Pt-coupled doublets in the $^{31}P\{^1H\}$ NMR would indicate that P-H activation had likely occurred. Indeed, after 4 h at 24 °C, two doublets approximately 20 % the size of the peaks for **2.5** were observed at $\delta\ ^{31}P = 28.9$ ($J = 9$ Hz) and 25.9 ($J = 9$ Hz), though platinum coupling was not observed. No further conversion was noted at 24 °C. Heating the sample at 50 °C resulted in decomposition, as evidenced by the disappearance of all peaks in the $^{31}P\{^1H\}$ NMR spectrum.

Continuing to investigate the reactivity of **2.5**, a variety of silanes were employed as E-H donors. While introduction of one equivalent of Ph_2SiH_2 or $PhSiH_3$ in C_6D_6 immediately led to multiple resonances and decomposition, both Ph_3SiH and Et_3SiH exhibited more uniform reactivity. In the case of Ph_3SiH, the appearance of a new peak at $\delta = 56.4$ (Pt satellites not resolved) in the $^{31}P\{^1H\}$ NMR spectrum suggested the formation of (κ^2-P,N-**1.19b**)Pt(SiPh$_3$)(Me) (**2.8a**). No platinum hydride resonances were observed, and the complex was found to be stable in solution at 50 °C for at least 7 days. Reacting **2.5** and one equivalent of Et_3SiH in C_6D_6 led to the observation of multiple resonances in the $^{31}P\{^1H\}$ spectrum. After heating at 50 °C for 7 days, a broad resonance at $\delta\ ^{31}P = 35.8$ was the largest peak, and no Si-H or Pt-H resonances were observed in the ^1H NMR spectrum. These observations suggest that a (κ^2-P,N-**1.19b**)Pt(SiEt$_3$)(Me) (**2.8b**) product may be formed in the course of this reaction.

Encouraged by reactivity observed with silanes and phosphines, a degassed

solution of **2.5** in C_6D_6 was exposed to an atmosphere of dihydrogen gas at 24 °C. After

2.5 h, the emergence of a peak at δ = 35.7 was evident in the $^{31}P\{^1H\}$ NMR spectrum. At

19 h, this resonance was the sole peak observed in the $^{31}P\{^1H\}$ spectrum (Figure 2.6),

and Pt coupling was discernable ($^1J_{PtP}$ = 3733 Hz) in addition to a second set of satellites

disposed about the center peak (J = 120 Hz, satellites of this magnitude were not

resolved about the Pt satellites), which may be related to the presence of a Pt-H (i.e.

"leakage" of $^2J_{PH}$ coupling through the decoupler). Analysis of the ^1H NMR spectrum

reveals the presence of resonances consistent with the κ^2-P,C mode observed in **2.5**,

though no resonances for ME_2S, Pt-Me or Pt-H were noted at 300 K. No change in

spectral features was noted on cooling to 250 K. However, upon heating to 340 K, a

resonance at δ = -5.78 (s, with Pt satellites $^1J_{PtH}$ = 376.6 Hz) was observed in the ^1H

NMR spectrum, consistent with the presence of a Pt hydride. These data lead to the

conclusion that a dimeric structure similar to **2.9** (Figure 2.5) may be the ultimate product

of this reaction. It is possible that oxidative addition of one unit of H_2 occurs rapidly to **2.5**,

liberating a unit of CH_4, thereby generating an intermediate of the type (κ^2-P,C-

1.19b)PtH, which may form a stable dimeric adduct through formation of a Pt-H

σ-complex with another molecule of (κ^2-P,C-**1.19b**)PtH. Interestingly, the confirmation of

such reactivity would provide insight into the strength of the N-CH_2-Pt interaction, relative

to the Pt-CH_3 bond in **2.5**.
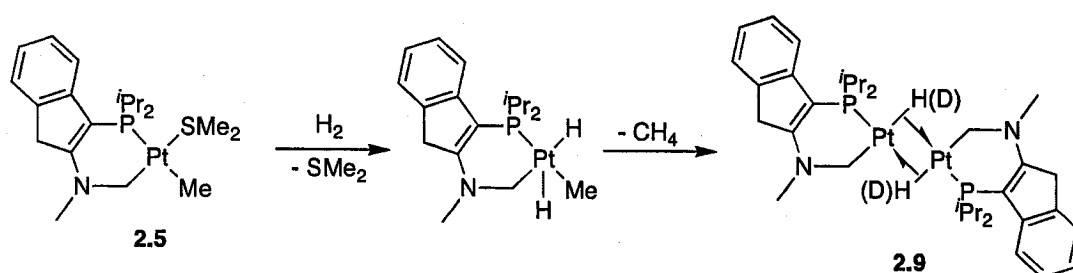
Figure 2.5 Proposed route to **2.9**, the product of the reaction of **2.5** with $H_{2(g)}$ at 24 °C in C_6D_6.
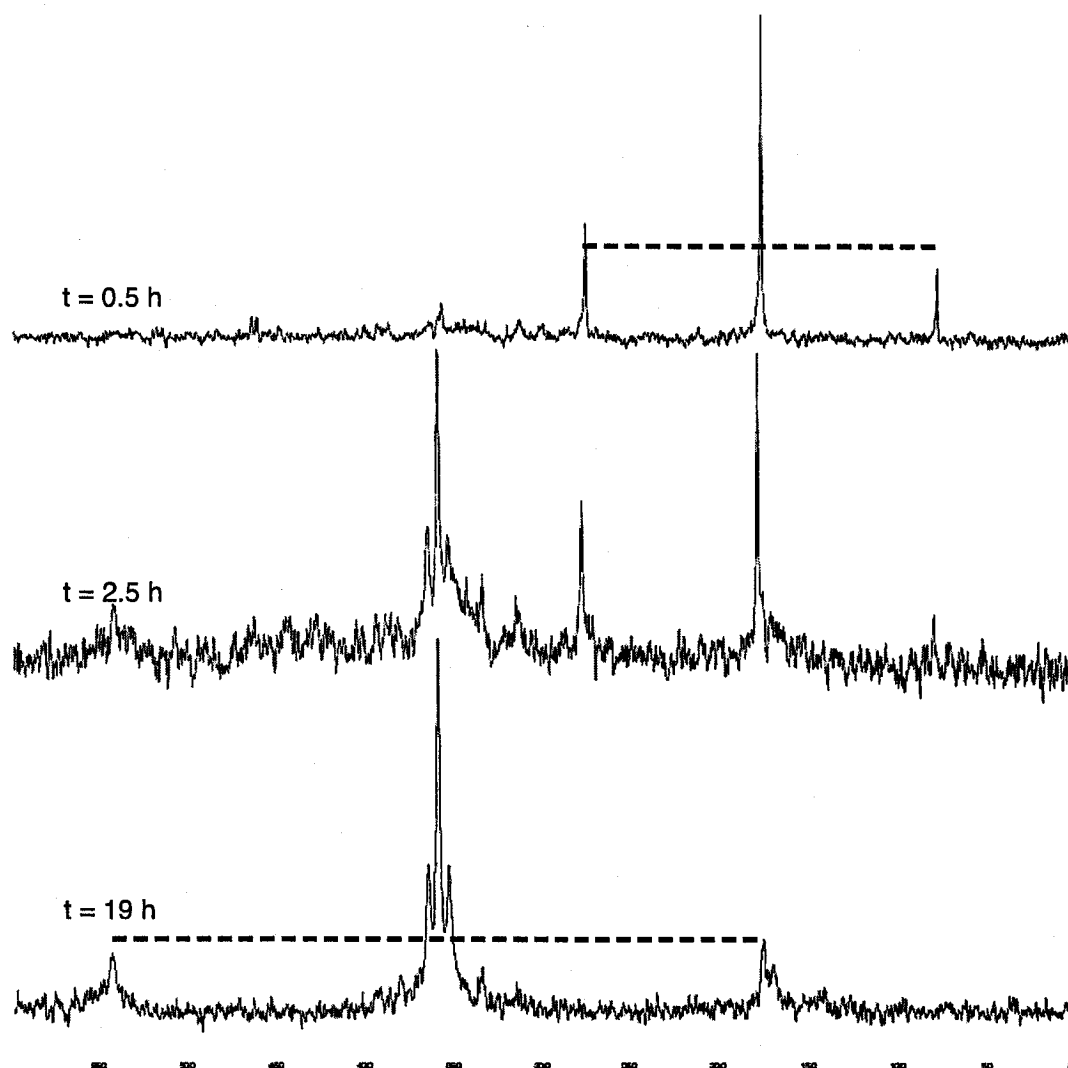
Figure 2.6 Stacked plot showing $^{31}P\{^1H\}$ NMR spectra for the reaction of **2.5** with $H_{2(g)}$ at 24 °C in C_6D_6 at indicated time intervals.

2.3   Conclusion

It has been shown that the P,N-substituted indene **1.19a** is a viable ligand for the preparation of complexes of the type $(\kappa^2\text{-}P,N\text{-}\mathbf{1.19})MX_2$ (M = Pd, Pt; X = Cl, Br, Me). While the benefits of a P,N ligand set have been established for some time with Pd, comparatively little research into such an effect on Pt has been conducted. As such, this work served to increase the scope of known $(\kappa^2\text{-}P,N)PtX_2$ complexes, and to add to known reactivity properties of such complexes. The design of the P,N ligand **1.19** was intended to promote the formation of unsaturated metal-complex intermediate species of the type $(\kappa^1\text{-}P,N\text{-}\mathbf{1.19})PtX_2$. While such a complex was not observed directly (for example, via the reaction of **2.3a** with various L donors), the formation of the cyclometalated complex **2.5** may be seen as arising from the intramolecular C-H activation of $(\kappa^1\text{-}P,N\text{-}\mathbf{1.19a})PtMe_2$, generated in situ from **2.3a** via dissociation of the NMe_2 fragment.

The reactivity of neutral complex **2.3a** with a variety of E-H bonds was explored, in most cases leading to a complex mixture of products that could not be unambiguously assigned. It is likely that intramolecular activation of the ligand fragment is playing some role in a number of these reactions, in a similar fashion to that observed in the generation of **2.5**. The observation that **2.3a** appears to react with a variety of E-H containing substrates to produce multiple products indicates that the ligand architecture is effective in providing a reactive Pt center capable of effecting intermolecular activation. **2.3a** was also found to be effective at mediating the dehydrogenative coupling of stannanes in a sub-stoichiometric fashion, though catalyst loadings lower than 10 mol% were not viable. Notably, the difference in reactivity with dihydrogen gas between **2.3a** and **2.5** was remarkable. Whereas **2.3a** was found to be completely inert to dihydrogen,

2.5 reacted readily under the same conditions to generate the putative Pt hydride, **2.9**. A

preliminary survey of the reactivity of **2.5** with various E-H bearing substrates revealed

significant differences from that observed under the same conditions with **2.3a**.

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Chapter 3 – Synthesis and Reactivity of Gold(III), and Related Neutral and Cationic Platinum(II) Complexes

3.1   Introduction

The preparation and evaluation of reactivity for a series of neutral Pt(II)

complexes supported by 1.19 has been reported previously (Chapter 2). In the course of

these studies, (κ^2-P,N-1.19b)PtMe$_2$ (2.3b) was observed to generate the "bit in" complex

2.5, presumably as a result of intramolecular C-H activation. This observation, in

combination with the known activity of neutral (κ^2-P,N)Pt(II) complexes,[1-18] prompted an

investigation of the competence of 2.3b as a catalyst for the hydrosilylation of alkenes. It

was hoped that the potentially hemilabile ligand 1.19 would provide access to key

intermediates of the type (κ^1-P,N-1.19)PtMe$_2$, thus serving to increase the rate of

oxidative addition of the Si-H functionality to the Pt center. Cationic complexes of Pt(II)

featuring the neutral ligands 1.19a/1.19b may be expected to display increased activity

in reactions involving the catalytic activation of an E-H bond due to the presence of a

potentially hemilabile donor (see section 1.4.1).

Also of interest was a comparison between the neutral Pt(II) complex 2.3b, and

the related zwitterionic Au(III) complex 3.1. While studies of related cationic and

zwitterionic complexes of the same late transition metal have appeared in recent years

(examples include Ru, Rh and Ir complexes supported by the indene/indenide system

employed herein,[19-22] and Rh, Pd and Pt complexes featuring BP/neutral silyl ligands,[23-25]

Figure 3.1), less common are studies featuring neutral and zwitterionic complexes of a

given platinum-group metal and its right-side neighbor. Such studies comparing neutral

group 3 and structurally related, cationic group 4 complexes have provided valuable

insight into the reactivity properties of olefin polymerization catalysts.[26]

Stradiotto and co-workers   Peters and co-workers
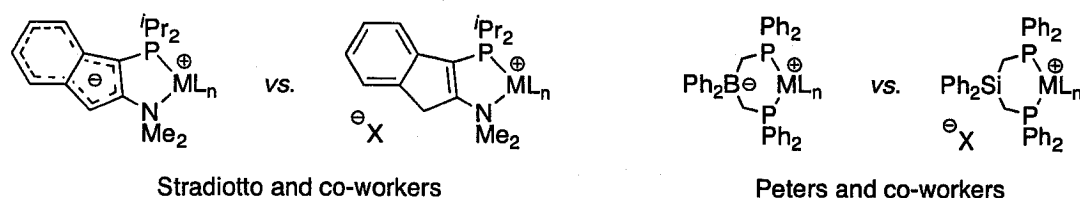
Figure 3.1   Comparison of isostructural zwitterionic and cationic complexes by Stradiotto and co-workers, and Peters and co-workers.

Fundamental studies of isostructural, isovalent cationic and zwitterionic complexes might be expected to provide a means of assessing how altering the electronic (and not steric) characteristics of an ancillary ligand influence the behavior of the associated metal fragment. The anionic ligand **1.23** provides a rare opportunity for such a study, given its similarity to the parent neutral ligand **1.19**. Similarly, the close relationship between Pt(II) and Au(III),[27-29] as well as the recent interest in Au-mediated catalysis (see section 1.6) validates such a study.

Herein is described the preparation of a zwitterionic $(\kappa^2\text{-}P,N\text{-}\mathbf{1.23})\text{AuMe}_2$ species (**3.1**) and the study of its reactivity with E-H bonds, competence as a catalyst for the hydrosilylation of styrene, and comparison to the related neutral Pt(II) complex **2.3b**. While a number of formally zwitterionic Au(I) and Au(III) complexes featuring a positive charge on Au are known,[30-33] no comparative structural and reactivity studies involving neutral Pt(II) and zwitterionic Au(III) supported by isosteric ancillary ligands have been reported. Also described are efforts to assess the catalytic utility of newly prepared mono- and dinuclear Pt(II) cations ligated by **1.19b**, for the addition of triethylsilane to styrene.

3.2 Results and Discussion

3.2.1 Preparation of a Gold Zwitterion, and Comparison with a Neutral Platinum Species

As shown in Scheme 3.1, a neutral (κ^2-P,N)PtMe$_2$ species, **2.3b** may be prepared

by reacting **1.19a** with one half an equivalent of [(μ-SMe$_2$)PtMe$_2$]$_2$, followed by treatment

with isopropanol, as described in Chapter 2. In the pursuit of an analogous Au(III)

species, **1.19a** was lithiated followed by the addition of one half an equivalent of

[Me$_2$AuCl]$_2$. After workup, (κ^2-P,N-**1.23**)AuMe$_2$ (**3.1**) was isolated as an analytically pure

bright yellow solid in 41% yield. Both spectroscopic and crystallographic data for **3.1**

(Figure 3.2, relevant crystallographic parameters are collected in Chapter 7) support the

structural formulation proposed for this formally zwitterionic complex. The geometric

relationship between **2.3b** and **3.1**, in which the Pt and Au metals each adopt a square-

planar geometry and are ligated by a chelating P,N-ligand as well as *cis*-methyl ligands,

is confirmed on the basis of both spectroscopic and crystallographic data. Though a

crystallographically characterized [(κ^2-P,N)AuMe$_2$]$^+$ complex has been reported,[34] the

disordered nature of the structure precludes a detailed comparison to **3.1**.
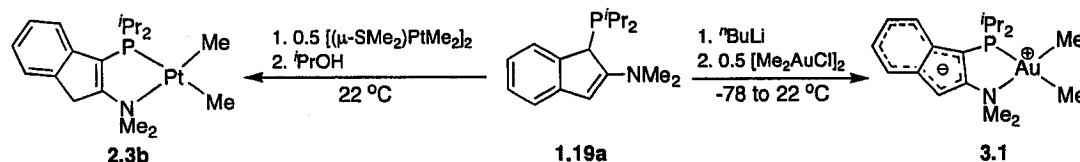
Scheme 3.1 Preparation of **2.3b** and **3.1** from **1.19a**.

The overall features in **3.1** mirror those observed in **2.3b**, with the Au-Me

distance trans to P being significantly longer than the Au-Me distance trans to N. While a

trend towards localized C-C and C=C bonds is observed within the indene backbone of

2.3b, the carbocyclic framework in **3.1** exhibits a more delocalized structure consistent

with a 10 π-electron indenide fragment, as is found in the related crystallographically

characterized zwitterions (κ^2-*P*,*N*-**1.23**)Rh(COD),[19] (κ^2-*P*,*N*-**1.23**)Ir(COD),[20] and (κ^2-*P*,*N*-

1.23)Ru(MeCN)(η^5-Cp*).[22] However, as with the platinum-group metal complexes of

1.23, the contracted P-C3 and C1-C2 distances in the formally zwitterionic **3.1** (1.749(3)

Å and 1.374(4) Å), when compared with those in **2.3b** (1.814(4) Å and 1.510(5) Å), point

to the existence of a less-conventional resonance contributor in **3.1** featuring a P=C3

bond that places the anionic formal charge on phosphorus.[35] The Au-P distance in **3.1** is

comparable to those found in other structurally related Au(III) complexes,[31] and the

observation of similar M-N distances (**2.3b**, 2.228(3); **3.1**, 2.195(3) Å) but significantly

different M-P distances (**2.3b**, 2.2474(9); **3.1**, 2.3523(8) Å) in **2.3b** and **3.1** is a trend that

has been noted in isostructural cation/zwitterion pairs of Rh or Ir supported by **1.19b** and

1.23, respectively.[19,20]
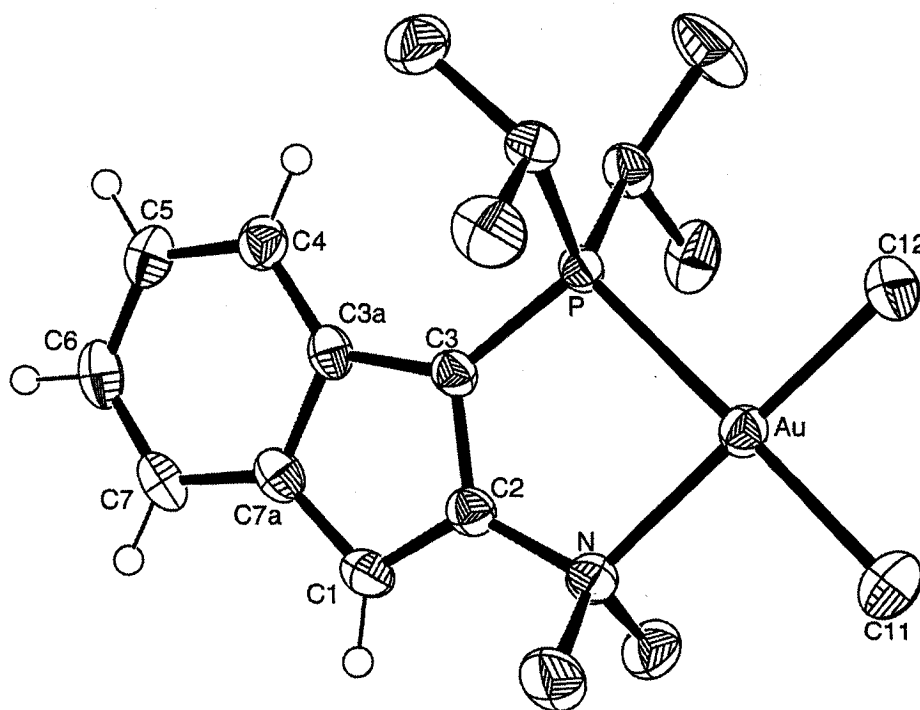
Figure 3.2   ORTEP diagram for **3.1**, showing the atomic numbering scheme for
selected atoms, with 50% displacement ellipsoids. Selected hydrogen
atoms have been omitted for clarity.

3.2.2 Stability and Reactivity of 2.3b and 3.1

While it was observed (Chapter 2) that heating a solution of **2.3a** (70 °C) results in conversion to **2.3b**, and ultimately generates a mixture of phosphorus-containing products, **3.1** exhibits remarkable thermal stability. Toluene solutions of **3.1** can be kept at 110 °C for 24 h with negligible decomposition to Au(0) or other phosphorus-containing products, as evidenced by ^{31}P NMR and visual examination. The stability of **3.1** contrasts with that of (κ^2-P,N-**1.23**)Ru(MeCN)(η^5-Cp*), which upon dissolution in benzene at 22 °C is rapidly transformed by way of double geminal C-H bond activation into a new complex featuring a Cp*Ru(H) fragment supported by a modified form of **1.19b**, whereby the NMe$_2$ unit has been transformed into a nitrogen-stabilized carbene donor group to give a κ^2-P,C complex.[22] Some differences in reactivity were also observed upon exposure of either **2.3b** or **3.1** to a stoichiometric equivalent (except where noted) of various E-H containing substrates in C$_6$D$_6$ (48 h, 50 °C). No observable reaction (^{1}H and ^{31}P{^{1}H} NMR) was noted for either complex upon treatment with H$_2$ (1 atm) or pinacolborane. While **2.3b** was observed to react to some extent with each of H$_2$O (ca. 350 equivalents in THF), Ph$_3$SiH, and PhSiH$_3$ to give a mixture of products including, in some cases, free **1.19**, complex **3.1** proved unreactive under these reaction conditions. The stability to hydrolysis of the indenide unit in **3.1** is remarkable (>48 h, 110 °C), especially when compared with the highly moisture-sensitive nature of **1.23**[Li].[36]

The reactivity differences observed for the structurally analogous complexes **2.3b** and **3.1** warrant further commentary. Complex **2.3b** can be viewed as reacting either directly with an E-H containing substrate by way of oxidative addition to give a Pt(IV) species, or by way of reductive elimination of ethane followed by oxidative addition of E-H to a putative (κ^2-P,N-**1.19b**)Pt species. While oxidative addition/reductive elimination

reaction cycles are likely the most appropriate mechanistic descriptors for reactions involving the addition of E-H bonds to relatively low oxidation state metal complexes, alternative reaction mechanisms featuring σ-bond metathesis in the absence of formal oxidation state changes may also be invoked. In the case of **3.1** direct oxidative addition would yield an unreasonable Au(V) addition product; as such, reductive elimination of ethane (or a σ-bond metathesis step) may be seen as a prerequisite for E-H additions. Given that reductive elimination of ethane from cis-$[L_2AuMe_2]^+$ complexes is greatly inhibited upon addition of excess L, it has been suggested that dissociation of L is the initial step in the reductive elimination process.[28] As such, the lack of reactivity observed for **3.1** may be attributed to the bidentate and anionic nature of the ancillary ligand **1.23**, which coordinates strongly to the $[AuMe_2]^+$ fragment, thereby preventing access to the three-coordinate $LAuMe_2$ intermediate required for reductive elimination. By comparison, similar dissociation of a ligand arm in **2.3b** to yield an $LPtMe_2$ species is anticipated to be much easier than in **3.1**, owing to the diminished electrostatic forces between the neutral ligand **1.19b** and the neutral $PtMe_2$ fragment. Given that dialkylgold(III) complexes are generally inert to protonolysis,[28] and in an effort to explore further the stability of the indenide unit in **3.1** to electrophilic attack, this complex was treated separately with HBF_4 and HCl at 22 °C (Scheme 3.2). In the case of HBF_4, clean conversion to the cationic complex $[(\kappa^2\text{-}P,N\text{-}1.19b)AuMe_2]^+ BF_4^-$ (**3.2**) was observed after 0.5 h,[20] while addition of anhydrous HCl yielded a κ^1-P,N species (**3.3**), which was isolated as an analytically pure, white solid in 82% yield. While **3.2** has not as yet been isolated as an analytically pure solid, its assignment as shown in Scheme 3.2 is based on the analysis of multinuclear NMR data (see Chapter 7).
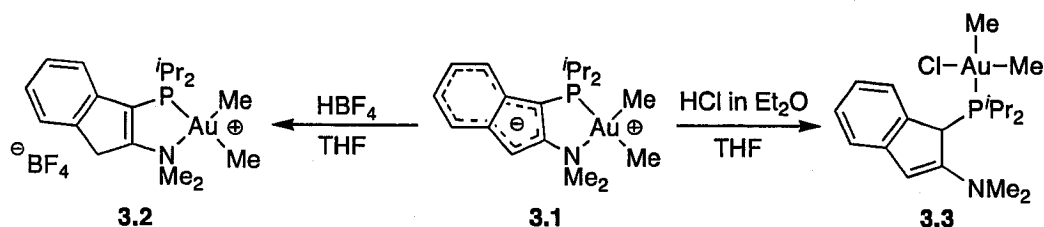
Scheme 3.2 Reactivity of **3.1** with Brønsted acids.

3.2.3 Metal-Mediated Addition of Triethylsilane to Styrene

The addition of triethylsilane to styrene was examined in a preliminary effort to compare the catalytic abilities of **2.3b** and **3.1** in E-H addition reactions; the predominant silicon-containing products of this reaction are given in Scheme 3.3.[37-39] While the activity of Pt-based catalysts in alkene hydrosilylation is well-established, such reactions are rarely regioselective (giving **3.4a** and **3.4c**) and are commonly accompanied by side-reactions including dehydrogenative silylation (giving **3.4b**, **3.4d**, and **3.4e**).[37-43] In light of the selectivity that has been observed in stoichiometric reactions of κ^2-(P,N)Pt(II) complexes with silanes,[6-11] investigation into whether similar selectivity benefits could be derived from employing **2.3b** and related Pt-complexes as catalysts for alkene hydrosilylation was of interest. A survey of the literature revealed that the use of P,N-ligands in tuning Pt-mediated hydrosilylation had not been examined thoroughly.
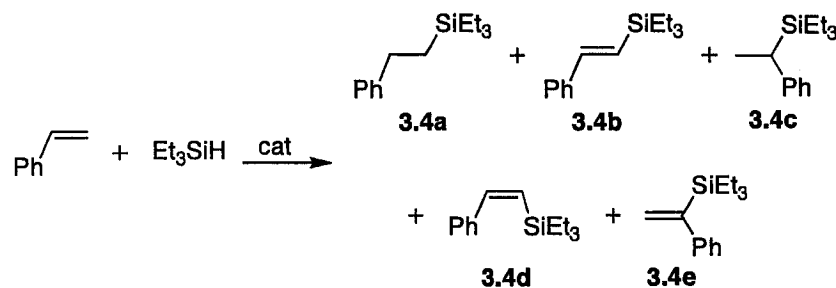
Scheme 3.3 Silicon-containing products of the hydrosilylation and dehydrogenative silylation of styrene using Et_3SiH.

The vinylsilanes **3.4b**, **3.4d**, and **3.4e** are presumed to arise by way of the modified Chalk-Harrod mechanism, which involves alkene 1,2-insertion into the M-Si bond in an intermediate of the type $L_nM(H)(SiR_3)$(alkene), followed by β-hydrogen elimination (see Chapter 1, Figure 1.3).[44-47] Gold complexes do not normally undergo β-hydrogen elimination,[28] and as such the use of **3.1** as a catalyst for this reaction was explored as a means of increasing the selectivity for **3.4a** and/or **3.4c** in Scheme 3.3. While the utilization of Au-based complexes as homogeneous catalysts for E-H additions to alkenes is gaining attention,[48-53] the ability of such complexes to mediate the addition of Si-H bonds to alkenes has not yet been demonstrated.

While negligible conversion was achieved by use of 5 mol% **2.3b** as a catalyst at 22 °C over 24 h, at 50 °C modest turnover was noted; 26% conversion was obtained using an equimolar substrate ratio (Table 3.1; entry 3-1), whereas 43% conversion was achieved by employing three equivalents of styrene (entry 3-2). Evidently, no selectivity advantages are brought about by the incorporation of the P,N-ligand in **2.3b**, as the observed product distributions mirror those obtained when employing a range of other Pt-based catalyst complexes.[37-43] Catalytic reactions employing 5 mol% $CODPtMe_2$ provided further evidence that the ancillary ligand **1.19b** serves to attenuate rather than enhance the activity of Pt-mediated hydrosilylations (entries 3-3 and 3-4). As well, in the case of hydrosilylation experiments employing 5 mol% **3.1** as catalyst and three equivalents of styrene, no conversion was noted at 22 °C, 50 °C, or 70 °C over a 24 h period (entry 3-15).

Table 3.1 Addition of Et_3SiH to styrene, in the presence of Pt(II) or Au(III).[a]

Entry	Catalyst	Styrene :Et_3SiH	Solvent	Total Yield (%)[b]	Yield 3.4a (%)[c]	Yield 3.4b (%)[c]	Yield 3.4c (%)[c]	Yield Other (%)[c]
3-1	**2.3b**	1:1	C_6H_6	26	10	8	5	3
3-2	**2.3b**	3:1	C_6H_6	43	25	12	3	3
3-3[d]	CODPtMe$_2$	1:1	C_6H_6	88	74	11	1	2
3-4[d]	CODPtMe$_2$	3:1	C_6H_6	> 99	66	32	< 1	2
3-5	**2.2**	1:1	C_6H_6	47	37	8	< 1	2
3-6	**2.2**	1:1	THF	33	20	8	2	3
3-7	**2.2** + 1 AgBF$_4$	1:1	C_6H_6	16	9	5	1	< 1
3-8	**2.2** + 1 AgBF$_4$	1:1	THF	43	15	20	3	5
3-9	**2.2** + 1 AgOTf	1:1	C_6H_6	26	14	5	7	< 1
3-10	CODPtClMe	1:1	C_6H_6	89	66	18	< 1	5
3-11	CODPtClMe + 1 AgBF$_4$	1:1	C_6H_6	78	59	14	< 1	5
3-12[e]	[**3.9**]$^+$ BF$_4^-$	1:1	C_6H_6	7	3	4	< 1	< 1
3-13	**2.1**	1:1	C_6H_6	< 1	< 1	< 1	< 1	< 1
3-14	**2.1** + 2 AgBF$_4$	1:1	C_6H_6	< 1	< 1	< 1	< 1	< 1
3-15	**3.1**	3:1	C_6H_6	< 1	< 1	< 1	< 1	< 1

[a] Reactions run for 24 h employing 5 mol% catalyst at 50 °C in C_6H_6, except where noted. [b] Based on consumption of Et_3SiH. [c] Product distribution based on GC-MS and GC-FID data, rounded to the nearest percent; other Si-containing products include **3.4d** and **3.4e**. [d] Experiment conducted at 24 °C. [e] 5 mol% catalyst was used, effectively providing 10 mol% Pt.

Encouraged by the work of Widenhoefer and co-workers, who have employed

(κ^2-N,N)PtMe$_2$ complexes activated by B(C_6F_5)$_3$ as catalysts for the

cyclization/hydrosilylation of functionalized diynes using triethylsilane,[54-56] and in light of

the observation that hydrosilylation catalysis is enhanced by the opening of a

coordination site at Pt,[40-43] efforts were made to improve the catalytic performance of

2.3b and **3.1** by employing B(C_6F_5)$_3$ as a methide-abstracting agent. A reaction between

2.3a and B(C_6F_5)$_3$ in a 1:1 toluene/THF mixture was observed, with the consumption of

the starting Pt complex (δ ^{31}P{^{1}H} = 27.6, $^1J_{PtP}$ = 2063 Hz) noted after 20 min, along with

the formation of two new phosphorus-containing products (δ ^{31}P{^{1}H} = 29.8, $^1J_{PtP}$ = 4924

Hz, *major*; δ ^{31}P{^{1}H} = 36.3, $^1J_{PtP}$ = 2873 Hz, *minor*); at this stage, two ^{11}B{^{1}H} NMR

signals were observed at 7.0 ppm and -14.1 ppm (Figure 3.3). It is possible that these

two sets of signals correspond to related compounds where a methide has been

abstracted either cis or trans to the phosphine, or that they represent isomers featuring

the related ligands **1.19a** and **1.19b**. The Au(III) complex **3.1** (δ ^{31}P$\{^1$H$\}$ = 46.3) was also

quantitatively consumed upon addition of an equivalent of borane, exhibiting two ^{31}P$\{^1$H$\}$

NMR resonances (δ = 50.2 and 43.0) as well as two ^{11}B$\{^1$H$\}$ NMR signals at δ = 0.0 and
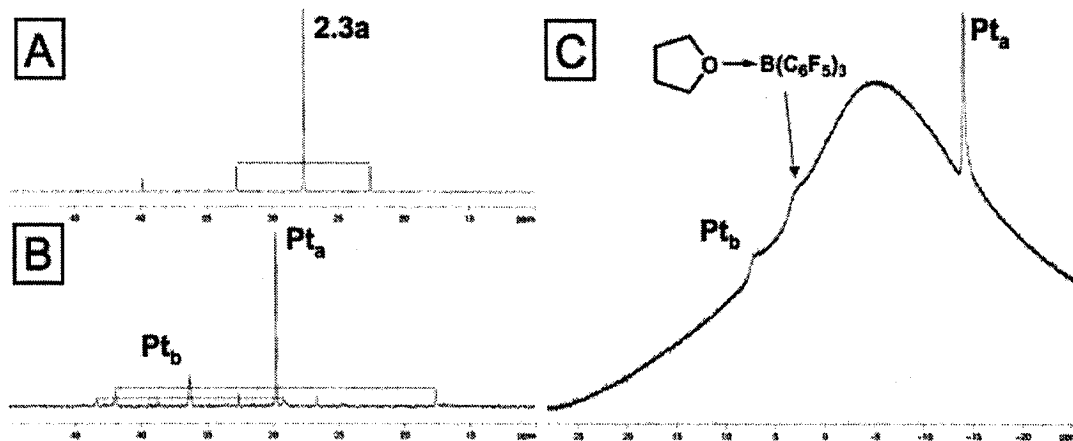
Figure 3.3 ^{31}P$\{^1$H$\}$ and ^{11}B$\{^1$H$\}$ NMR spectra of the addition of B(C$_6$F$_5$)$_3$ to a solution of **2.3a**. Shown are: A) ^{31}P$\{^1$H$\}$ NMR spectrum of **2.3a** before addition of B(C$_6$F$_5$)$_3$; B) ^{31}P$\{^1$H$\}$ NMR spectrum of **2.3a** after addition of B(C$_6$F$_5$)$_3$; and C) ^{11}B$\{^1$H$\}$ NMR spectrum of **2.3a** after addition of B(C$_6$F$_5$)$_3$.
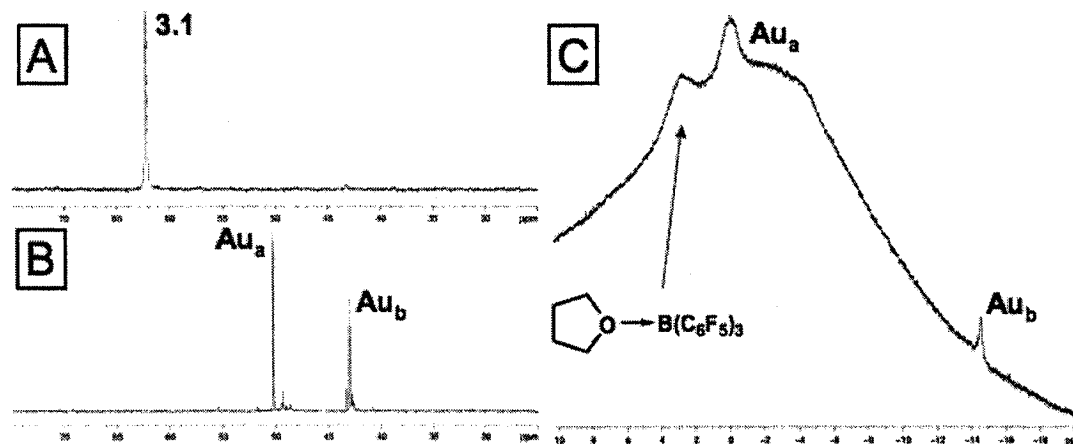
Figure 3.4 ^{31}P$\{^1$H$\}$ and ^{11}B$\{^1$H$\}$ NMR spectra of the addition of B(C$_6$F$_5$)$_3$ to a solution of **3.1**. Shown are: A) ^{31}P$\{^1$H$\}$ NMR spectrum of **3.1** before addition of B(C$_6$F$_5$)$_3$; B) ^{31}P$\{^1$H$\}$ NMR spectrum of **3.1** after addition of B(C$_6$F$_5$)$_3$; and C) ^{11}B$\{^1$H$\}$ NMR spectrum of **3.1** after addition of B(C$_6$F$_5$)$_3$.

-14.3 (Figure 3.4). Again, it is possible that these two sets of signals relate to abstraction of a methide unit from either the *cis* or the *trans* position relative to the phosphine. Tentative assignments of the peaks in Figures 3.3 and 3.4 are made on the basis of relative integration of the peaks from $^{31}P\{^1H\}$ and $^{11}B\{^1H\}$ NMR experiments.

The hydrosilylation of styrene with equimolar triethylsilane (22 °C) was subsequently attempted in a 1:1 toluene/THF mixture, employing 10 mol% of **2.3a** or **3.1** pre-treated with an equivalent of the borane activator. After 1 h, greater than 80% conversion to ^{n}BuOSiEt$_3$ (presumably derived from the ring-opening of THF) was observed, in the absence of alkene addition products. In contrast to the aforementioned cyclization/hydrosilylation process examined by Widenhoefer and co-workers, which is not mediated by $(\kappa^2\text{-}N,N)PtMe_2$ complexes or $B(C_6F_5)_3$ alone,[54-56] control experiments revealed that the formation of ^{n}BuOSiEt$_3$ described herein can be attributed entirely to the borane, in keeping with previous reports by both Piers and Chivers.[57-61] The mechanism for this transformation (Figure 3.5) most likely resembles that proposed for the $B(C_6F_5)_3$-catalyzed hydrosilylation of carbonyl compounds,[61] in which activation of the Si-H bond by the Lewis acidic borane renders subsequent attack by oxygen on silicon possible, despite the predominant formation of a Lewis acid-base adduct between the borane and THF. When the reactions were conducted in toluene, CH_2Cl_2, or MeCN, negligible metal-mediated catalysis was observed.
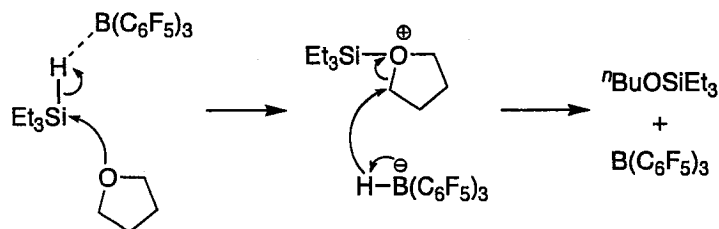
Figure 3.5 Proposed mechanism for the borane-catalyzed hydrosilylation of THF.

In an alternative approach to the generation of a potentially reactive [(κ^2-P,N-1.19b)PtMe]$^+$ fragment, the catalytic abilities of (κ^2-P,N-1.19b)PtClMe (**2.2**), as well as products derived from in situ chloride abstraction, were evaluated. While **2.2** proved to be a more effective alkene hydrosilylation catalyst than **2.3b** in benzene (compare Table 3.1; entries 3-1 and 3-5), CODPtClMe out-performed both of these catalyst complexes under analogous conditions (entry 3-10), in keeping with the aforementioned L_2PtMe_2 system (vide supra). Treatment of **2.2** with either an equivalent of AgOTf (entry 3-9) or AgBF$_4$ (entry 3-7) in benzene gave rise to a progressively poorer catalyst system versus **2.2**, while a less pronounced reduction in activity was noted upon treatment of CODPtClMe with AgBF$_4$ in benzene (entry 3-11).[28] Conversely, the **2.2**/AgBF$_4$ catalyst system performed somewhat better than **2.2** in THF (entries 3-6 and 3-8). The use of (κ^2-P,N-1.19b)PtCl$_2$ (**2.1**) in both the presence and absence of two equivalents of AgBF$_4$ resulted in negligible conversion (entries 3-13 and 3-14), likely due to the formation of an unstable [(κ^2-P,N-1.19b)Pt]$^{2+}$ fragment. The decrease in activity of **2.2** and (COD)PtMeCl observed when AgX was employed as an activator prompted an investigation into the nature of the species formed under these reaction conditions.

3.2.4 Rational Preparation of Mono- and Dinuclear (κ^2-P,N)Pt(II) Cations

In an effort to characterize cationic Pt(II) species derived from **2.2** that may have been generated in the course of the previously described catalytic experiments, a study of the reactivity of **2.2** in THF or benzene with various halide-abstracting agents was conducted (Scheme 3.5). Treatment of **2.2** with AgBF$_4$ in THF resulted in an observed change in the chemical shift and Pt-P coupling constant (δ ^{31}P{^{1}H} = 29.9; $^1J_{Pt-P}$ = 4893 Hz) that was consistent with the quantitative formation of a THF-stabilized cation, [**3.5**]$^+$

BF_4^-. Subsequent addition of one equivalent of either MeCN or SMe_2 resulted in a corresponding shift in $^{31}P\{^1H\}$ NMR signal, as well as a substantial decrease in $^1J_{Pt-P}$ (4600 Hz for L = MeCN, a decrease of ~300 Hz). Characterization of the resulting complexes by NMR prompted their assignment as $[(\kappa^2\text{-}P,N)PtMe(L)]^+$ BF_4^- (L = MeCN, $[3.6]^+$ BF_4^-; L = SMe_2, $[3.7]^+$ BF_4^-). In the case of $[3.7]^+$ BF_4^-, this structural formulation was confirmed on the basis of a single crystal X-ray diffraction experiment. The crystal structure of $[3.7]^+$ BF_4^- is presented in Figure 3.6, and relevant crystallographic parameters are collected in Chapter 7. While the Pt-P, Pt-N, and Pt-Me distances, as well are related angles in $[3.7]^+$ BF_4^-, are consistent with those observed in 2.3b, the Pt-S distance is significantly longer than those found in some structurally related
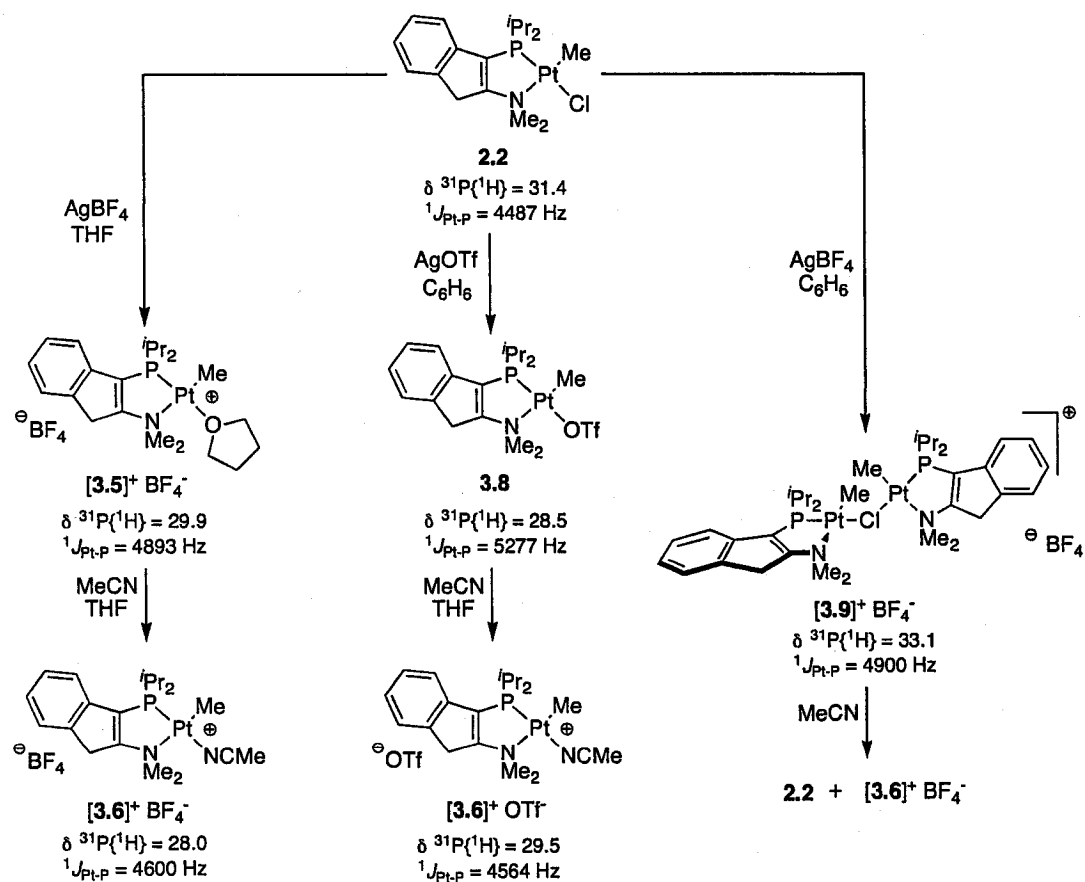
Scheme 3.5 Reactivity of 2.2 with various halide-abstracting agents in THF and C_6H_6.
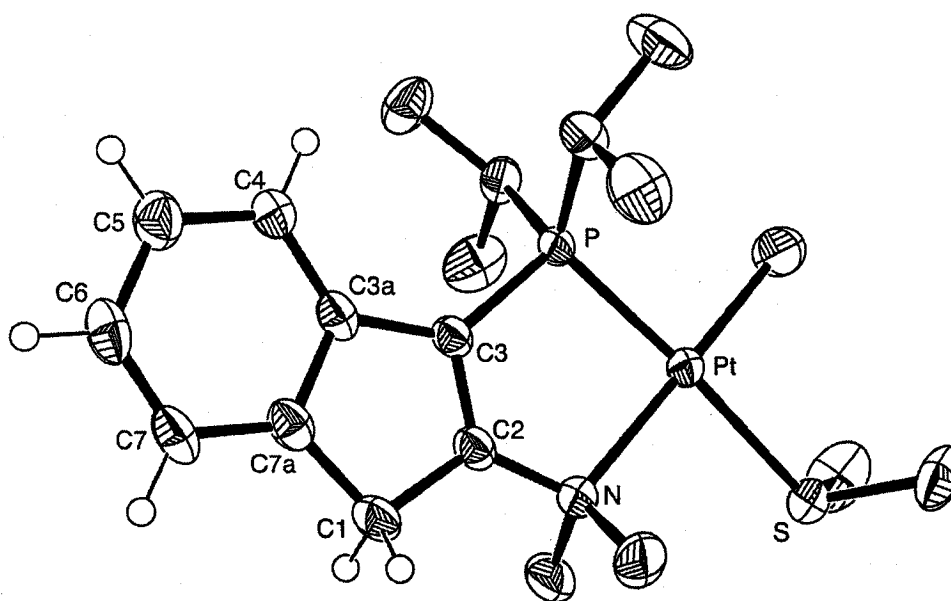
Figure 3.6 ORTEP diagram for [**3.7**]⁺ BF₄⁻, showing the atomic numbering scheme for selected atoms, with 50% displacement ellipsoids. Selected hydrogen atoms and the tetrafluoroborate counterion have been omitted for clarity.

[(κ²-N,N)PtMe(SMe₂)]⁺ complexes.[62] Both complexes were isolated as analytically pure powders in good yield (L = MeCN, 84 %; L = SMe₂, 77 %).

In contrast to the expected reactivity observed in THF, when either 0.5 or 1.0 equivalents of AgBF₄ were added to **2.2** in benzene or toluene solution, a precipitate was noted to form, and was isolated in 61 % yield as an analytically pure solid after trituration with pentane. Analysis of the supernatant solution revealed the presence of only minute quantities of unreacted **2.2**, while a solution of the dissolved precipitate in CH₂Cl₂ exhibited a single resonance in the ³¹P{¹H} NMR (δ = 33.1; ¹J_{Pt-P} = 4900 Hz) assigned to the compound [**3.9**]⁺ BF₄⁻. When one equivalent of MeCN was added to a solution of [**3.9**]⁺ BF₄⁻, the ³¹P{¹H} NMR signal at δ = 33.1 was immediately consumed, and a 1:1 mixture of **2.2** and [**3.6**]⁺ BF₄⁻ was returned. The structure of [**3.9**]⁺ BF₄⁻ was ultimately elucidated on the basis of a single crystal X-ray diffraction experiment, and is presented in Figure 3.7, with relevant crystallographic parameters collected in Chapter 7.
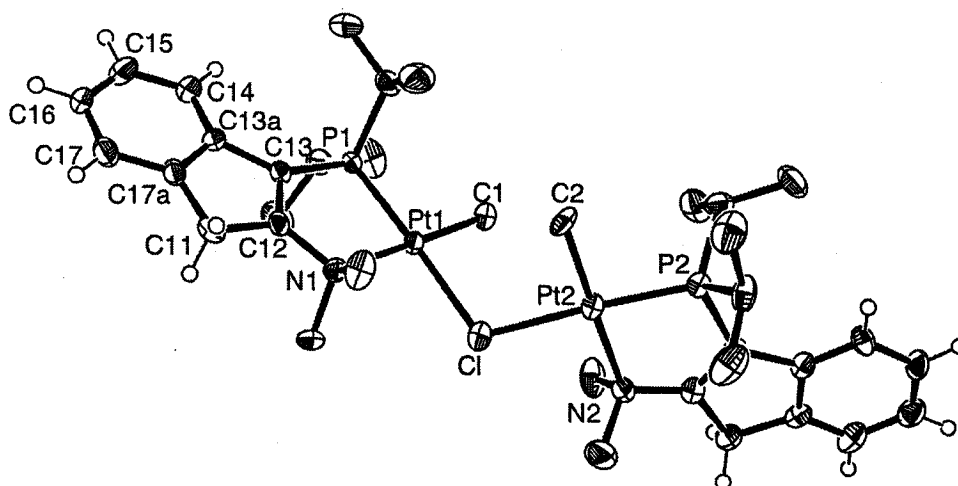
Figure 3.7   ORTEP diagram for [**3.9**]$^+$ BF$_4^-$, showing the atomic numbering scheme for selected atoms, with 50% displacement ellipsoids. Selected hydrogen atoms and the tetrafluoroborate counterion have been omitted for clarity.

The structure for [**3.9**]$^+$ BF$_4^-$ features two corner-sharing square-planar Pt(II) moieties that are offset by 73.4(1) °, bridged through a single chloride atom. The Pt-N, Pt-Me and Pt-P distances are in keeping with those observed for **2.2**, as well as a related [{(κ^2-P,N)PtMe}$_2$Cl]$^+$ complex reported by Braunstein and co-workers.[13] Dinuclear cations of this type featuring two Pt fragments bridged by a single chloride are relatively uncommon.[13,63-65] The formation of [**3.9**]$^+$ BF$_4^-$ may be viewed as arising from the trapping of [(κ^2-P,N-**1.19b**)PtMe]$^+$ BF$_4^-$ by **2.2**, supporting the claim that an η^2-arene does not provide sufficient stability to isolate such cationic Pt(II) complexes in the absence of an alternative lone-pair donor such as MeCN or Me$_2$S.

Reacting **2.2** with one equivalent of AgOTf in benzene solution resulted in quantitative conversion, as evidenced by ^{31}P{^{1}H} NMR (δ = 28.5; $^1J_{Pt-P}$ = 5277 Hz), to a proposed (κ^2-P,N-**1.19b**)PtMe(OTf) complex (**3.8**) as shown in Scheme 3.5. This assignment is proposed on the basis of the marked increase in $^1J_{Pt-P}$, consistent with an inner-sphere triflate adduct, and the assumption that an η^2-benzene coordination would

not provide sufficient stabilization for a $[(\kappa^2\text{-}P,N\text{-}\textbf{1.19b})PtMe]^+$ fragment (vide supra).

Addition of one equivalent of MeCN to this solution resulted in quantitative formation of

$[\textbf{3.6}]^+$ OTf⁻, based on in situ NMR characterization.

These synthetic studies provided some insight regarding the catalytic behavior of

cationic Pt species supported by **1.19b**. Given the poor catalytic performance exhibited

by purified $[\textbf{3.9}]^+ BF_4^-$, which contains two moles of Pt per mole of catalyst (Table 3.1;

entry 3-12), it seems plausible that the modest catalytic conversion observed upon

treatment of **2.2** with $AgBF_4$ in benzene (entry 3-7) can be attributed to residual **2.2**

(entry 3-5). The activity of CODPtClMe is only slightly diminished upon exposure to

$AgBF_4$ in benzene. It is conceivable that a related $[(CODPtMe)_2Cl]^+$ complex, if formed, is

either significantly more active than $[\textbf{3.9}]^+ BF_4^-$, or is more prone to dissociation to give

catalytically active CODPtClMe and/or $[CODPtMe(solvent)]^+$ species. Conversely, in THF

$[\textbf{3.9}]^+ BF_4^-$ is not formed upon addition of $AgBF_4$ to **2.2**. Instead, **2.2** is quantitatively

converted to a new phosphorus-containing complex, which may correspond to $[\textbf{3.5}]^+ BF_4$.

In this context, the modestly increased conversion observed upon treatment of **2.2** with

$AgBF_4$ in THF (entry 3-8) may reflect the heightened activity of this proposed cationic

intermediate, relative to **2.2**. As well, **2.2** and AgOTf react cleanly in benzene to give the

putative inner-sphere complex **3.8** (entry 3-9), thereby circumventing the formation of the

related dimer, $[\textbf{3.9}]^+$ OTf⁻.

3.3   Conclusion

Notwithstanding the structural, "right-hand neighbor" relationship between **2.3b**

and **3.1**, the reactivity properties of these species differ considerably. For example, while

2.3b has been shown to react in a stoichiometric and catalytic fashion with silanes, no

such reactivity was noted for **3.1** under similar conditions. It is likely that these

observations can be attributed in part to differences both in the metal formal oxidation state (Pt(II) versus Au(III)), as well as the charge of the ancillary bidentate ligand (neutral in **2.3b** versus anionic in **3.1**). In addition, catalytic studies employing **2.3b** and related Pt(II) cations supported by **1.19b** revealed that no selectivity advantages for the Pt-mediated addition of triethylsilane to styrene are brought about by the incorporation of this bidentate ligand, despite the established precedent of P,N-ligands in providing heightened selectivity in myriad transformations mediated by platinum-group metal complexes.[66-68]

In the course of this catalytic survey it was discovered that the identity of the Pt(II) species formed in situ upon treatment of **2.2** with AgX (X = BF_4 or OTf) is dictated by the solvent employed, as well as the nature of X. In benzene, **2.2** and $AgBF_4$ combine to give $[3.9]^+ BF_4^-$, while in THF $[3.5]^+ BF_4^-$ is presumably formed, which can be converted to $[3.6]^+ BF_4^-$ or $[3.7]^+ BF_4^-$ upon treatment with MeCN or Me_2S, respectively. These latter findings underscore the problems that can arise when attempting to develop thorough structure-reactivity relationships based on the investigation of reactive metal species formed in situ. Despite the wealth of reactivity displayed by cationic Pt(II) complexes, the most active catalysts for the hydrosilylation of styrene under these conditions were found to be neutral (COD)Pt(II) species. This may indicate that ion-pairing or irreversible solvent coordination to a cationic Pt center plays a significant role in attenuating catalyst activity.

3.4   References

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Chapter 4 – Gold(I) Complexes Supported by P,N and P Ligands

4.1   Introduction

While soluble platinum-group metal catalysts are employed widely in mediating a diversity of synthetically useful chemical reactions, the application of Au complexes in homogeneous catalysis had, until relatively recently, received little attention (see section 1.6). However, the numerous reports documenting Au-catalyzed substrate transformations that have emerged over the last decade serve to confirm the utility of such catalyst complexes; indeed, soluble Au complexes in some instances have provided access to reaction manifolds that cannot be reached by use of more traditional catalysts. Notwithstanding this remarkable progress, and despite an early report by Hayashi and co-workers that highlights the reactivity benefits of employing appropriately selected phosphine ancillary ligands in Au-mediated transformations,[1] one consequence associated with the delayed recognition of Au catalysis is that the influence of supporting ligands on metal-centered reactivity has not been explored exhaustively. Given the central role that fundamental ligand design studies have played in advancing the field of transition metal-mediated homogeneous catalysis,[2-5] related studies involving Au are likely to further the collective understanding of the factors that influence Au-centered reactivity, and may ultimately enable the development of new or improved Au-catalyzed substrate transformations.

As a step toward probing the influence of ligands on Au-mediated reactions, the preparation and characterization of a variety of new Au(I) complexes featuring the P,N ligands **1.19a** and **1.20a**, as well as the P ligands **1.21** and **1.22**, including a comparison of structural and spectroscopic features was desired. Also of interest was the ability for

such species to catalyze the addition of various E-H bonds to unsaturated organic fragments. While several such Au-mediated addition reactions have been reported, the addition of Si-H bonds is limited to a single communication by Hosomi and co-workers,[6] in which they report the hydrosilylation of various aldehydes and an aldimine catalyzed by a mixture of Ph_3PAuCl and $^nBu_3P$ (a recent report by Ito and co-workers demonstrates selective dehydrocoupling of silanes and primary alcohols catalyzed by a Au(I)/XANTPHOS system in the presence of tertiary alcohols, ketones and aldehydes).[7] The hydrosilylation of alkynes catalyzed by Au nanoparticles supported on carbon or alumina has also been reported,[8] though it is obvious that a different, heterogeneous mechanism is operational in this case. In the interest of probing the effect of P,N ligation (versus P ligation), phosphine substituent, coordination number and counterion effects, as well as extending the scope of the reaction reported by Hosomi and co-workers, Au(I) complexes derived from **1.19a**, **1.20a**, **1.21** and **1.22**, as well as various phosphines (R_3P, R = Et, ^nBu, ^tBu, Cy, Ph) and one *N*-heterocyclic carbene, were explored as catalysts for the hydrosilylation of aldehydes.

4.2 Results and Discussion

4.2.1 Synthesis of New Au(I) Complexes

Treatment of **1.21** or **1.22** with one equiv of Me_2SAuCl afforded (κ^1-*P*-**1.21**)AuCl (**4.1**) and (κ^1-*P*-**1.22**)AuCl (**4.2**) in 88% and 75% isolated yield, respectively (Scheme 4.1). The proposed structures of **4.1** and **4.2** are supported by data obtained from solution NMR studies, with the C_s symmetry of these complexes being evident in the ^1H and $^{13}C\{^1H\}$ NMR spectra. In the case of **4.1**, the connectivity was confirmed on the basis of data obtained from single-crystal X-ray diffraction studies. The crystal structure of **4.1**

is presented in Figure 4.1, and relevant crystallographic parameters are collected in

Chapter 7. The structure of **4.1** is quite similar to that of the related complex ^{i}Pr$_3$PAuCl,[9]

with the Au center in **4.1** deviating only modestly from linearity (177.20(3)°).

1.21 R = ^{i}Pr
1.22 R = Ph

4.1 R = ^{i}Pr
4.2 R = Ph
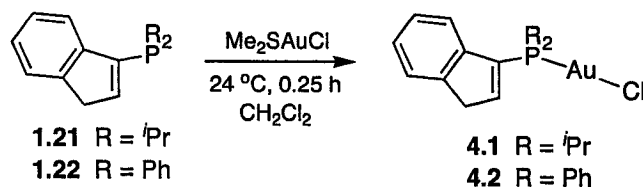
Scheme 4.1   Preparation of (κ^1-*P*)Au(I) complexes derived from **1.21** and **1.22**.
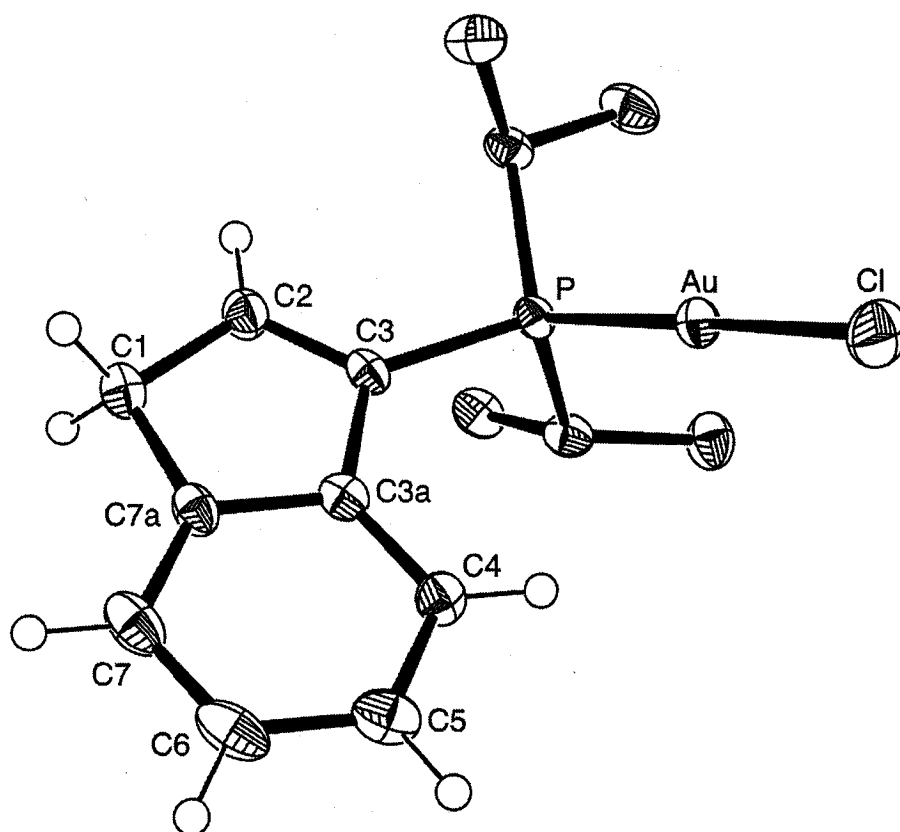
Figure 4.1   ORTEP diagram for **4.1**, showing the atomic numbering scheme for selected atoms, with 50% displacement ellipsoids. Selected hydrogen atoms have been omitted for clarity.

The utility of P,N-ligands in supporting catalytically active platinum-group

complexes is well-established (see section 1.2). In this regard, the Stradiotto group has

demonstrated previously that such metal complexes featuring **1.19** and related P,N-substituted indenes can participate in a range of stoichiometric and/or catalytic transformations involving E-H bond activation.[10-15] In the pursuit of related Au(I) coordination complexes, **1.19a** was treated with Me_2SAuCl, affording $(\kappa^1\text{-}P,N\text{-}\textbf{1.19a})AuCl$ **(4.3)** in 67% isolated yield (Scheme 4.2). Data obtained from solution NMR spectroscopic studies revealed that the connectivity within the monodentate ligand **1.19a** is retained in **4.3**. This is in keeping with previously established behavior of **1.19**, in which κ^2 metal complexes are observed to isomerize exclusively to the C3 isomer, while κ^1 complexes maintain a C1 conformation. This structural formulation of **4.3** was confirmed through a single crystal X-ray diffraction experiment; the crystal structure of **4.3** is presented in Figure 4.2, and relevant crystallographic parameters are collected in Chapter 7. The nearly linear geometry at Au (177.60(8)°) as well as the Au-P (2.247(2) Å) and Au-Cl (2.294(2) Å) distances in **4.3** are indistinguishable from those in **4.1** (vide supra), and can be compared with other structurally related Au(I) complexes.[16-19] The Au⋯N separation (3.667 Å) lies outside the sum of the van der Waals radii for these elements (3.25 Å),[20] thereby confirming the $\kappa^1\text{-}P,N$ binding mode of **1.19a** in **4.3**; similar $(\kappa^1\text{-}P,N)AuCl$ coordination complexes of potentially bidentate P,N-ligands have been reported.[16-19] While this coordination motif for **1.19a** is also observed in $(\kappa^1\text{-}P,N\text{-}\textbf{1.19a})Rh(COD)Cl$,[10,12] the ability of **1.19a** to function as a bidentate $\kappa^2\text{-}P,N$ ligand for neutral later transition metal complexes has been demonstrated for both Pt (see Chapter 2) and Ru.[11]
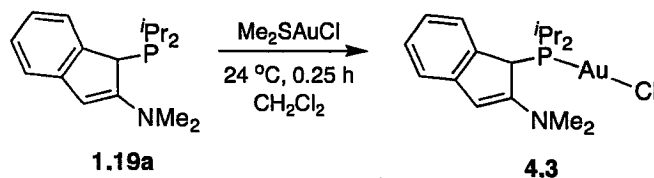
Scheme 4.2   Preparation of a $(\kappa^1\text{-}P,N)Au(I)$ complex derived from **1.19a**.
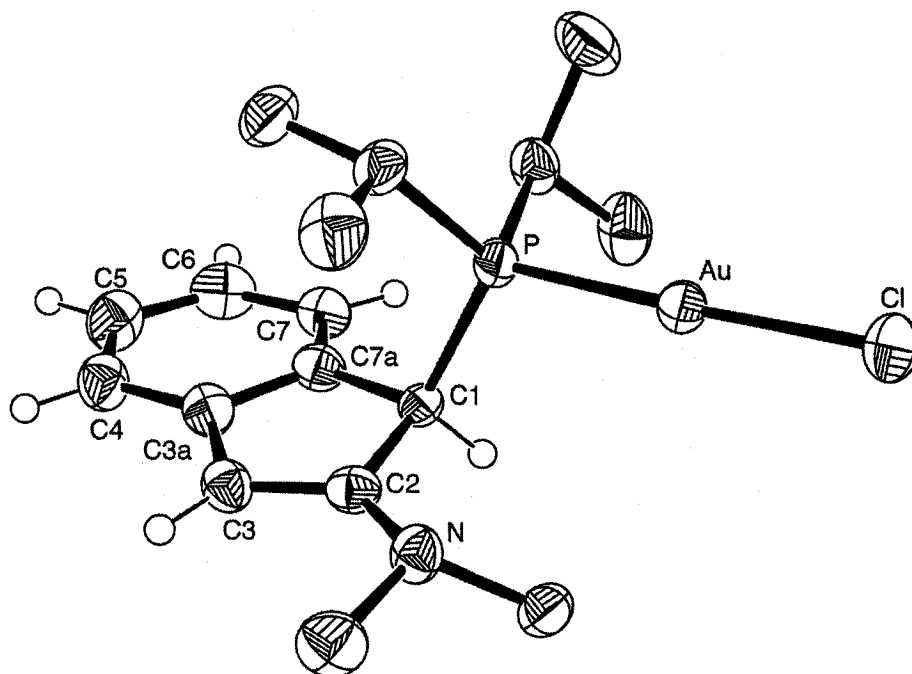
Figure 4.2 ORTEP diagram for **4.3**, showing the atomic numbering scheme for selected atoms, with 50% displacement ellipsoids. Selected hydrogen atoms have been omitted for clarity.

In contrast to the preparation of **4.3**, during which products derived from the isomerization of the ancillary ligand **1.19a** were not detected by use of NMR spectroscopic methods, treatment of **1.20a** with Me_2SAuCl generated cleanly (^1H and $^{31}P\{^1H\}$ NMR) an inseparable 2:3 isomeric mixture of (κ^1-P,N-**1.20a**)AuCl (**4.4a**) and (κ^1-P,N-**1.20b**)AuCl (**4.4b**), which was isolated in 56% yield and characterized by use of 1D- and 2D-NMR techniques (Scheme 4.3). It has been shown previously that the ligands **1.19a** and **1.20a**, when heated or upon treatment with NEt_3, convert to an isomeric mixture of **1.19a** and **1.19b** or **1.20a** and **1.20b**; under similar conditions, 1-R_2P-indenes (R = ^iPr, Ph) are readily converted to **1.21** and **1.22**, respectively.[10] Consistent with these observations, and in keeping with (κ^1-P,N-**1.19a**)Rh(COD)Cl, which also resists rearranging to (κ^1-P,N-**1.19b**)Rh(COD)Cl,[10,12] neither **4.4a** nor **4.4b** could be converted to

its isomer, either with heating (50 °C, 6 days), or upon exposure to NEt_3, ^iPrOH, or H_2O in THF solution. Notably, under similar conditions Pt (see Chapter 2) and Ru^{11} (κ^2-P,N-1.19a)ML_n species have been observed to isomerize to the corresponding (κ^2-P,N-1.19b)ML_n complexes.

1.20a   **4.4a**   **4.4b**
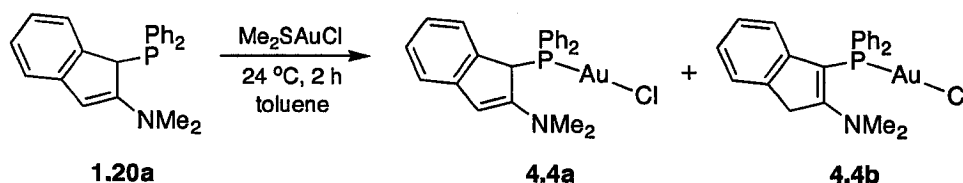
Scheme 4.3 Preparation of (κ^1-P,N)Au(I) complexes derived from **1.20a**.

In the pursuit of an L_2AuCl species, **4.1** was treated with one equiv of **1.21**, thereby allowing for the isolation of (κ^1-P-**1.21**)$_2$AuCl (**4.5**) as an analytically pure light brown crystalline solid in 69% yield (Scheme 4.4). The crystal structure of **4.5** is presented in Figure 4.3, and relevant crystallographic parameters are collected in Chapter 7. The structure as determined by a single crystal X-ray diffraction experiment highlights a distorted trigonal planar coordination geometry at Au ($\Sigma_{angles\ at\ Au} \sim 360°$) that is also evident in some other crystallographically characterized $(R_3P)_2AuCl$ complexes.[21-24] Notably, the Au-P (2.3181(5) Å and 2.3050(5) Å) and Au-Cl (2.6577(6) Å) distances in **4.5** are lengthened significantly relative to those found in both **4.1** and **4.3**. In contrast to the asymmetric Au-P distances in **4.5** that may arise due to crystal packing effects, both ^1H and $^{13}C\{^1H\}$ NMR data for this complex are consistent with an effective C_{2v} symmetric solution structure for **4.5**. While the $^{31}P\{^1H\}$ spectrum of **4.5** at 300 K consists of a single broad resonance centered at δ = 35 ($\Delta v_{1/2} \sim 950$ Hz), upon cooling to 170 K a sharp singlet at δ = 37 is observed, along with a low intensity multiplet centered at δ = 48. While de-coalescence of signals is clearly occurring, attempts to assign the species involved in this behavior in an unambiguous fashion have proven unsuccessful to date.
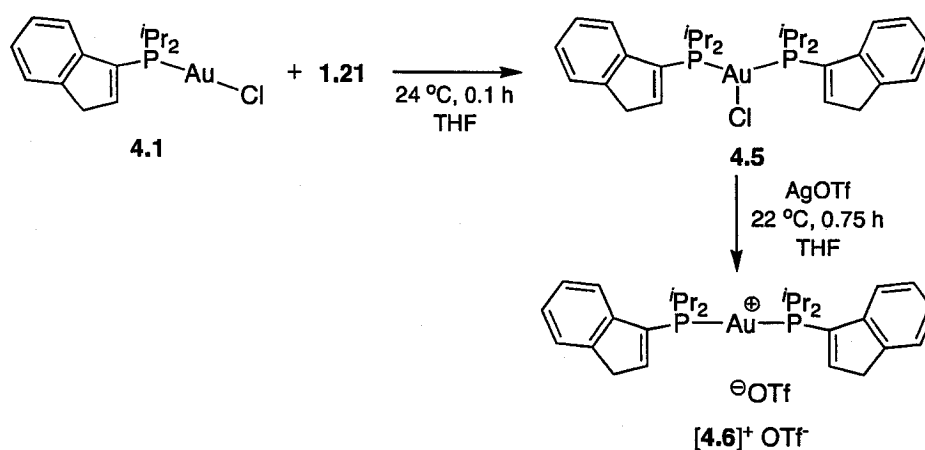
Scheme 4.4 Preparation of (κ¹-*P*,N)₂AuX (X = Cl, OTf) complexes.
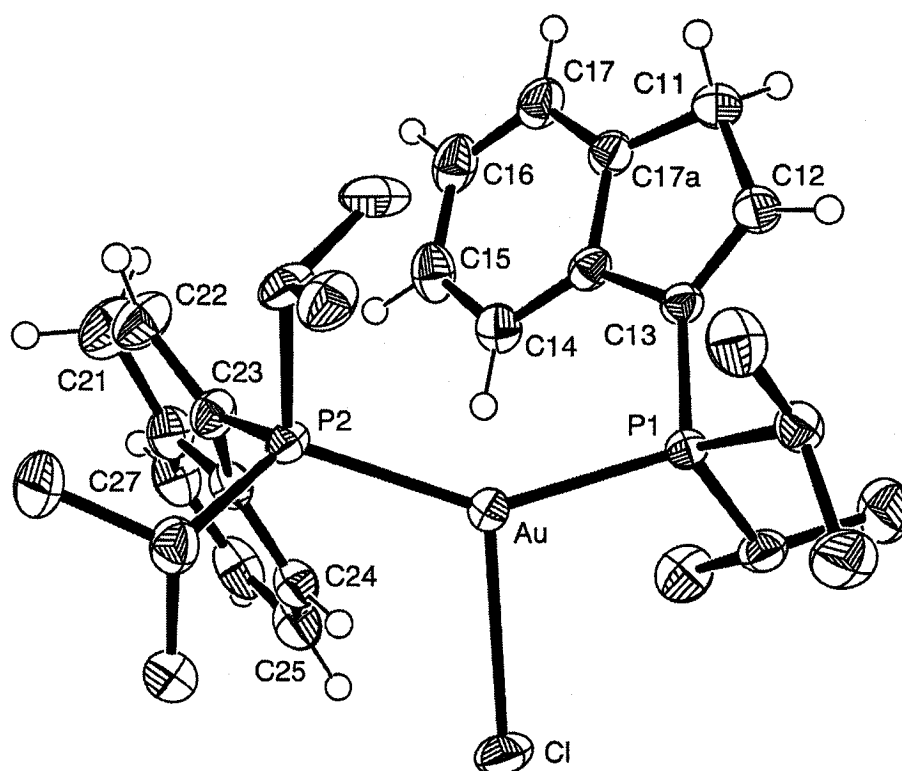
Figure 4.3 ORTEP diagram for **4.5**, showing the atomic numbering scheme for selected atoms, with 50% displacement ellipsoids. Selected hydrogen atoms have been omitted for clarity.

The preparation of $(\kappa^1\text{-}P,\text{N-}\textbf{1.19a})_2\text{AuCl}$ complexes proved less straightforward.

Following the addition of one equivalent of **1.19a** to **4.3** in THF, the $^{31}P\{^1H\}$ NMR

spectrum of the reaction mixture revealed multiple broad resonances centered around

$\delta = 62$ and -5. Upon cooling from 300 K to 170 K, several de-coalescence events were

noted, eventually resulting in a complicated spectrum that could not be unambiguously

assigned. In addition to the spectral complexities arising from the anticipated presence

of isomeric *meso* and *rac* $(\kappa^1\text{-}P,\text{N-}\textbf{1.19a})_2\text{AuCl}$ and/or $[(\kappa^1\text{-}P,\text{N-}\textbf{1.19a})_2\text{Au}]^+$ Cl⁻ products in

this reaction, it is possible that oligomeric Au complexes, in which **1.19a** serves to bridge

metal centers, are also formed.[9,21,25] All efforts to isolate pure materials from such

reactions were unsuccessful.

In exploring the synthetic viability of $[(\kappa^1\text{-}P\text{-}\textbf{1.21})_2\text{Au}]^+X^-$ species, complex **4.5** was

treated with one equiv of AgOTf (Scheme 4.4). Subsequent examination of the reaction

mixture by use of $^{31}P\{^1H\}$ NMR methods revealed the consumption of **4.5**, along with the

clean formation of a single phosphorus-containing product $([(\kappa^1\text{-}P\text{-}\textbf{1.21})_2\text{Au}]^+$ OTf⁻, $\textbf{[4.6]}^+$

OTf⁻) giving rise to a sharp singlet at $\delta = 53$ (300 K). Complex $\textbf{[4.6]}^+$ OTf⁻ was isolated in
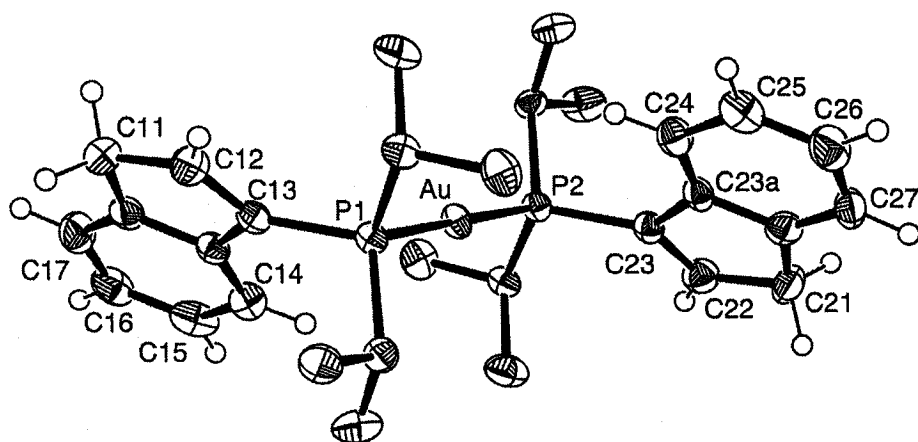
Figure 4.4 ORTEP diagram for $\textbf{[4.6]}^+$ OTf⁻, showing the atomic numbering scheme for selected atoms, with 50% displacement ellipsoids. Selected hydrogen atoms and the triflate counterion have been omitted for clarity.

72% yield and characterized by use of NMR spectroscopic and X-ray crystallographic

methods. The crystal structure of [**4.6**]$^+$OTf$^-$ is presented in Figure 4.4, and relevant

crystallographic parameters are collected in Chapter 7. The linear Au coordination

environment in [**4.6**]$^+$OTf$^-$ (179.26(4)°) is found commonly in $[L_2Au]^+X^-$ complexes.[16,26-31]

As well, no close Au⋯OTf or Au⋯Au contacts were found in [**4.6**]$^+$OTf$^-$, and the Au-P

distances in this complex (2.310(1) Å and 2.315(1) Å) differ only modestly from those

found in **4.5**. Although [**4.6**]$^+$OTf$^-$ itself is not chiral, this complex crystallized in a chiral

space group ($Pna2_1$); the final refined value for the absolute structure (Flack) parameter

(0.183(6)) indicated that the correct absolute configuration had been determined.[32,33] The

solution characterization of [**4.6**]$^+$OTf$^-$ is consistent with the solid state structure of this
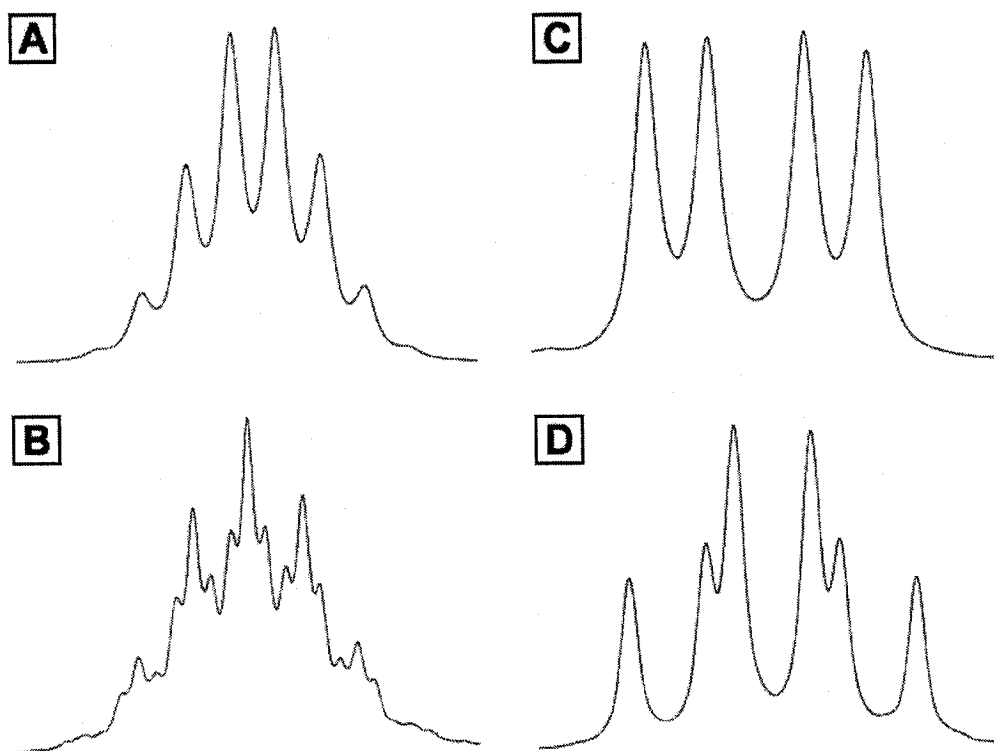
Figure 4.5 ^{1}H NMR spectra demonstrating the presence of virtual coupling in [**4.6**]$^+$
            OTf$^-$ as compared to **4.5**, which does not display such features. Shown
            are: A) ^{i}Pr CH resonance in **4.5**; B) ^{i}Pr CH resonance in [**4.6**]$^+$OTf$^-$,
            displaying virtual coupling; C) ^{i}Pr CH$_3$ resonance in **4.5**; and D) ^{i}Pr CH$_3$
            resonance in [**4.6**]$^+$OTf$^-$, displaying virtual coupling.

complex. Interestingly, virtual coupling to phosphorus is observed in the ^{1}H and ^{13}C{^{1}H}

NMR spectra of [4.6]$^+$OTf.[34] For example, whereas the ^{1}H NMR signal for each of the

diastereotopic methyl groups within the ^{i}Pr$_2$P fragments of 1.21 and 4.5 appears as a

doublet of *doublets*, similar signals in [4.6]$^+$OTf appear as a virtual *doublet* of *triplets* – a

result of coupling to both P-atoms that presumably is enabled by the linearity of the P-

Au-P unit in [4.6]$^+$OTf (see Figure 4.5).

4.2.2 Au(I)-Catalyzed Hydrosilylation of Aldehydes

The addition of Si-H bonds to carbonyl compounds provides a direct and atom-

economical route to synthetically useful silyl ethers.[35,36] While a diversity of carbonyl

hydrosilylation catalysts have been identified, Cu complexes supported by phosphine or

N-heterocyclic carbene ligands have proven particularly effective, and the development

of such catalysts continues to attract attention.[37-47] In contrast, only a single report for

each of Ag (see Chapter 5) and Au[6] documents the catalytic abilities of the heavier group

11 elements in hydrosilylation chemistry. With regard to the study of ligand effects in Au-

catalyzed hydrosilylations, Hosomi and co-workers noted that while catalysts comprised

of 3 mol% Ph$_3$PAuCl and X mol% Ph$_3$P (X = 0 or 20) were ineffective in mediating the

addition of Me$_2$PhSiH to benzaldehyde at 70 °C, a catalyst mixture comprised of 3 mol%

Ph$_3$PAuCl and 20 mol% ^{n}Bu$_3$P proved effective for the hydrosilylation of various aldehyde

substrates under similar conditions.[6] Building upon these preliminary observations, the

evaluation of the catalytic abilities of the new Au(I) complexes 4.1, 4.2, 4.3, 4.4a/4.4b,

4.5 and [4.6]$^+$ OTf reported herein, as well as those of Me$_2$SAuCl/L mixtures (L = 1,3-

diisopropyl-4,5-dimethylimidazol-2-ylidene or R$_3$P, R = Et, ^{n}Bu, ^{t}Bu, Cy, or Ph), in the

hydrosilyation of aldehydes (Scheme 4.5). For convenience, and due to the success of

previous catalysis in this medium (see Chapter 5),[6] THF was chosen as a solvent for all

transformations. Preliminary experiments were conducted using benzaldehyde and

Me_2PhSiH as substrates; the results of these studies are summarized in Table 4.1.
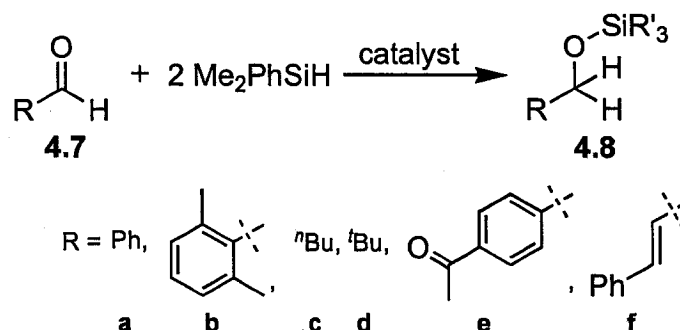
Scheme 4.5 Au(I) catalyzed hydrosilylation of aldehydes.

While the $(\kappa^1\text{-}P)$ complexes **4.1** and **4.2** were both moderately effective catalysts (see

Table 4.1, entries 1-1 and 1-5), complexes featuring $(\kappa^1\text{-}P,N)$ ligands (**4.3** and **4.4a/4.4b**)

proved significantly less successful (entries 1-7 and 1-9). Indeed, addition of two

equivalents of NEt_3 to a solution of **4.1** prior to catalysis was sufficient to render the

catalyst ineffective (entry 1-2). While it is premature to draw mechanistic conclusions

based on such an observation, it seems apparent that the presence of an amine or

amino functionality is detrimental to the Au metal center, possibly promoting

deactivation, as opposed to temporarily stabilizing coordinatively unsaturated reactive

intermediates as originally intended. In contrast, addition of one equivalent of the ligand

1.21 to a solution of **4.1** prior to catalysis resulted in only a slight decrease in yield (entry

1-3), relative to **4.1** by itself; identical numbers were obtained when the isolated

compound **4.5** (prepared from **4.1** and 1 equivalent of **1.21**) was employed. Interestingly,

the cationic complex $[4.6]^+$ OTf^- was also found to be ineffective as a catalyst, possibly

due to competitive coordination of solvent or substrate molecules to the presumably

more electrophilic metal center (entry 1-13).

Table 4.1   Au(I) catalyzed hydrosilylation of benzaldehyde with Me_2PhSiH at 70 °C.[a]

Entry	(mol%) catalyst	Time (h)	Yield **4.8a** (%)[b]	Yield Other (%)[b]	TOF (h^{-1})[c]
1-1	3% **4.1**[d]	24	50	2	< 1
1-2	3% **4.1** + 6% NEt_3[d]	24	1	< 1	< 1
1-3	3% **4.1** + 3% **1.21**[d]	24	42	< 1	1
1-4	3% **4.1** + 20% **1.21**[d]	12	99	1	4
1-5	3% **4.2**[d]	24	47	1	< 1
1-6	3% **4.2** + 20% **1.22**	24	4	< 1	2
1-7	3% **4.3**	24	< 1	< 1	< 1
1-8	3% **4.3** + 20% **1.19a**	24	7	4	< 1
1-9	3% **4.4a/4.4b**	24	5	< 1	< 1
1-10	3% **4.4a/4.4b** + 20% **1.20a**	24	31	1	5
1-11	3% **4.5**[d]	24	42	< 1	1
1-12	3% **4.5** + 20% **1.21**	12	99	1	4
1-13	3% **[4.6]**⁺ OTf⁻	24	< 1	< 1	< 1
1-14	3% **[4.6]**⁺ OTf⁻ + 20% **1.21**	24	52	1	1
1-15	3% Me_2SAuCl	3	27	< 1	3
1-16	3% Me_2SAuCl + 20% Et_3P[d,e]	3	97	< 1	51
1-17	3% Me_2SAuCl + 20% $^nBu_3P$[d]	3	98	2	40
1-18	3% Me_2SAuCl + 20% $^tBu_3P$	3	98	1	34
1-19	3% Me_2SAuCl + 20% Cy_3P	3	53	2	1
1-20	3% Me_2SAuCl + 20% Ph_3P[d]	3	2	< 1	3
1-21	3% Me_2SAuCl + 20% NHC	3	31	1	21
1-22	3% Ph_3PAuCl + 20% $^nBu_3P$	3	99	< 1	10

[a] Reactions conducted in THF at 70 °C with 2 equivalents of Me_2PhSiH relative to benzaldehyde (**4.7a**). [b] Yields quoted with respect to **4.7a** consumed at the time quoted based on GC-MS and GC-FID data (average of two runs). [c] Turnover frequency (TOF, h^{-1}) calculated at t = 0.25 h, based on the consumption of **4.7a**. [d] A precipitate of metallic gold was observed at the conclusion of the reaction. [e] Under these conditions, Ph_2SiH_2 (86 %, <3 % "double hydrosilylation" product), Et_3SiH (34 %) and $(EtO)_3SiH$ (7 %) all proved inferior to Me_2PhSiH.

In an attempt to provide added support to the Au center, and in keeping with the observations of Hosomi and co-workers,[6] this study of isolated $(\kappa^1\text{-}P,N)_2AuX$ (X = Cl, OTf) complexes was extended to compounds supported by excess ligand. While a slight increase in the effectiveness of $(\kappa^1\text{-}P,N)_2AuCl$ complexes **4.3** and **4.4a/4.4b** was noted on the addition of 20 mol% of the corresponding ligand (entries 1-8 and 1-10, relative to 1-7 and 1-9), as well as a decrease in the case of **4.2** (entry 1-6), addition of 20 mol% **1.21** to a solution of **4.1** had a profoundly beneficial effect (entry 1-4). Indeed, 99%

conversion was achieved in 12 h, with high selectivity, clearly distinguishing this catalyst system from its counterparts. Again, identical results were obtained using **4.5** in combination with 20 mol% **1.21** (entry 1-12). While an improvement in the performance of cationic complex [**4.6**]$^+$ OTf was observed when 20 mol% **1.21** was added (entry 1-14), the % conversion was not as high as that observed when 20 mol% of the appropriate ligand was added to **4.1** or **4.5**. It is possible that the addition of free ligand generates a catalytically more competent L_nAuCl (n ≥ 3) species, or that such an excess simply drives an equilibrium mixture away from less competent LAuCl species.

For convenience, Me_2SAuCl was employed as a source of "AuCl" instead of Ph_3PAuCl, though use of either species in combination with 20 mol% $^nBu_3P$ (entries 1-17 and 1-22) confirmed the results originally reported by Hosomi and co-workers.[6] As a control, Me_2SAuCl by itself was noted to catalyze the hydrosilylation of styrene with limited success (entry 1-15). Previous studies have shown that neither Et_3P (see Chapter 5) nor $^nBu_3P$[6] catalyzes this transformation in the absence of a metal catalyst. Cy_3P and the N-heterocyclic carbene 1,3-diisopropyl-4,5-dimethylimidazolyl-2-ylidene (NHC) provided a slight improvement over Me_2SAuCl alone (entries 1-19 and 1-21), while the addition of Ph_3P was noted to be detrimental to catalytic effectiveness (entry 1-20). In sharp contrast, both Et_3P and $^tBu_3P$ (entries 1-16 and 1-18) provided the desired product in high yield after 3 h. These findings suggest that Au-mediated catalysis is aided by a strongly donating phosphine, while cone angle appears to have little effect (Et_3P ~130° vs. $^tBu_3P$ ~180°).[48] While it is surprising that the strongly σ-donating NHC does not perform as well as the trialkylphosphines Et_3P, $^nBu_3P$ and $^tBu_3P$, studies involving other electron-releasing phosphines or carbenes may offer further insight. Notably, no

detectable trimerized benzaldehyde was observed, in contrast to observations made using an analogous Ag system (see Chapter 5).

Since the original report by Hosomi and co-workers of a 3 mol% Ph_3PAuCl/20 mol% $^nBu_3P$ catalyst system only highlighted reactions at 70 °C using the one phosphine ($^nBu_3P$), it was desirable to expand the scope of this reaction beyond a single temperature and phosphine. Thus, the catalyst species giving rise to > 95% conversion at 70 °C (3% **4.1** + 20% **1.21**; 3% Me_2SAuCl + 20% $Et_3P/^nBu_3P/^tBu_3P$) were examined for catalytic activity at 24 °C. While **4.1** did not accomplish the hydrosilylation of benzaldehyde to a reasonable extent under these conditions (Table 4.2, entry 2-1), use of any of the trialkylphosphines resulted in exceptional yield and selectivity (entries 2-2 to 2-4). A brief survey of aldehydes was undertaken. Little difference in either yield or selectivity is noted on switching to a 2,6-dimethylbenzaldehyde (**4.7b**, entries 2-5 to 2-7), though in the case of Et_3P, a drop of ~10 % may be attributed to the increased bulk of **4.7b** versus **4.7a** decreasing the rate of association to the catalyst. Conversion dropped dramatically when the alkyl aldehydes **4.7c** and **4.7d** were employed (entries 2-8 to 2-10 and 2-11 and 2-13, respectively). In the case of **4.7c**, lower yields were also accompanied by a lower selectivity, though aldehyde trimer was still not a significant contributor to product distribution. Remarkably, chemoselective hydrosilylation of both 4-acetylbenzaldehyde (**4.7e**) and *trans*-cinnamaldehyde (**4.7f**) was achieved in high yield at 24 °C (entries 2-14 to 2-16 and 2-17 to 2-19, respectively). Stryker's reagent ($[Ph_3PCuH]_6$) has proven to be effective at chemoselective hydrosilylation of aldehydes in the presence of ketones or alkenes,[44,49] though 1,4-conjugate addition to α,β-unsaturated aldehydes such as **4.7f** is observed, in contrast to the 1,2 (direct) addition observed herein; 1,4-addition is also observed when Wilkinson's catalyst (($Ph_3P)_3RhCl$)

is employed.[50] Selective, room temperature hydrosilylation has not been previously reported for Au systems of this type and despite prolonged reaction times relative to those conducted at 70 °C (24 h vs. 3 h), represents a significant advance.

Table 4.2   Au(I) catalyzed hydrosilylation of aldehydes with Me_2PhSiH at 24 °C.[a]

Entry	(mol%) catalyst	Aldehyde	Yield 4.8 (%)[b]	Yield Other (%)[b]	TOF (h^{-1})[c]
2-1	3% **4.1** + 20% **1.21**	**4.7a**	3	1	1
2-2	3% Me_2SAuCl + 20% Et_3P	**4.7a**	99	< 1	10
2-3	3% Me_2SAuCl + 20% $^nBu_3P$	**4.7a**	98	1	9
2-4	3% Me_2SAuCl + 20% $^tBu_3P$	**4.7a**	99	1	9
2-5	3% Me_2SAuCl + 20% Et_3P	**4.7b**	88	1	2
2-6	3% Me_2SAuCl + 20% $^nBu_3P$	**4.7b**	98	2	3
2-7	3% Me_2SAuCl + 20% $^tBu_3P$	**4.7b**	97	2	3
2-8	3% Me_2SAuCl + 20% Et_3P	**4.7c**	74	4	3
2-9	3% Me_2SAuCl + 20% $^nBu_3P$	**4.7c**	85	7	8
2-10	3% Me_2SAuCl + 20% $^tBu_3P$	**4.7c**	85	5	7
2-11	3% Me_2SAuCl + 20% Et_3P	**4.7d**	45	< 1	1
2-12	3% Me_2SAuCl + 20% $^nBu_3P$	**4.7d**	79	3	2
2-13	3% Me_2SAuCl + 20% $^tBu_3P$	**4.7d**	78	2	2
2-14	3% Me_2SAuCl + 20% Et_3P	**4.7e**	> 99	< 1	69
2-15	3% Me_2SAuCl + 20% $^nBu_3P$	**4.7e**	98	2	42
2-16	3% Me_2SAuCl + 20% $^tBu_3P$	**4.7e**	98	2	54
2-17	3% Me_2SAuCl + 20% Et_3P	**4.7f**	97	< 1	29
2-18	3% Me_2SAuCl + 20% $^nBu_3P$	**4.7f**	97	2	19
2-19	3% Me_2SAuCl + 20% $^tBu_3P$	**4.7f**	90	3	16

[a] Reactions conducted in THF at 24 °C with 2 equiv. Me_2PhSiH relative to aldehyde (**4.7**). [b] Yields quoted with respect to **4.7** consumed at 24 h based on GC-MS and GC-FID data (average of two runs). [c] Turnover frequency (TOF, h^{-1}) calculated at t = 0.25 h, based on the consumption of **4.7**.

While the mechanism by which the hydrosilylation of aldehydes occurs remains unclear, it is possible that a process such as that outlined in Scheme 4.6 occurs. Reaction of the precursor Au(I) species with Me_2PhSiH would generate a gold hydride active catalyst, which subsequently coordinates and reduces the carbonyl functionality. The activation of C-H by a Au(I) catalyst to generate an active Au-H intermediate has been proposed to be a key step in several recently reported reactions.[51-55] Lipshutz and co-workers have also proposed that related processes mediated by "CuH" proceed via a

similar route to give a copper alkoxide intermediate, similar to the gold alkoxide

proposed below.[43,44] While the process by which the carbonyl functionality is reduced

remains unclear, it likely involves insertion of the aldehyde into the Au-H bond without a

formal oxidation to a Au(III) intermediate. Further studies directed at identifying reactive

intermediates and the active catalyst involved in these transformations are warranted,

and should be a focus of related future work.
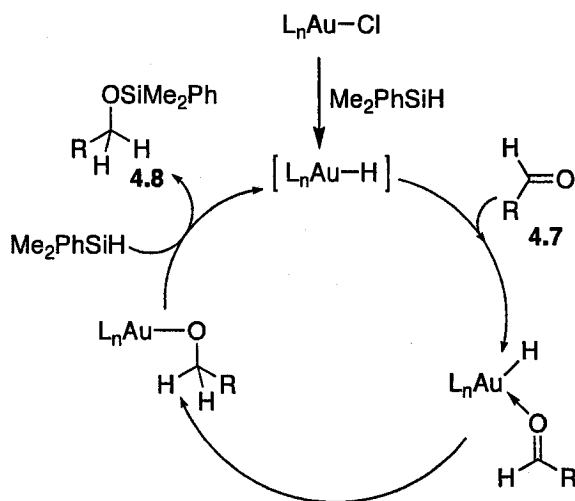
Scheme 4.6 Proposed mechanism for the Au(I) catalyzed hydrosilylation of aldehydes.

4.3 Conclusion

In summary, a series of new Au(I) complexes featuring κ^1-3-R_2P-indene (R = ^{i}Pr

(**1.21**), Ph (**1.22**)) and κ^1-1-R_2P-2-NMe$_2$-indene (R = ^{i}Pr (**1.19**), Ph (**1.20**)) ligands were

prepared and structurally characterized. The structural features of the resultant

complexes are in keeping with those observed in previously reported complexes, though

few such related complexes have been reported. Indeed, **4.5** represents the first

crystallographically characterized monomeric P_2AuCl complex. In the case of [**4.6**]$^+$ OTf$^-$,

a textbook example of virtual coupling was observed. Evaluation of the ability of these

Au(I) complexes to catalyze the hydrosilylation of benzaldehyde revealed that the P,N

ligands **1.19** and **1.20** proved inferior to the P ligands **1.21** and **1.22**, and that the

presence of 20 mol% ligand led to a more active system. This last finding prompted

extension of this study to investigate other ligands. The alkyl phosphines Et_3P, $^nBu_3P$ and

$^iBu_3P$ proved most effective, maintaining high conversion and selectivity at both 70 °C (3

h) and 24 °C (24 h). This is exemplified by the facile chemoselective hydrosilylation of 4-

acetylbenzaldehyde (**4.7e**) and *trans*-cinnamaldehyde (**4.7f**) at 24 °C. These findings

underscore the importance of mapping the potential of Au(I) complexes to mediate such

transformations in a selective fashion under mild conditions. While catalysis by colloidal

species resulting from the reduction of Au(I) precursors cannot be ruled out on the basis

of these findings, the undeniable presence of a ligand effect, as well as the similarity to

related proposed mechanisms for other Au and Cu systems lends credence to a

homogeneous mechanism.

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Chapter 5 – Silver Catalyzed Hydrosilylation of Aldehydes

5.1   Introduction

The metal-catalyzed hydrosilylation of carbonyl compounds is an atom-economical methodology that provides direct access to synthetically useful silyl ethers.[1] In addition to the diversity of transition metal catalysts for carbonyl hydrosilylation that have been identified over the past three decades, including those based on Ti,[2-4] Ru,[5] and Rh,[6-10] effective group 11 catalysts have also emerged. The groups of Stryker,[11] Lipshutz,[12-16] Nolan,[17,18] and others have demonstrated that Cu complexes featuring either phosphine or *N*-heterocyclic carbene (NHC) ligands can function as active and selective catalysts for carbonyl hydrosilylations, while a single report by Hosomi and co-workers highlights the catalytic utility of Au species for such transformations.[19] In contrast, reports focused on the application of Ag species as hydrosilylation catalysts are absent from the literature. Indeed, Ag salts are often viewed as being catalytically inactive in hydrosilylation chemistry, and in this context are commonly employed as innocent anion exchange agents for the in situ generation of cationic transition (and other) metal catalysts. In a report pertaining to carbonyl hydrosilylations catalyzed by (pybox)RhCl₃/AgX (pybox = pyridine bis-oxazoline), the ability of unligated AgX salts to mediate such transformations to a limited extent is mentioned briefly in a footnote; pybox/AgX mixtures did not exhibit any catalytic activity.[20]

Inspired by recent reports from the groups of He,[21,22] and Li,[23-26] in which Ag complexes have been shown to mediate the addition of σ-bonds to unsaturated organic molecules (see section 1.7), the evaluation of the catalytic utility of Ag species in carbonyl hydrosilylations, including examining the influence of supporting ligands on

such Ag-mediated transformations became an interest. Herein is reported the Ag-catalyzed chemoselective addition of silanes to aldehydes, which represents the first systematic application of Ag species as catalysts for the hydrosilylation of unsaturated organic compounds.

5.2   Results and Discussion

5.2.1   Hydrosilylation of Benzaldehyde Catalyzed by Ag Salts

The hydrosilylation of benzaldehyde (**5.1a**) with Me_2PhSiH to give the silyl ether **5.2a** was selected as a preliminary test reaction for Ag-mediated carbonyl hydrosilylations (Scheme 5.1). While reactions conducted in THF at 24 °C employing 3 mol% $AgSbF_6$ generated the benzaldehyde trimer (**5.3a**) in 97% yield after 15 minutes (Table 5.1, entry 1-1), under analogous conditions employing 3 mol% AgOTf, **5.2a** was obtained in 94% yield, along with only 6% of **5.3a** (entry 1-2). Similar results were obtained for reactions conducted at 70 °C using 3 mol% AgOTf. Although the initial rates and overall reaction rates were lowered considerably upon the addition of 20 mol% Et_3P to 3 mol% AgOTf (see Table 5.1, entry 1-3 TOF value), the use of this catalyst mixture enabled the clean formation of **5.2a** in 98% yield after 24 h at 70 °C, in the absence of **5.3a** or other by-products. By comparison, reactions employing 3 mol% Me_3SiOTf at 70 °C afforded **5.3a** quantitatively, while no reaction was observed when a Et_3P/Me_3SiOTf catalyst system was used at 70 °C (entries 1-4 and 1-5, respectively). Control experiments showed that no catalysis was observed when 20% Et_3P alone was employed. Moreover, though the experiments described herein were conducted using 99+ % purity AgOTf (Aldrich), no change in catalytic behavior was noted for reactions employing 99.95+ % purity AgOTf (Aldrich) that was found to contain only the following

trace elements by ICP analysis (ppm): Na (13.5), Ca (1.6), B (0.8), Mg (0.3), Zn (0.1), Sb (0.1).
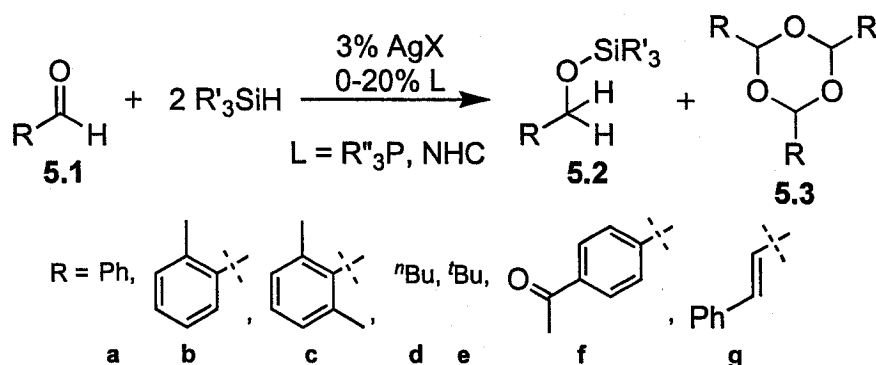
Scheme 5.1 Ag catalyzed addition of silanes to aldehydes.

The conversion of **5.1a** to **5.2a** mediated by Et_3P/AgX mixtures was found to vary based on the counteranion employed, with catalysts derived from AgCl (Table 5.1, entry 1-6, 57%) proving inferior to those based on AgOTf (98%), $AgBF_4$ (entry 1-7, 93%), or $AgSbF_6$ (entry 1-8, 95%). For convenience, AgOTf was used for all subsequent catalytic investigations. The observation that a $R_3P/AgCl$ mixture is capable of mediating such transformations is noteworthy, given that AgCl elimination in the presence of excess phosphine is often exploited during the in situ preparation of cationic metal catalysts for carbonyl hydrosilylations. The choice of solvent was also found to have an impact on the ability of $Et_3P/AgOTf$ mixtures to mediate this transformation at 70 °C. While the yield of **5.2a** obtained in THF was reduced modestly in changing the reaction medium to toluene (entry 1-9, 91%) or DMSO (entry 1-10, 93%), a lower yield was achieved on going to 1,2-dichloroethane (entry 1-11, 36%). A drop in the yield of **5.2a** was also noted for reactions catalyzed by $Et_3P/AgOTf$ in THF, either upon lowering the reaction temperature from 70 °C to 50 °C (entry 1-12, 89%), or upon reducing the Et_3P from 20 mol% to 10 mol% (entry 1-13, 25%). Other tertiary silanes, such as Et_3SiH (entries 1-14 and 1-15) and $(EtO)_3SiH$ (entries 1-18 and 1-19), as well as the secondary silane Ph_2SiH_2 (entries 1-16

and 1-17), proved to be less effective than Me_2PhSiH in mediating this transformation; as such, Me_2PhSiH was used for the remainder of this study.

Table 5.1   Ag catalyzed hydrosilylation of benzaldehyde with Me_2PhSiH.[a]

Entry	Catalyst (mol%)	Solvent	Temp. (°C)	Yield 5.2a (%)[b]	Yield 5.3a (%)[b]	Yield other (%)[b]	TOF (h⁻¹)[c]
1-1	3% $AgSbF_6$[d]	THF	24	< 1	97	3	133
1-2	3% $AgOTf$[d]	THF	24	94	6	< 1	133
1-3	20% Et_3P / 3% $AgOTf$	THF	70	98	< 1	< 1	29
1-4	3% Me_3SiOTf	THF	70	< 1	> 99	< 1	133
1-5	20% Et_3P / 3% Me_3SiOTf	THF	70	< 1	< 1	< 1	< 1
1-6	20% Et_3P / 3% $AgCl$	THF	70	57	< 1	< 1	1
1-7	20% Et_3P / 3% $AgBF_4$[d]	THF	70	93	< 1	< 1	7
1-8	20% Et_3P / 3% $AgSbF_6$	THF	70	95	< 1	< 1	41
1-9	20% Et_3P / 3% $AgOTf$	toluene	70	91	< 1	< 1	4
1-10	20% Et_3P / 3% $AgOTf$[d]	DMSO	70	93	< 1	< 1	51
1-11	20% Et_3P / 3% $AgOTf$	DCE[e]	70	36	< 1	< 1	< 1
1-12	20% Et_3P / 3% $AgOTf$	THF	50	89	< 1	< 1	17
1-13	10% Et_3P / 3% $AgOTf$	THF	70	25	< 1	< 1	< 1
1-14	3% $AgOTf$[f]	THF	24	< 1	85	15	124
1-15	20% Et_3P / 3% $AgOTf$[f]	THF	70	59	< 1	2	1
1-16	3% $AgOTf$[g]	THF	24	17	< 1	83	133
1-17	20% Et_3P / 3% $AgOTf$[g]	THF	70	25	< 1	9	43
1-18	3% $AgOTf$[h]	THF	24	78	< 1	16	93
1-19	20% Et_3P / 3% $AgOTf$[h]	THF	70	< 1	< 1	< 1	2

[a] Reactions run for 24 h employing two equivalents of Me_2PhSiH (or other hydrosilane, where noted) with respect to benzaldehyde (**5.1a**), with the exception of entries 1-1, 1-2, 1-4, 1-22, and 1-24, where the yield is quoted after 0.25 h. [b] Yields are quoted with respect to **5.1a** consumed, and are based on GC-MS and GC-FID data (average of two runs). [c] Turnover frequency (TOF) reported at 0.25 h, based on the consumption of **5.1a** relative to AgX employed. [d] A precipitate of Ag metal was noted to form during the course of the reaction. [e] DCE = 1,2-dichloroethane. [f] Two equivalents of Et_3SiH were used in place of Me_2PhSiH. [g] Two equivalents of Ph_2SiH_2 were used in place of Me_2PhSiH, with the double hydrosilylation product $Ph_2Si(OCH_2Ph)_2$ constituting <1% of the converted **5.1a**. [h] Two equivalents of $(EtO)_3SiH$ were used in place of Me_2PhSiH.

Intrigued by these preliminary catalytic results, the effectiveness of alternative

ligands was explored. Given the exceptional selectivity exhibited by the catalyst system

derived from a combination of excess Et_3P relative to AgOTf (20:3), it was anticipated

that the structurally related bidentate ligand 1,2-bis(diethylphosphino)ethane (DEPE)

might give rise to an even more effective catalyst system. Surprisingly, catalysts derived

from the combination of either 10 or 20 mol% DEPE with 3 mol% AgOTf afforded

significantly lower yields of **5.2a** (Table 5.2, entries 2-1 and 2-2, 45% and 68%,

respectively) than were obtained in analogous reactions employing 20 mol% Et_3P (98%).

Table 5.2   L/AgOTf catalyzed hydrosilylation of benzaldehyde with Me_2PhSiH.[a]

Entry	Catalyst (mol%)	Yield 5.2a (%)[b]	Yield 5.3a (%)[b]	Yield other (%)[b]	TOF (h⁻¹)[c]
2-1	10% DEPE / 3% AgOTf[e]	45	< 1	< 1	< 1
2-2	20% DEPE / 3% AgOTf[e]	68	< 1	< 1	< 1
2-3	20% $^nBu_3P$ / 3% AgOTf[d]	95	< 1	< 1	21
2-4	20% Cy_3P / 3% AgOTf	13	< 1	< 1	< 1
2-5	20% $^iPr_3P$ / 3% AgOTf[d]	21	< 1	< 1	< 1
2-6	20% $^tBu_3P$ / 3% AgOTf	51	< 1	< 1	29
2-7	20% Ph_3P / 3% AgOTf	3	9	< 1	< 1
2-8	20% NHC / 3% AgOTf[d,e]	94	< 1	4	82

[a] Reactions run for 24 h in THF solution at 70 °C employing two equivalents of Me_2PhSiH (except where noted) with respect to benzaldehyde (**5.1a**). [b] Yields are quoted with respect to **5.1a** consumed, and are based on GC-MS and GC-FID data (average of two runs). [c] Turnover frequency (TOF) reported at 0.25 h, based on the consumption of **5.1a** relative to AgX employed. [d] A precipitate of Ag metal was noted to form during the course of the reaction. [e] DEPE = 1,2-bis(diethylphosphino)ethane; NHC = 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene.

Though detailed mechanistic conclusions are not merited solely on the basis of

such an observation, it appears likely that one of three scenarios is leading to poor

catalyst performance. Firstly, the DEPE ligands may serve to bridge rather than chelate

in this system, thereby generating what may be catalytically less-competent oligomeric

structures (silver is known to self-assemble in the presence of appropriate ligation).[27]

Secondly, it is possible that a chelate complex is being formed, and that a related bis-phosphine architecture was not the predominant catalyst when Et_3P was employed. In such a case, the preferential formation of a bis-phosphine complex would detract from the activity previously observed when mono- or multi-phosphine species were generated using Et_3P. The last likely explanation for poorer performance when DEPE was employed in place of Et_3P is that though a bis-phosphine complex may be the most active, the natural bite angle of DEPE ($\sim$78 °)[28] is too severe for the favored geometry about the silver center.

In returning the focus to mono-phosphines, the use of 20 mol% $^nBu_3P$ afforded an Ag-catalyst system that provided cleanly a yield of **5.2a** (Table 5.2, entry 2-3, 95%) comparable to that obtained by use of 20 mol% Et_3P (see Table 5.1). In contrast, the combination of 3 mol% AgOTf and 20 mol% of one of the more sterically hindered branched trialkylphosphines Cy_3P (entry 2-4, 13%), $^iPr_3P$ (entry 2-5, 21%), or $^tBu_3P$ (entry 2-6, 51%), or the triarylphosphine Ph_3P (entry 2-7, 3%), afforded significantly lower yields of **5.2a**. To test the generality of ligation with a strong σ-donor, 20 mol% of the N-heterocyclic carbene 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene (NHC) was used successfully in place of PR_3, giving **5.2a** in 94% yield (entry 2-8).

5.2.2 Hydrosilylation of Aldehydes Catalyzed by AgOTf

Using favorable conditions identified from the reactivity survey involving **5.1a** (3 mol% AgOTf, 20 mol% Et_3P, Me_2PhSiH, THF, 70 °C), the generality of the Ag-catalyzed hydrosilylation of aldehydes was investigated. Whereas ortho-tolualdehyde (**5.1b**) was reduced to **5.2b** in 94% yield (Table 5.3, entry 3-1a), lower conversions were obtained for the reduction of the more sterically hindered 2,6-dimethylbenzaldehyde **5.1c** (entry 3-2a,

76%). Much faster reaction rates under more mild conditions were observed when 3 mol% AgOTf alone was employed as a catalyst for these transformations. However, significantly poorer selectivity for the desired hydrosilylation product **5.2** was obtained (entries 3-1b and 3-2b). The aliphatic aldehydes **5.1d** and **5.1e** were also reduced more efficiently by use of Et_3P/AgOTf catalyst mixtures (entries 3-3a and 3-4a) versus AgOTf alone (entries 3-3b and 3-4b). When triethylphosphine was employed in the reduction of **5.1d** (the only aldehyde employed that may form an enol tautomer), products derived from aldol condensation processes represented less than 3% of the consumed aldehyde.

Table 5.3 Et_3P/AgOTf catalyzed hydrosilylation of aldehydes with Me_2PhSiH.[a]

Entry	Aldehyde	% Et_3P	Yield 5.2 (%)[b]	Yield 5.3 (%)[b]	Yield other (%)[b]	TOF (h^{-1})[c]
3-1a	**5.1b**	20	94	< 1	1	49
3-1b	**5.1b**	0	88	< 1	2	121
3-2a	**5.1c**	20	76	< 1	1	< 1
3-2b	**5.1c**	0	50	< 1	40	121
3-3a	**5.1d**	20	86	1	12	1
3-3b	**5.1d**	0	9	58	20	117
3-4a	**5.1e**	20	48	< 1	6	1
3-4b	**5.1e**	0	7	< 1	1	11
3-5a	**5.1f**	20	> 99	< 1	< 1	37
3-5b	**5.1f**	0	62	< 1	24	114
3-6a	**5.1g**	20	99	< 1	1	37
3-6b	**5.1g**	0	48	< 1	17	87

[a] Reactions employing 20 mol% Et_3P were run for 24 h at 70 °C in THF, while those using no Et_3P were run for 0.25 h at 24 °C. All reactions employed two equivalents of Me_2PhSiH and 3 mol% AgOTf with respect to aldehyde (**5.1**). For all reactions conducted in the absence of Et_3P, the introduction of the hydrosilane resulted in rapid change of the solution color from colorless to yellow, followed by the immediate precipitation of Ag metal. [b] Yields are quoted with respect to **5.1** consumed, and are based on GC-MS and GC-FID data (average of two runs). [c] Turnover frequency (TOF) reported at 0.25 h, based on the consumption of **5.1** relative to AgOTf employed.

In an effort to assess the chemoselectivity of Ag-mediated aldehyde

hydrosilylation in the presence of either ketone or alkene functionalities, the reduction of

4-acetylbenzaldehyde (**5.1f**) and *trans*-cinnamaldehyde (**5.1g**) was examined. Whereas

a mixture of products was obtained by using AgOTf as a catalyst (entries 3-5b and 3-6b),

both substrates were reduced cleanly by use of a Et_3P/AgOTf catalyst system, with 1,2

Si-H addition occurring exclusively at the aldehyde (entries 3-5a and 3-6a). The identities

of **5.2g** and **5.2f** were confirmed on the basis of NMR studies, in which the persistence of

signals corresponding to the ketone and alkene moieties established chemoselectivity.

Notably, $(Ph_3PCuH)_6$ (Stryker's reagent) has also proven effective for the chemoselective

hydrosilylation of aldehydes in the presence of ketones and alkenes.[13] However, this Cu

catalyst,[29] like $(Ph_3P)_3RhCl$ (Wilkinson's catalyst),[30] has been shown to mediate the 1,4-

conjugate hydrosilylation of α,β-unsaturated aldehydes, in contrast to the 1,2-addition

brought about by the Et_3P/AgOTf catalyst system described herein for the hydrosilylation

of **5.1g**. In a series of control experiments, it was found that Et_3P/AgOTf did not catalyze

the hydrosilylation of either styrene or acetophenone under the conditions employed

herein.

5.2.3 Characterization of Ag Species Present in Solution

Though there is some uncertainty as to whether the Ag-catalyzed hydrosilylation

reactions detailed above are homogeneous or heterogeneous in nature, the identification

of $Me_2PhSiOTf$ as a by-product in these reactions suggests the possible intermediacy of

AgH species (see Scheme 5.2). It is unlikely that $Me_2PhSiOTf$ is responsible for the

observed reduction chemistry, given the distinct lack of hydrosilylation observed when

Me_3SiOTf is employed in place of AgOTf, in the presence or absence of Et_3P (vide

supra). Association of the aldehyde to a AgH species, followed by 1,2-insertion might

generate a silver alkoxide, which can be attacked by another molecule of hydrosilane to yield the desired product, regenerate the L_nAgH species, and complete the catalytic cycle. While this mechanism remains largely speculative, it is supported by similarities to mechanisms proposed for related copper systems,[13,15-18,31] as well as that proposed in Chapter 4. Speculation that a silver species, and not an unidentified minor impurity, is the active catalyst is also supported by the similarity of results obtained using AgOTf of various purity, as described above in section 5.2.1. While $(R_3P)_nAgSiR'_3$ species are known and may represent important reactive intermediates,[32,33] they are not invoked in this proposed cycle. Studies were undertaken to characterize the silver species present in solution under reaction conditions.
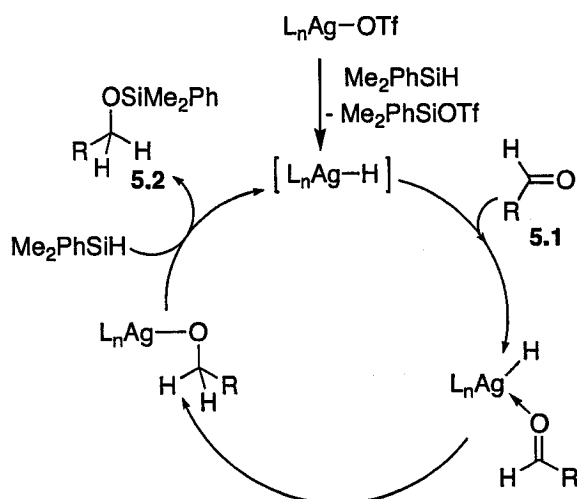
Scheme 5.2 Proposed mechanism for the Ag catalyzed hydrosilylation of aldehydes.

While ESI-MS has received much attention as a tool for structural elucidation,[34] less attention has been paid to its use with metal-containing molecules. However, recent studies have marked an increase in the role of ESI-MS as a tool for characterization of organometallic complexes in solution,[35-37] with one literature report in which ligated silver has been studied.[38] A solution similar in composition to the reaction conditions used for

catalysis studies above was analyzed by use of ESI-MS in positive ion mode. Though

the ratio of AgOTf to Et_3P was kept at 3:20, solutions were prepared using CH_2Cl_2 as a

solvent instead of THF, to ensure compatibility with the instrumentation. Solutions were

diluted to approximately 5×10^{-5} M, or about 1/1000th the concentration employed for

catalysis. Runs using both CH_2Cl_2 and MeCN as flow solvents were conducted, and will

be described presently. Assignment of peaks was supported by evidence gathered from

ESI-MS-MS (tandem) data gathered throughout the runs.
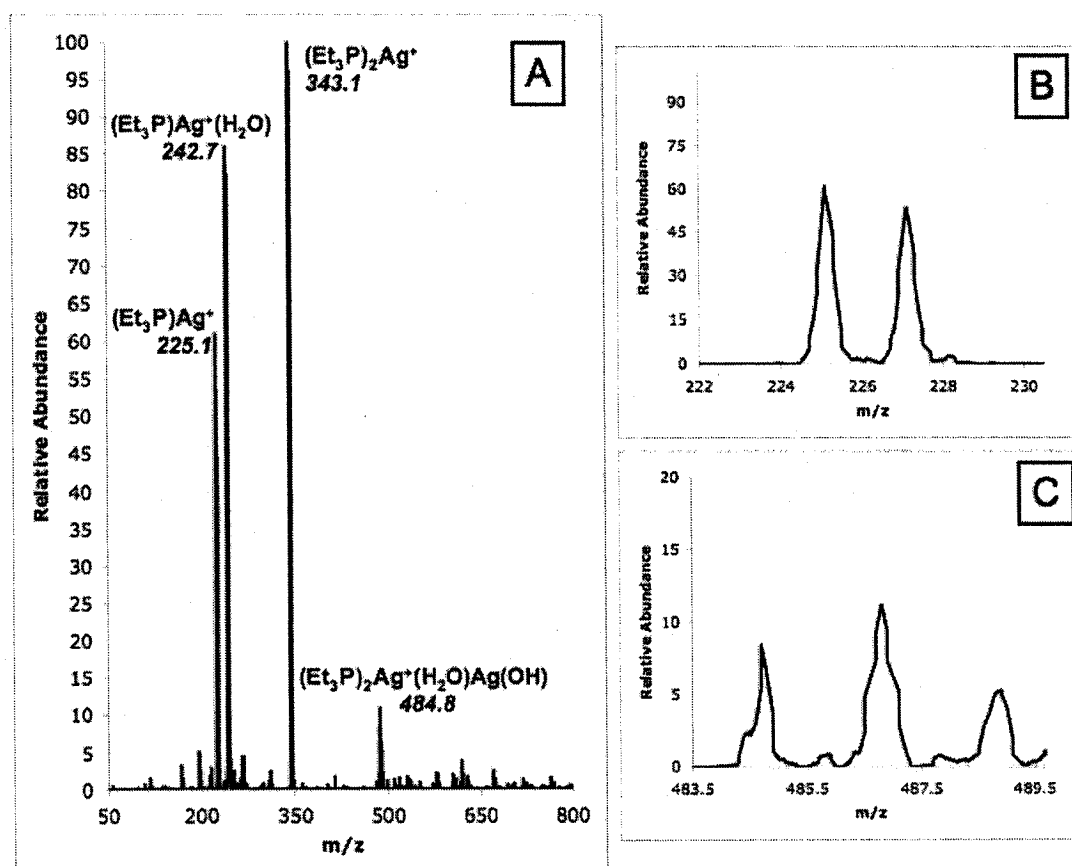
Figure 5.1   Positive mode ESI mass spectrometry data from a solution of 3:20 AgOTf and Et_3P in CH_2Cl_2. Shown are: A) Full spectrum with m/z of isotopologue containing only ^{107}Ag, and peak assignments; B) Expansion of m/z 225.1 demonstrating an isotope pattern consistent with one silver atom; and C) Expansion of m/z 484.8 demonstrating an isotope pattern consistent with two silver atoms.

There are two naturally occurring isotopes of silver; 107 and 109, with natural abundances of 51.8 and 48.2 %, respectively. As such, one would predict that species containing one silver atom would exhibit an isotope pattern showing two peaks separated by two mass units, where the lighter mass to charge peak is slightly higher in intensity. Similarly, for a species containing two silver atoms, the expected isotope pattern is derived from a statistical distribution of binary isotope pairs. Compounds featuring isotopes 107/107, 107/109 and 109/109 would occur in a 1:2:1 ratio, with the intensities of peaks observed by the MS experiment varying moderately to the lighter mass due to the slightly more abundant ^{107}Ag. Using a solution of 3:20 AgOTf and Et$_3$P in CH$_2$Cl$_2$, with CH$_2$Cl$_2$ as the flow solvent, four peaks dominated the spectrum (see Figure 5.1A). Peaks at mass-to-charge ratios (for species containing only the ^{107}Ag isotope) of 225.1, 242.7 and 343.1 were readily assigned to species containing only one silver atom, on the basis of the observed isotope pattern (see Figure 5.1B). Similarly, the peak at mass-to-charge ratio 484.8 exhibited an isotope pattern of roughly 1:2:1 relative intensity, suggested the presence of two silver atoms (see Figure 5.1C).

On the basis of these data, peaks at 225.1, 242.7, 343.1 and 484.8 were tentatively assigned to (Et$_3$P)Ag$^+$, (Et$_3$P)Ag$^+$(H$_2$O), (Et$_3$P)$_2$Ag$^+$ and (Et$_3$P)$_2$Ag$^+$(H$_2$O)AgOH, respectively. To confirm these assignments and establish any interconnectivity between these species, ESI-MS-MS was conducted. When mass-to-charge 484.8 was fragmented, a large peak for 343.1 was observed. In turn, when 343.1 was fragmented, peaks for both 242.7 and 225.1 were noted. This implies that 242.7 (assigned to (Et$_3$P)Ag$^+$(H$_2$O)) is forming as a result of water coordination inside the fragmentation chamber, rather than entering as a discrete species. This assertion is further supported by fragmentation of the peak at 225.1, which in addition to producing a peak corresponding to protonated Et$_3$P (mass to charge 119.1), also gives rise to the

proposed water adduct with a mass to charge ratio of 242.7. These observations are summarized schematically in Figure 5.2.

$$(Et_3P)_2Ag^+(H_2O)Ag(OH) \dashrightarrow (Et_3P)_2Ag^+ \dashrightarrow \begin{array}{c} (Et_3P)Ag^+ \dashrightarrow [(Et_3P)+H]^+ \\ 225.1 \qquad\qquad 119.1 \\ \\ (Et_3P)Ag^+(H_2O) \\ 242.7 \end{array}$$

$$484.8 \qquad\qquad 343.1$$
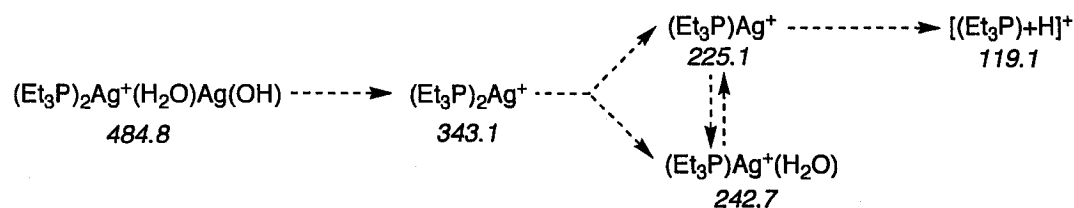
Figure 5.2   Proposed fragmentation pathway for ESI-MS experiment.

When similar experiments were conducted using MeCN as the flow solvent instead of CH_2Cl_2, differences were noted in the spectrum. Though all four major peaks observed with CH_2Cl_2 flow solvent were noted to occur in roughly the same proportions, the spectrum was dominated by a set of peaks at mass-to-charge ratio (for species containing only the ^{107}Ag isotope) of 265.8. This peak is assigned to an adduct of the formula $(Et_3P)Ag^+(MeCN)$. Implications of this observation are that the Et_3P ligands are labile, and that strongly coordinating solvents may play an important role in ligation of the silver center. Peaks corresponding to a compound of the formula $(MeCN)_2Ag^+$ were not observed, suggesting that the presence of at least one trialkylphosphine ligand is required to impart stability to the resultant complex.

As a complementary study, $^{31}P\{^1H\}$ and $^{109}Ag\{^1H\}$ NMR experiments were conducted on THF solutions of approximately the same concentration and composition as those employed for catalysis. For $^{31}P\{^1H\}$ NMR studies, a solution of 3:20 AgOTf and Et_3P in THF (~0.5 M in Ag) at 300 K gave rise to a sharp singlet at $\delta = -17.8$. Ag coupling was not noted, and indeed, to a first approximation, appeared much the same as Et_3P alone at the same concentration in THF solution ($\delta = -18.4$). Upon cooling the sample to 200 K, three small singlets at $\delta = 56.3$, 47.8 and 35.8 were observed, in addition to a

large sharp singlet at δ = -15.9 (see Figure 5.3). Slow warming of this sample led to a

reduction in intensity of the three new peaks relative to the large upfield singlet, without

coalescence. The process was found to be reversible, though no silver coupling was

observed throughout the experiment. This implies that the system is undergoing rapid

exchange of bound and free triethylphosphine, as has been observed for similar

silver/R_3P systems.[39-42] Moreover, the appearance of three distinct resonances that do

not appear to couple to one another suggests the presence of several AgOTf/Et_3P

adducts in the solution phase, or at a minimum, a complex in which Et_3P inhabits several

unique environments.
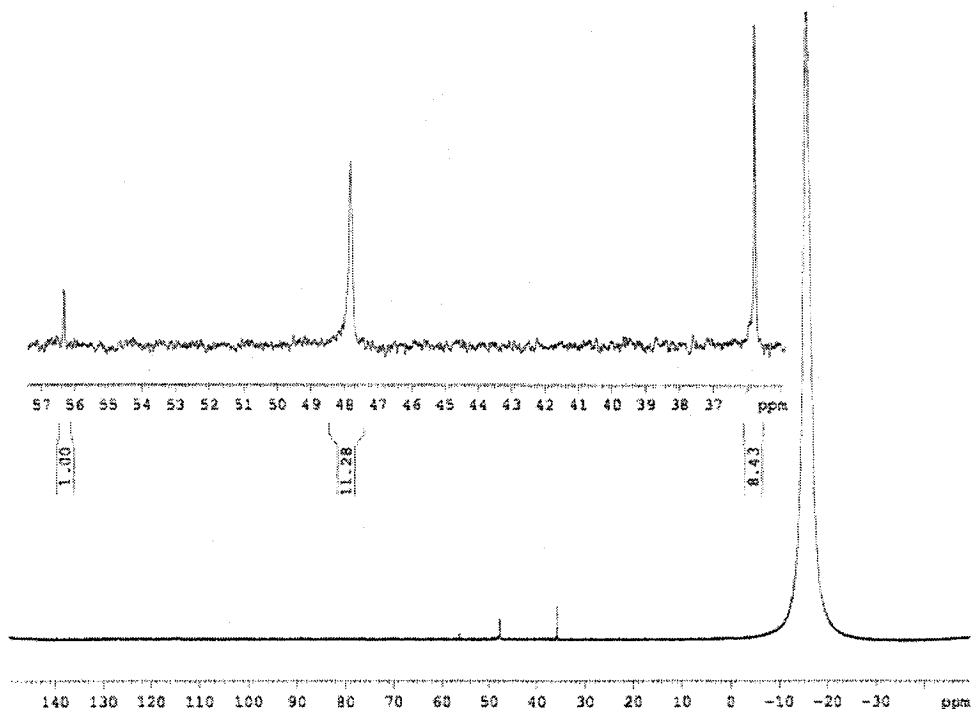
Figure 5.3 $^{31}P\{^1H\}$ NMR spectrum of a mixture of AgOTf and Et_3P (3:20, ~0.5 M in Ag) in THF solution at 200 K, with expansion of the region from δ = 57 to 35 shown.

Though the signals arising from both ^{109}Ag and ^{107}Ag are extremely difficult to

detect, ^{109}Ag$\{^1H\}$ NMR has been used to some extent in the characterization of

homogeneous Ag complexes.[39-41,43-48] [109]Ag{^{1}H} NMR studies were also undertaken in an

attempt to elucidate the nature of the silver-containing species under catalytic conditions.

When a solution of the same composition and concentration as that employed in the

[31]P{[1]H} studies was examined at 300 K, a sharp singlet at δ = 1309 was noted in the

[109]Ag{^{1}H} NMR spectrum (see Figure 5.4). Notably, this peak was resolved after

relatively few (~100) scans using a short relaxation time of 5 seconds. Upon lengthening

the relaxation time to 20 seconds, no change was noted, despite prolonged acquisition

(>2500 scans); no other signals were observed between δ = 2125 and -875. Upon

cooling the system to 200 K, a sharp singlet was noted at δ = 1488, though despite this

temperature-related change in chemical shift, no other differences from the room

temperature spectrum were noted. When a sample containing AgOTf only (~0.5 M, in
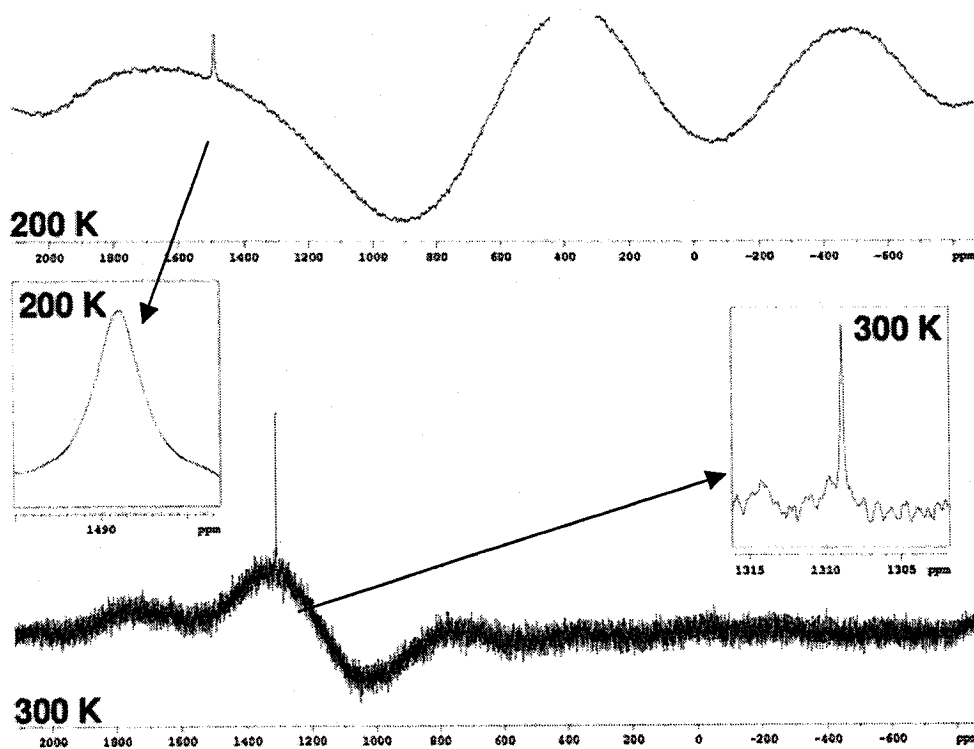
Figure 5.4   [109]Ag{^{1}H} NMR spectra of a mixture of AgOTf and Et$_3$P (3:20, ~0.5 M in
Ag) in THF solution at 200 and 300 K, with expansions of peaks shown.

THF) was run at 300 K, no peaks were resolved. The reason behind the lack of signal is unclear at this time, though ^{109}Ag{^{1}H} NMR signals are notoriously difficult to detect. The appearance of a singlet in the ^{109}Ag{^{1}H} NMR spectrum, as opposed to the expected doublet or triplet from coupling to either one or two ^{31}P nuclei is in keeping with the observed singlets in the ^{31}P{^{1}H} spectrum at low temperature. While a lone singlet in the ^{109}Ag{^{1}H} NMR would suggest that all silver atoms in the sample conform to a single chemical environment, it is likely that peaks for less-abundant species in solution were not observed due to the low sensitivity of the ^{109}Ag nucleus (~5 x 10^{-5} relative to ^{1}H), and/or reduced signal intensity due to dynamic exchange.[49]

5.3   Conclusion

Presented above is the first systematic evaluation of silver-catalyzed hydrosilylation of an unsaturated organic molecule. While AgOTf is itself capable of catalyzing the reduction of simple aldehydes (i.e. benzaldehyde) by hydrosilanes under mild conditions in an exceptionally efficient fashion, it is less effective for other substrates. In contrast, though a mixture of trialkylphosphine and AgOTf was found to be a much slower catalyst system, both simple and more complex aldehydes were successfully reduced in high yield in the presence of a hydrosilane. Chemoselective reduction of the aldehyde fragment in the presence of either a ketone or an alkene functional group demonstrates the utility of catalyst systems derived from R$_3$P/AgOTf. While such a catalytic system is not currently competitive with more active catalysts such as "(L)$_n$CuH" (Stryker's reagent, and relatives) or (Ph$_3$P)$_3$RhCl (Wilkinson's catalyst), the observed selectivity for the aldehyde functionality justifies further study. The observation that Et$_3$P/AgCl serves as a moderately effective catalyst for the hydrosilylation of benzaldehyde is interesting due to the assumed innocence for AgCl elimination as a

means of activating late transition metal complexes. Indeed, it is conceivable that AgCl and an excess of phosphine may be present in reaction mixtures, and that catalysis mediated by such a system could obscure the performance of the intended catalyst. This warrants further study of the range and scope of transformations catalyzed by such a system.

Studies directed at determining the composition of species in solution for the $Et_3P/AgOTf$ system described herein yielded mixed results. While unequivocal NMR evidence for Et_3P/Ag interaction was not obtained, this does not preclude the possibility of such an association. The appearance of resonances in both the $^{109}Ag\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra that could not be attributed to naked AgOTf or Et_3P suggest that discrete complexes are in fact formed. ESI-MS studies revealed the formation of several cationic adducts in solution, the proportion and identity of which could be significantly altered by varying the solvent. These data, coupled with the control experiments that highlight the need for AgOTf in this catalyst system, are consistent with the proposed mechanism in which ligated silver forms a hydride complex in situ (see Figure 5.2). While a colloidal catalyst cannot be discounted on the basis of these data, there is precedence for oligomeric $(L)_nAgH$ species,[48] supporting a homogeneous model. Further studies will undoubtedly lead to increased understanding of the active catalyst in this and related systems.

5.4   References

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Chapter 6 – Experimental

6.1 General Considerations

Except where noted, all manipulations were conducted in the absence of oxygen and water under an atmosphere of dinitrogen, either by use of standard Schlenk methods or within an inert atmosphere glovebox (mBraun), utilizing glassware that was oven-dried (130 °C) and evacuated while hot prior to use. Celite (Aldrich) and Al_2O_3 (Fisher, neutral, Brockman Activity I, 60-325 mesh) were oven dried (130 °C) for 5 d and then evacuated for 24 h prior to use. Non-deuterated solvents THF, CH_2Cl_2, diethyl ether, toluene, benzene, and pentane were deoxygenated and dried by sparging with dinitrogen gas, followed by passage through a double-column solvent purification system (mBraun). THF, CH_2Cl_2 and diethyl ether were purified over two alumina-packed columns, while toluene, benzene, and pentane were purified over one alumina-packed column and one column packed with copper-Q5 reactant. Purification of CH_3CN was achieved by refluxing over CaH_2 for 4 days under dinitrogen, followed by distillation. Purification of NEt_3 was achieved by stirring over KOH for 7 days, followed by distillation; the distilled NEt_3 was then refluxed over CaH_2 for 3 days under dinitrogen, followed by distillation. Technical grade 2-propanol was not purified prior to use. The solvents used within the glovebox were stored over activated 4 Å molecular sieves. All liquid reagents, including the deuterated solvents C_6D_6 (Aldrich), CD_2Cl_2 (Cambridge Isotope Laboratories), $CDCl_3$ (CIL), CD_3CN (CIL), THF-d_8 (CIL), styrene (Aldrich, containing 10 – 15 ppm 4-tert-butylcatechol as an inhibitor) and all silanes (Aldrich) were degassed using three repeated freeze-pump-thaw cycles and stored over 4 Å molecular sieves for a minimum of 24 h prior to use, unless otherwise noted.

Benzaldehyde (ACP) was washed with 10 % aqueous sodium bicarbonate until no further CO_2 was evolved, followed by saturated aqueous sodium sulfite, then dried over magnesium sulfate and distilled under reduced pressure. With the exception of phosphines, which were obtained from either Alfa (Et_3P) or Strem (all others), dihydrogen (99.999%, Air Liquide – UHP Grade), $PtCl_2$ (Fisher), Ph_3SiH (Strem), all chemicals were obtained from Aldrich in high purity. AgCl (Fisher) and all other Ag salts were dried in vacuo for a minimum of 48 h prior to use. Compounds **1.19a**,[1] **1.23[Li]**,[1] **1.20a**,[2] **1.21**,[2] **1.22**,[3] (η^4-COD)PtClMe,[4] (η^4-COD)PtMe$_2$,[4] cis/trans-[(Me_2S)$_2$PtCl$_2$],[5] [(μ-Me_2S)PtMe$_2$]$_2$,[5] $Ph_2PH \cdot BH_3$,[6] (Me_2AuCl)$_2$,[7] Me_2SAuCl[8] and 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene[9] were prepared employing reported methods.

6.1.1 Reactions Involving Ph$_3$SnH (Chapter 2)

All experiments were conducted in duplicate using Ph_3SnH that was purified by extraction into diethyl ether, followed by filtration through Celite to remove insoluble impurities, and removal of the solvent to yield purified Ph_3SnH (based on ^1H and ^{119}Sn NMR data). Unless otherwise stated, each reaction was carried out without exclusion of ambient light by adding a solution of an appropriate amount of either **2.3a** or **2.3b** in 0.75 mL of either C_6D_6 or CD_2Cl_2 to a glass vial containing Ph_3SnH (30 mg, 0.086 mmol). A homogeneous mixture formed instantly, and this mixture was then transferred immediately to an NMR tube, which was subsequently capped and sealed with PTFE tape. The resulting light brown solutions were observed to darken to orange-brown over 1 min, and then to dark orange after 10 min. Clear, homogeneous mixtures were maintained throughout, and for reactions employing a Ph_3Sn:**2.3a** ratio of 10:1, gas evolution was also observed. The progress of each reaction was monitored periodically by use of NMR techniques, with the relative product distribution estimated from the ratio

of the peak heights in the spectrum (for ^{31}P and ^{119}Sn NMR). Details of specific experiments are provided in Chapter 2.

6.1.2 General Protocol for the Hydrosilylation of Alkenes (Chapter 3)

The protocol used for hydrosilylation reactions employing 5 mol% catalyst loading in C_6H_6 is provided as a representative procedure. A solution of the catalyst compound in C_6H_6 (0.05 mmol in 4 mL of solvent) was allowed to equilibrate for 5 min under the influence of magnetic stirring, at which point styrene (1.0 mmol or 3.0 mmol, as noted) was added by use of an Eppendorf pipette. The resultant solution was stirred for an additional 10 min to ensure equilibration of the styrene with the catalyst, after which triethylsilane (1.0 mmol) was added. Subsequently, 0.7 mL aliquots were placed in NMR tubes and sealed with polypropylene tube caps and PTFE tape. For runs conducted at elevated temperatures, the NMR tubes were immediately transferred to a Schlenk tube filled partially with heavy mineral oil, which in turn was placed within a temperature-controlled mineral oil bath. No precipitates were observed throughout the course of all catalytic reactions, with the exception of reactions employing $AgBF_4$ or AgOTf, in which case AgCl was presumably generated. At the desired sampling time, NMR tubes were opened and filtered through a short Al_2O_3 column (5 cm long x 0.5 cm diameter) from which clear, colorless solutions eluted. Benzene was passed through the column to increase the total eluted volume to between 1.0 and 1.5 mL. 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 and compared to standards prepared using literature methods.[10,11] When GC analysis was not conducted immediately following workup, vials were stored in a conventional freezer at 0 °C. Tabulated data represent the average of two experimental runs.

6.1.3 General Protocol for the Hydrosilylation of Aldehydes (Chapters 4 & 5)

The protocol used for the hydrosilylation of benzaldehyde with dimethylphenylsilane, employing 3 mol% AgOTf (or 3 mol% Me_2SAuCl) and 20 mol% Et_3P in THF, is provided as a representative procedure. To a solution of AgOTf in THF (0.018 g, 0.072 mmol in 1.6 mL THF) or Me_2SAuCl in THF (0.022 g, 0.072 mmol in 1.6 mL THF) was added Et_3P (0.071 mL, 0.057 g, 0.48 mmol). The clear, colorless solution was allowed to equilibrate for 5 min under the influence of magnetic stirring, at which point benzaldehyde (0.25 mL, 2.4 mmol) was added by use of an Eppendorf pipette. The resultant solution was stirred for an additional 5 min to ensure equilibration of the benzaldehyde with the catalyst, after which dimethylphenylsilane (0.73 mL, 0.65 g, 4.8 mmol) was added. Subsequently, 0.7 mL aliquots were placed in 13 x 100 mm borosilicate tubes and sealed with a PTFE valve. Reactor cells were immediately transferred to a temperature-controlled mineral oil bath. Magnetic stirring of the solutions was initiated, and the headspace vapor pressure was reduced to approximately 0.5 mmHg. Occasionally, color changes and/or formation of metal precipitate was noted during the course of the reaction, as noted in Chapters 4 and 5. At the desired sampling time the reactor cells were opened and filtered through a short Al_2O_3 column (5 cm long x 0.5 cm diameter) from which clear, colorless solutions eluted. Benzene was passed through the column to increase the total eluted volume to between 1.0 and 1.5 mL. 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. In some reactions in which no ligand was employed, polymerization of the THF solvent was observed at reaction times greater than 6 hours. In some instances tetramethyldiphenyldisiloxane was observed as a side-product. The ratio of disiloxane formed to aldehyde reacted was found to vary

between undetectable and 1:6 when a ligand was employed, and between undetectable and 3:1 in the absence of ligand. We view this disiloxane as arising from a competing pathway involving adventitious water, as has been observed previously.[12] Control experiments show that the Ag or Au salt is required to generate disiloxane, the identity of which was confirmed by comparison with a rationally prepared sample.[13]

6.2   Characterization Techniques

6.2.1   Nuclear Magnetic Resonance (NMR)

All ^{1}H, ^{13}C, ^{11}B, ^{31}P, ^{109}Ag, ^{119}Sn and ^{195}Pt NMR characterization data were collected at 300 K (except where explicitly noted) on a Bruker AV-500 spectrometer operating at 500.1, 125.8, 160.5, 202.5, 23.3, 186.5 and 107.1 MHz (respectively) with chemical shifts reported in parts per million downfield of $SiMe_4$ (for ^{1}H and ^{13}C), BF_3 in diethyl ether (for ^{11}B), 85% H_3PO_4 in D_2O (for ^{31}P), $AgNO_3$ in D_2O (for ^{109}Ag), $SnMe_4$ (for ^{119}Sn), or K_2PtCl_4 in D_2O (for ^{195}Pt). In some cases, slightly fewer than expected independent ^{1}H or ^{13}C NMR resonances were observed, despite prolonged data acquisition times. ^{1}H and ^{13}C NMR chemical shift assignments are based on data obtained from ^{1}H-^{1}H COSY, ^{1}H-^{13}C HSQC, ^{1}H-^{13}C HMBC, and DEPT NMR experiments. Where coupling could not be accurately distinguished, resonances corresponding to a single magnetic environment are reported as their centroid, and those corresponding to multiple magnetic environments as the range over which the signals were observed. Acknowledgement is made to Drs. Mike Lumsden and Bob Berno for their assistance in the acquisition of NMR data.

6.2.2 Single Crystal X-ray Diffraction

Crystallographic data were obtained at 193($\pm$2) K on a Bruker

PLATFORM/SMART 1000 CCD diffractometer using a graphite-monochromated Mo Kα

(λ = 0.71073 Å) radiation, employing samples that were mounted in inert oil and

transferred to a cold gas stream on the diffractometer. The structures were solved by

use of direct methods in the case of **2.1, 2.3b, 2.4, 2.5, 3.1, [3.7]$^+$ BF$_4^-$, 4.1,** and **4.5,** or

Patterson search/structure expansion in the case of **[3.9]$^+$ BF$_4^-$, 4.3** and **[4.6]$^+$ OTf$^-$,** and

refined by use of full-matrix least-squares procedures (on F^2) with R_1 based on $F_o^2 \geq 2\sigma$

(F_o^2) and wR_2 based on $F_o^2 \geq -3\sigma(F_o^2)$. 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. Data were collected and refined at the University of Alberta X-ray Crystallography

Laboratory, by Drs. Robert McDonald and Michael Ferguson. Crystal structure diagrams

were generated by use of the ORTEP-3 program.[14] Data from X-ray crystallographic

studies (with the exception of **2.4**) is available via the Cambridge Structural Database at

http://www.ccdc.cam.ac.uk.

6.2.3 Gas Chromatography (GC)

GC-MS and GC-FID were performed on a Perkin Elmer AutoSystem XL gas

chromatograph equipped with a TurboMass mass spectrometer. GC-MS analyses were

performed using a Supelco 30 m x 0.25 mm MDN-5S column with 5% phenyl

methylsiloxane, film thickness 0.50 μm, temperature programmed: 60 °C, 1 min; 20

°C/min to 200 °C, 7 min; 45 °C/min to 280 °C, 7 min. GC-FID analyses were done in a

similar way except on a Supelco DB200 column. Acknowledgement is made to Dr. Jim

Pincock and Alex Pincock for their assistance in the acquisition of GC data.

6.2.4 Electrospray Ionization Mass Spectrometry (ESI-MS)

Mass spectra were obtained using a Finnigan LCQ Duo electrospray ionization

ion trap mass spectrometer. Samples were injected (in 2 or 5 μL aliquots) directly into

the electrospray ionization source of the mass spectrometer. The solvent flow rate was

set at 1.5 mL/h, the heated capillary temperature at 200 °C. The sheath gas (N_2 (g)) flow

rate at 20 (arbitrary units), and the spray voltage at a magnitude of 4.00 kV. Spectra

were collected over a mass-to-charge range of 50 to 2000 units. ESI-MS-MS (tandem)

spectra were obtained using helium as the collision gas, by applying a collision energy

between 10 and 25 %.

6.2.5 Elemental Analyses (EA)

Elemental analyses for all compounds (% C, H, N content) were performed by

Canadian Microanalytical Service Ltd., Delta, British Columbia, Canada, with the

exception of **3.1** and **4.3**, which were performed by Desert Analytics, Tucson, AZ, USA.

6.3   Preparative Procedures and Characterization Data for New Compounds

6.3.1   Preparation of 2.1

Method A: To a Schlenk flask containing a magnetic stir bar was added **1.19a**

(0.017 g, 0.63 mmol) and a mixture of cis- and trans-[(SMe$_2$)$_2$PtCl$_2$] (0.025 g, 0.63 mmol).

The flask was then sealed with a septum, and toluene (30 mL) was added via cannula to

generate a light yellow solution. Magnetic stirring was initiated, and the solution was

stirred for 16 h at 24 °C. At this time, toluene and other volatile materials were removed

in vacuo, and the residue was washed with pentane (2 x 6 mL) and diethyl ether (6 mL)

and residual solvent evaporated in vacuo, to leave a light yellow powder, **2.1** (0.29 g, 0.53 mmol, 84%).

Method B: To a vial containing a magnetically stirred suspension of platinum dichloride (0.049 g, 0.18 mmol) in toluene (2 mL) was added a solution of **1.19a** (0.050 g, 0.18 mmol) in toluene (2 mL). The resulting mixture was stirred for 16 h at 24 °C, at which time toluene and other volatiles were evaporated in vacuo to yield a light brown solid residue. This solid was dissolved in a minimal amount of CH_2Cl_2 (5 mL) and filtered through Celite to yield a clear, orange solution. CH_2Cl_2 was removed in vacuo, and the residue was washed with pentane (2 x 6 mL) to yield a light yellow powder, **2.1** (0.054 g, 0.10 mmol, 55%).

Pale yellow crystals suitable for X-ray diffraction were obtained by diffusing diethyl ether into a CH_2Cl_2 solution of **2.1**, and placing the resulting mixture in a freezer at -35 °C. Melting point 218 – 221 °C. Anal.(%): calcd. for $C_{17}H_{26}Cl_2NPPt$: C 37.72, H 4.84, N 2.59, found: C 37.43, H 4.72, N 2.47. ^1H NMR: δ 7.07-7.04 (m, 2H, aryl-CH's), 7.01-6.99 (m, 2H, aryl-CH's), 3.06 (s, 6H, $N(CH_3)_2$), 2.64 (s, 2H, CH_2), 2.46 (m, 2H, $P(CHCH_3CH_3)_2$), 1.32 (dd, $^3J_{PH}$ = 18.1 Hz, $^3J_{HH}$ = 7.2 Hz, 6H, $P(CHCH_3CH_3)_2$), 0.89 (dd, $^3J_{PH}$ = 16.9 Hz, $^3J_{HH}$ = 7.2 Hz, 6H, $P(CHCH_3CH_3)_2$); $^{13}C\{^1H\}$ NMR: δ 178.5 (C2), 143.1 (C3a or C7a), 134.7 (C3), 130.0 (C7a or C3a), 125.8 (aryl-CH), 125.2 (aryl-CH), 124.6 (aryl-CH), 121.2 (aryl-CH), 52.7 ($N(CH_3)_2$), 29.4 (d, $^3J_{PC}$ = 10 Hz, CH_2), 22.7 (d, $^1J_{PC}$ = 36 Hz, $P(CHCH_3CH_3)_2$), 17.3 ($P(CHCH_3CH_3)_2$), 17.0 ($P(CHCH_3CH_3)_2$); $^{31}P\{^1H\}$ NMR: δ 31.2 (s, with Pt satellites $^1J_{PtP}$ = 3788 Hz).

6.3.2 Preparation of 2.2

To a Schlenk flask containing a magnetic stir bar was added **1.19a** (0.13 g, 0.49 mmol) and (η^4-COD)PtClMe (0.16 g, 0.45 mmol). The flask was then sealed with a

septum, and toluene (7 mL) was added via cannula to generate a yellow-brown solution.

Magnetic stirring was initiated, and the solution was stirred for 16 h at 24 °C. At this time,

stirring was arrested, and toluene and other volatile materials were removed in vacuo.

The residue was washed with pentane (2 x 6 mL) and diethyl ether (2 x 6 mL) and

residual solvent evaporated in vacuo, to leave a finely divided, off-white powder, **2.2**

(0.21 g, 0.41 mmol, 91%). Melting point 177 – 180 °C. Anal.(%): calcd. for

$C_{18}H_{29}ClNPPt$: C 41.50, H 5.61, N 2.69, found: C 41.12, H 5.53, N 2.68. ^{1}H NMR: δ 7.10-

7.06 (m, 3H, aryl-CH's), 6.99 (m, 1H, aryl-CH), 2.79 (s, 6H, $N(CH_3)_2$), 2.48 (s, 2H, CH_2),

2.21 (m, 2H, $P(CHCH_3CH_3)_2$), 1.42 (d, $^3J_{PH}$ = 2.2 Hz, with Pt satellites, $^2J_{PtH}$ = 72 Hz, 3H,

Pt-CH_3 *trans* to N), 1.05 (dd, $^3J_{PH}$ = 17.1 Hz, $^3J_{HH}$ = 6.6 Hz, 6H, $P(CHCH_3CH_3)_2$), 0.85 (dd,

$^3J_{PH}$ = 16.5 Hz, $^3J_{HH}$ = 7.1 Hz, 6H, $P(CHCH_3CH_3)_2$); $^{13}C\{^1H\}$ NMR: δ 177.1 (d, $^2J_{PC}$ = 13 Hz,

C2), 143.8 (d, J_{PC} = 6 Hz, C3a or C7a), 138.4 (C7a or C3a), 131.9 (d, $^1J_{PC}$ = 41 Hz, C3),

126.9 (aryl-CH), 125.8 (aryl-CH), 125.4 (aryl-CH), 122.2 (aryl-CH), 49.8 ($N(CH_3)_2$), 30.2

(d, $^3J_{PC}$ = 10 Hz, CH_2), 24.2 (d, $^1J_{PC}$ = 37 Hz, $P(CHCH_3CH_3)_2$), 19.1 ($P(CHCH_3CH_3)_2$), 18.6

($P(CHCH_3CH_3)_2$), -27.2 (d, $^2J_{PC}$ = 7 Hz, Pt satellites not resolved, Pt-CH_3 *trans* to N);

$^{31}P\{^1H\}$ NMR: δ 31.4 (s, with Pt satellites $^1J_{PtP}$ = 4487 Hz); ^{195}Pt NMR: δ -2558 (d, $^1J_{PtP}$ =

4497 Hz).

6.3.3   Preparation of 2.3a

In a vial containing a magnetic stir bar, $[(\mu\text{-}SMe_2)PtMe_2]_2$ (0.031 g, 0.054 mmol)

was suspended in toluene (3 mL), and stirring was initiated. A light brown solution of

1.19a (0.027 g, 0.098 mmol) in toluene (3 mL) was then added rapidly to the platinum-

containing solution. The resulting mixture was stirred for 3 h at 24 °C, after which time

$^{31}P\{^1H\}$ NMR indicated quantitative formation of the allylic isomer, **2.3a**. The solution was

filtered through Celite to remove unreacted $[(\mu\text{-}SMe_2)PtMe_2]_2$, and toluene and other

volatiles were removed in vacuo, yielding a light brown solid, **2.3a** (0.047 g, 0.095 mmol, 97%). Since **2.3a** isomerizes to **2.3b**, elemental analysis data are only provided for **2.3b** (see **7.3.4**, below). Additionally, ^{13}C NMR chemical shift assignments are made based on projections of the cross-peaks from ^{1}H-^{13}C HSQC, and ^{1}H-^{13}C HMBC NMR experiments.

^{1}H NMR: δ 7.14-7.01 (m, 4H, aryl-CH's), 5.70 (s, 1H, vinylic CH), 3.82 (d, $^2J_{PH}$ = 10.5 Hz, 1H, allylic CH), 2.72 (s with Pt satellites, $^3J_{PtH}$ = 14.5 Hz, 3H, NCH_3aCH$_3$b), 2.68 (s with Pt satellites, $^3J_{PtH}$ = 16.3 Hz, 3H, NCH$_3$aCH_3b), 2.14 (m, 1H, P(CHCH$_3$aCH$_3$b)), 2.08 (s with Pt satellites, $^2J_{PtH}$ = 20.0 Hz, 3H, Pt-CH$_3$ *trans* to N), 1.85 (m, 1H, P(CHCH$_3$cCH$_3$d)), 1.39 (dd, $^3J_{PH}$ = 16.8 Hz, $^3J_{HH}$ = 7.2 Hz, 3H, P(CHCH_3cCH$_3$d)), 1.04 (dd, $^3J_{PH}$ = 18.0 Hz, $^3J_{HH}$ = 7.5 Hz, 3H, P(CHCH$_3$cCH_3d)), 0.99 (s, Pt satellites not resolved, 3H, Pt-CH$_3$ *trans* to P), 0.83 (dd, $^3J_{PH}$ = 14.7 Hz, $^3J_{HH}$ = 7.3 Hz, 3H, P(CHCH_3aCH$_3$b)), 0.62 (dd, $^3J_{PH}$ = 16.5 Hz, $^3J_{HH}$ = 6.7 Hz, 3H, P(CHCH_3aCH$_3$b)); ^{13}C{^{1}H} NMR: δ 170.0 (C2), 144.2 (C3a), 137.0 (C7a), 127.0 (aryl-CH), 124.4 (aryl-CH's), 121.3 (aryl-CH), 113.6 (vinylic C), 50.8 (NCH$_3$aCH_3b), 46.7 (NCH_3aCH$_3$b), 45.8 (allylic C), 23.3 (P(CHCH$_3$aCH$_3$b)), 21.4 (P(CHCH$_3$cCH$_3$d)), 20.1 (Pt-CH$_3$ *trans* to N), 19.3 (P(CHCH$_3$cCH$_3$d)), 18.5 (P(CHCH$_3$cCH$_3$d)), 18.1 (P(CHCH$_3$aCH$_3$b)), 17.4 (P(CHCH$_3$aCH$_3$b)), -7.1 (Pt-CH$_3$ *trans* to P); ^{31}P{^{1}H} NMR: δ 27.6 (s, with Pt satellites $^1J_{PtP}$ = 2063 Hz).

6.3.4 Preparation of 2.3b

To a magnetically stirred solution of **2.3a** (0.103 g, 0.206 mmol) in THF (10 mL) was added ^{i}PrOH (2.5 mL). After 1 h at 24 °C, clean conversion to **2.3b** (^{31}P NMR) was achieved. Stirring was arrested, and solvents and other volatiles were removed *in vacuo* to yield **2.3b** (0.102 g, 0.204 mmol, 99%) as an analytically pure light brown solid. Decomposition point 109 – 114 °C (charring, effervescence). Crystals suitable for X-ray diffraction studies were obtained by slow evaporation of a solution of **2.3b** in pentane at

24 °C. Anal.(%): calcd. For $C_{19}H_{32}NPPt$: C 45.59, H 6.44, N 2.80, found: C 45.22, H 6.38,

N 2.67. ^{1}H NMR (C_6D_6): δ 7.28-7.10 (m, 4H, aryl-CH's), 2.62 (s, 6H, N(CH$_3$)$_2$), 2.60 (s,

2H, CH$_2$), 2.44 (m, 2H, P(CHCH$_3$CH$_3$)$_2$), 1.49 (d, $^3J_{PH}$ = 6.5 Hz, with Pt satellites, $^2J_{PtH}$ =

90.5 Hz, 3H, Pt-CH$_3$ *trans* to N), 1.29 (dd, $^3J_{PH}$ = 16.0 Hz, $^3J_{HH}$ = 7.0 Hz, 6H,

P(CHCH_3CH$_3$)$_2$), 1.09 (d, $^3J_{PH}$ = 7.0 Hz, with Pt satellites, $^2J_{PtH}$ = 63.5 Hz, 3H, Pt-CH$_3$ *trans*

to P), 1.00 (dd, $^3J_{PH}$ = 14.8 Hz, $^3J_{HH}$ = 6.9 Hz, 6H, P(CHCH$_3$CH_3)$_2$); ^{13}C{^{1}H} NMR: δ 176.7

(d, $^2J_{PC}$ = 20 Hz, C2), 144.0 (d, $^1J_{PC}$ = 4 Hz, C3), 139.9 (C7a), 136.1 (C3a), 126.8 (C6 or

C7), 125.5 (C4), 125.2 (C5), 122.3 (C7 or C6), 49.8 (N(CH$_3$)$_2$), 29.5 (d, $^3J_{PC}$ = 9 Hz, C1),

24.7 (d, $^1J_{PC}$ = 23 Hz, P(CHCH$_3$CH$_3$)$_2$), 19.7 (P(CHCH$_3$CH_3)$_2$), 19.3 (d, $^2J_{PC}$ = 7 Hz,

P(CHCH_3CH$_3$)$_2$), 17.4 (d, $^2J_{PC}$ = 111 Hz, Pt satellites not resolved, Pt-CH$_3$ *trans* to P),

-27.2 (d, $^2J_{PC}$ = 4 Hz, Pt satellites not resolved, Pt-CH$_3$ *trans* to N); ^{31}P{^{1}H} NMR: δ 39.2

(s, with Pt satellites $^1J_{PtP}$ = 2039 Hz).

6.3.5 Preparation of 2.4

To a magnetically stirred suspension of PdBr$_2$ (0.10 g, 0.38 mmol) in toluene (2

mL) was added a solution of **1.19a** (0.11 g, 0.39 mmol) in toluene (2 mL). The resulting

solution was stirred for 20 h at 24 °C, at which time an opaque olive-green suspension

was observed. The reaction mixture was filtered through Celite, leaving a dark brown

solid, which was dissolved in CH$_2$Cl$_2$ (4 mL) to yield an orange solution. The solution

was filtered through Celite, and CH$_2$Cl$_2$ and other volatiles were removed in vacuo to give

an orange powder, **2.4** (0.15 g, 0.28 mmol, 73%). Crystals suitable for X-ray diffraction

experiments were grown from a concentrated toluene solution at 24 °C. Melting point

188-190 °C. Anal. (%): Calcd for $C_{17}H_{26}Br_2NPPd$: C, 37.70; H, 4.84; N, 2.59. Found: C,

40.67; H, 5.03; N, 2.55. ^{1}H NMR (CDCl$_3$): δ 7.60-7.30 (m, 4H, aryl C-H's), 3.70 (s, 2H,

CH$_2$), 3.43 (s, 6H, N(CH$_3$)$_2$), 2.95 (m, 2H, P(CHCH$_3$CH$_3$)$_2$), 1.63 (dd, $^3J_{PH}$ = 18.5 Hz, $^3J_{HH}$

= 7.0 Hz, 6H, P(CHCH_3CH$_3$)$_2$), 1.47 (dd, $^3J_{PH}$ = 17.5 Hz, $^3J_{HH}$ = 7.0 Hz, 6H,

P(CHCH$_3$CH_3)$_2$); ^{13}C{^{1}H} NMR: δ 177.8 (d, $^1J_{PC}$ = 15 Hz, C3), 144.2 (d, $^3J_{PC}$ = 6 Hz, C7a),

136.3 (C3a), 130.3 (C2), 127.5 (aryl C-H), 127.2 (aryl C-H), 125.8 (aryl C-H), 122.9 (aryl

C-H), 54.0 (N(CH$_3$)$_2$), 31.0 (d, $^3J_{PC}$ = 10 Hz, CH$_2$), 26.6 (d, $^1J_{PC}$ = 29 Hz, P(CHCH$_3$CH$_3$)$_2$),

19.4 (P(CHCH$_3$CH_3)$_2$), 19.2 (P(CHCH_3CH$_3$)$_2$); ^{31}P{^{1}H} NMR: δ 62.6.

6.3.6 Preparation of 2.5

In a Schlenk tube containing a magnetic stir bar, **2.3a** (0.047 g, 0.095 mmol) was

dissolved in toluene (3 mL) to form a light brown solution. Dimethyl sulfide (0.018 mL,

0.25 mmol, 2.5 equiv) was added, and the tube was sealed with a rubber septum and

placed in a 70 °C oil bath. Stirring was initiated, and after 0.33 h the solution was noted

to be dark brown (nearly black) in color. The solution was stirred for 20 h, at which time

toluene and other volatiles were removed in vacuo. The product was dissolved in

benzene (6 mL) and filtered through Celite to remove small quantities of insoluble

materials. Removal of benzene in vacuo left a dark brown solid, **2.5** (0.031 g, 0.057

mmol, 61%). Slow evaporation of a pentane solution of **2.5** at 24 °C yielded brown

crystals suitable for X-ray diffraction. Decomposition point 135 – 137 °C (charring,

effervescence). Anal.(%): calcd. For C$_{20}$H$_{34}$NPPtS: C 43.95, H 6.27, N 2.56, found: C

44.24, H 6.20, N 2.51. ^{1}H NMR: δ 7.30-7.23 (m, 2H, aryl-CH's), 7.17 (m, 1H, aryl-CH), 6.99

(td, $^3J_{HH}$ = 7.0 Hz, $^4J_{HH}$ = 1.5 Hz, 1H, C5 or C6), 4.08 (d, $^3J_{PH}$ = 8.5 Hz, with Pt satellites, $^2J_{PtH}$

= 93.5 Hz, 2H, N-CH$_2$), 3.01 (s, 2H, C(1)H$_2$), 2.98 (m, 2H, P(CHCH$_3$CH$_3$)$_2$), 2.60 (s, 3H, N-

CH$_3$), 1.93 (s with Pt satellites, $^3J_{PtH}$ = 25.0 Hz, 6H, S(CH$_3$)$_2$), 1.28 (dd, $^3J_{PH}$ = 15.5 Hz, $^3J_{HH}$ =

7.0 Hz, 6H, P(CHCH_3CH$_3$)$_2$), 1.24 (dd, $^3J_{PH}$ = 14.5 Hz, $^3J_{HH}$ = 7.0 Hz, 6H, P(CHCH$_3$CH_3)$_2$),

1.10 (d, $^3J_{PH}$ = 6.5 Hz, with Pt satellites, $^2J_{PtH}$ = 64.3 Hz, 3H, Pt-CH$_3$); ^{13}C{^{1}H} NMR: δ 169.2

(d, $^2J_{PC}$ = 13 Hz, C2), 149.3 (C3a or C7a), 135.5 (d, J = 7 Hz, C7a or C3a), 126.5 (aryl-CH),

122.9 (aryl-CH), 119.6 (aryl-CH), 118.3 (aryl-CH), 88.8 (d, $^1J_{PC}$ = 51 Hz, C3), 41.7 (s with Pt

satellites, $^3J_{PtC}$ = 31 Hz, N-CH$_3$), 39.8 (d, $^3J_{PC}$ = 6 Hz, C1), 38.0 (d, $^2J_{PC}$ = 8 Hz, N-CH$_2$), 25.3

(d, $^1J_{PC}$ = 27 Hz, P(CHCH$_3$CH$_3$)$_2$), 20.6 (P(CHCH$_3$CH$_3$)$_2$), 20.1 (d, $^2J_{PC}$ = 6 Hz,

P(CHCH$_3$CH$_3$)$_2$), 19.1 (S(CH$_3$)$_2$), 9.6 (d, $^2J_{PC}$ = 99 Hz, with Pt satellites, $^1J_{PtC}$ = 667 Hz, Pt-

CH$_3$); ^{31}P{^{1}H} NMR: δ 16.8 (s, with Pt satellites $^1J_{PtP}$ = 2006 Hz).

6.3.7   Preparation of 3.1

To a magnetically stirred suspension of [Me$_2$AuCl]$_2$ (0.098 g, 0.19 mmol) in 3 mL

toluene was rapidly added a light brown solution of **1.23**[Li] (0.11 g, 0.39 mmol) in 3 mL

toluene. The resulting mixture was stirred for 4 h at 24 °C, after which time toluene and

other volatiles were removed in vacuo, yielding a bright yellow solid, interspersed with

white powder. To this solid was added pentane (5 mL) and the resulting mixture was

filtered through Celite, giving a bright yellow solution. Removal of the pentane in vacuo

yielded a bright yellow solid, **3.1** (0.079 g, 0.16 mmol, 41 %). Crystals suitable for X-ray

diffraction analysis were grown from a concentrated pentane solution at -35 °C.

Decomposition point 122 °C (charring; effervescence noted at 143 – 144 °C). Anal.(%):

calcd. for C$_{19}$H$_{31}$AuNP: C 45.51, H 6.23, N 2.79, found: C 45.23, H 6.34, N 2.86. ^{1}H NMR

(C$_6$D$_6$): δ 7.93 (d, J = 7.5 Hz, 1H, aryl-CH), 7.66 (d, J = 8.0 Hz, 1H, aryl-CH), 7.45-7.25

(m, 2H, aryl-CH's), 6.25 (d, $^4J_{PH}$ = 4.0 Hz, 1H, C1-H), 2.74 (s, 6H, N(CH$_3$)$_2$), 2.49 (m, 2H,

P(CHCH$_3$CH$_3$)$_2$), 1.06 (d, $^3J_{PH}$ = 5.5 Hz, 3H, Au-CH$_3$ *trans* to P), 1.01 (dd, $^3J_{PH}$ = 16.0 Hz,

$^3J_{HH}$ = 7.0 Hz, 6H, P(CHCH$_3$CH$_3$)$_2$), 0.85 (dd, $^3J_{PH}$ = 17.5 Hz, $^3J_{HH}$ = 7.5 Hz, 3H,

P(CHCH$_3$CH$_3$)$_2$), 0.58 (d, $^3J_{PH}$ = 7.0 Hz, 3H, Au-CH$_3$ *trans* to N); ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ

162.2 (d, $^2J_{PC}$ = 25 Hz, C2), 139.2 (d, $^2J_{PC}$ = 16 Hz, C3a), 129.3 (C7a), 121.8 (aryl-CH),

119.5 (aryl-CH), 117.7 (aryl-CH), 117.5 (aryl-CH), 90.7 (d, $^3J_{PC}$ = 12 Hz, C1), 53.7

(N(CH$_3$)$_2$), 26.4 (Au-CH$_3$ *trans* to P), 25.4 (d, $^1J_{PC}$ = 33 Hz, P(CHCH$_3$CH$_3$)$_2$), 19.5

$(P(CHCH_3CH_3)_2)$, 18.6 $(P(CHCH_3CH_3)_2)$, -2.0 (d, $^2J_{PC}$ = 5 Hz, Au-CH$_3$ *trans* to N); $^{31}P\{^1H\}$

NMR (C_6D_6): δ 46.3.

6.3.8 Characterization of 3.2

To a solution of **3.1** (0.015 g, 0.031 mmol) in THF (0.7 mL) was added a solution

of technical grade HBF$_4$ in H$_2$O, diluted 1/10th with THF (0.1 mL, 0.16 mmol) in an NMR

tube sealed with a natural rubber septum. $^{31}P\{^1H\}$ NMR revealed the presence of a lone

singlet at δ = 51.6. THF and other volatiles were removed in vacuo, and the solid

material was subsequently dissolved in CDCl$_3$ for further NMR characterization. No yield,

melting point, elemental analysis, or X-ray data were obtained. ^1H NMR (CDCl$_3$): δ 7.56

(m, 1H, aryl-CH), 7.42-7.33 (m, 3H, aryl-CH's), 3.98 (s, 2H, CH$_2$), 3.18 (s, 6H, N(CH$_3$)$_2$),

3.09 (m, 2H, P(C*H*CH$_3$CH$_3$)$_2$), 1.52 (d, $^3J_{PH}$ = 7.0 Hz, 3H, Au-CH$_3$ *trans* to P), 1.41 (dd,

$^3J_{PH}$ = 19.0 Hz, $^3J_{HH}$ = 7.0 Hz, 6H, P(CHC*H*$_3$CH$_3$)$_2$), 1.32 (dd, $^3J_{PH}$ = 17.5 Hz, $^3J_{HH}$ = 7.0

Hz, 6H, P(CHCH$_3$C*H*$_3$)$_2$), 1.08 (d, $^3J_{PH}$ = 7.5 Hz, 3H, Au-CH$_3$ *trans* to N); $^{13}C\{^1H\}$ NMR

(CDCl$_3$): δ 178.0 (d, $^2J_{PC}$ = 16 Hz, C2), 143.8 (d, J_{PC} = 6 Hz, C7a or C3a), 136.5 (C3a or

C7a), 127.8 (aryl-CH), 127.5 (aryl-CH), 126.5 (aryl-CH), 122.0 (aryl-CH), 50.7 (N(CH$_3$)$_2$),

33.1 (d, $^3J_{PC}$ = 9 Hz, CH$_2$), 27.6 (d, $^2J_{PC}$ = 100 Hz, Au-CH$_3$ *trans* to P), 24.4 (d, $^1J_{PC}$ = 26

Hz, P(*C*HCH$_3$CH$_3$)$_2$), 19.6 (P(CHCH$_3$*C*H$_3$)$_2$), 18.7 (d, $^2J_{PC}$ = 3 Hz, P(CH*C*H$_3$CH$_3$)$_2$), 1.8 (d,

$^2J_{PC}$ = 5 Hz, Au-CH$_3$ *trans* to N); $^{31}P\{^1H\}$ NMR (CDCl$_3$): δ 51.6.

6.3.9 Preparation of 3.3

A solution of **3.1** (0.050 g, 0.099 mmol) in a mixture of diethyl ether (0.80 mL) and

THF (0.85 mL) was cooled to -35 °C. Magnetic stirring was initiated, and HCl (0.052 mL

of a 2.0 M solution in diethyl ether, 0.10 mmol) was added. After 2 h, the solvent and

other volatiles were removed in vacuo. The resulting solid was rinsed with pentane (2 x

1.5 mL) to leave a white solid, **3.3** (0.044 g, 0.082 mmol, 82%). Anal.(%): calcd. for

$C_{19}H_{32}AuClNP$: C 42.43, H 6.00, N 2.60, found: C 42.67, H 5.92, N 2.41. ^1H NMR (C_6D_6):

δ 8.39 (d, J = 7.0 Hz, 1H, aryl-CH), 7.14-7.01 (m, 2H, aryl-CH's), 6.97 (m, 1H, aryl-CH),

5.50 (s, 1H, vinylic CH), (broad s, 1H, allylic CH), 3.04 (m, 1H, P($CHCH_3aCH_3b$)), 2.22

(s, 6H, N(CH_3)$_2$), 2.16 (m, 1H, P($CHCH_3cCH_3d$)), 1.71 (d, $^3J_{PH}$ = 9.0 Hz, 3H, Au-CH_3 *trans*

to P), 1.38 (dd, $^3J_{PH}$ = 16.5 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, P(CHCH_3aCH$_3$b)), 0.98 (d, $^3J_{PH}$ = 7.5

Hz, 3H, Au-CH_3 *cis* to P), 0.94 (dd, $^3J_{PH}$ = 12.0 Hz, $^3J_{HH}$ = 7.5 Hz, 3H, P(CHCH_3cCH$_3$d),

0.87 (dd, $^3J_{PH}$ = 15.0 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, P(CHCH$_3$aCH_3b)), 0.41 (dd, $^3J_{PH}$ = 15.5 Hz,

$^3J_{HH}$ = 7.0 Hz, 3H, P(CHCH$_3$cCH_3d)); $^{13}C\{^1H\}$ NMR (C_6D_6): δ 160.6 (d, $^2J_{PC}$ = 8 Hz, C2),

144.9 (d, J_{PC} = 4 Hz, C7a or C3a), 137.7 (C3a or C7a), 125.7 (aryl-CH), 122.9 (aryl-CH),

119.1 (aryl-CH), 109.5 (vinylic C), 43.0 (N(CH_3)$_2$), 41.1 (d, $^1J_{PC}$ = 7 Hz, allylic C), 22.1 (d,

$^1J_{PC}$ = 18 Hz, P(CHCH$_3$cCH$_3$d)), 21.3 (d, $^2J_{PC}$ = 111 Hz, Au-CH_3 *trans* to P), 21.2 (d, $^2J_{PC}$

= 4 Hz, P(CHCH$_3$aCH$_3$b), 20.7 (d, $^1J_{PC}$ = 17 Hz, P(CHCH$_3$aCH$_3$b)), 18.5

(P(CHCH$_3$cCH$_3$d)), 18.4 (P(CHCH$_3$cCH$_3$d)), 16.7 (d, $^2J_{PC}$ = 6 Hz, P(CHCH$_3$aCH$_3$b), 5.5 (d,

$^2J_{PC}$ = 5 Hz, Au-CH_3 *cis* to P); $^{31}P\{^1H\}$ NMR (C_6D_6): δ 53.3.

6.3.10 Preparation of [3.6]$^+$ BF$_4^-$

To a magnetically stirred solution of **2.2** (0.10 g, 0.20 mmol) in 3 mL of THF was

added solid AgBF$_4$ (0.044 g, 0.23 mmol). The reaction mixture was stirred for 0.5 h at 24

°C, after which time acetonitrile (0.10 mL, 1.9 mmol) was added, and the solution stirred

for an additional 1 h. The solvent and other volatiles were removed in vacuo, and the

solid was treated with 5 mL CH$_2$Cl$_2$. Insoluble materials were removed by filtration

through a Celite column, from which the filtrate was collected, and the CH$_2$Cl$_2$ and other

volatiles were then removed in vacuo. The residual white solid was rinsed with pentane

(2 x 3 mL) to leave a white powder, [3.6]$^+$ BF$_4^-$ (0.098 g, 0.16 mmol, 84 %). Melting point

111 – 114 °C. Anal.(%): calcd. for $C_{20}H_{32}BF_4N_2PPt$: C 39.16, H 5.26, N 4.57, found: C

39.02, H 4.98, N 4.19. ^1H NMR (CD_3CN): δ 7.56 (m, 1H, aryl-CH), 7.49 (m, 1H, aryl-CH),

7.38-7.31 (m, 2H, aryl-CH's), 3.68 (s, 2H, CH_2), 3.08 (s, 6H, $N(CH_3)_2$), 2.79 (m, 2H,

$P(CHCH_3CH_3)_2$), 1.31 (dd, $^3J_{PH}$ = 18.0 Hz, $^3J_{HH}$ = 7.5 Hz, 6H, $P(CHCH_3CH_3)_2$), 1.22 (dd,

$^3J_{PH}$ = 17.5 Hz, $^3J_{HH}$ = 7.0 Hz, 6H, $P(CHCH_3CH_3)_2$), 0.67 (d, $^3J_{PH}$ = 2.0 Hz, with Pt

satellites, $^2J_{PtH}$ = 70.0 Hz, 3H, Pt-CH_3 trans to N); $^{13}C\{^1H\}$ NMR (CD_3CN): δ 178.0 (d, $^2J_{PC}$

= 11 Hz, C2), 145.7 (d, J_{PC} = 7 Hz, C3a or C7a), 138.0 (C7a or C3a), 131.0 (d, $^1J_{PC}$ = 47

Hz, C3), 128.1 (aryl-CH), 127.7 (aryl-CH), 126.7 (aryl-CH), 123.7 (aryl-CH), 53.5

($N(CH_3)_2$), 31.9 (d, $^3J_{PC}$ = 9 Hz, CH_2), 24.9 (d, $^1J_{PC}$ = 39 Hz, P($CHCH_3CH_3)_2$), 19.7 (s, with

Pt satellites, $^3J_{PtC}$ = 39 Hz, $P(CHCH_3CH_3)_2$), 19.2 ($P(CHCH_3CH_3)_2$), -28.0 (d, $^2J_{PC}$ = 8 Hz,

with Pt satellites, $^1J_{PtC}$ = 600 Hz, Pt-CH_3 trans to N); ^1H and ^{13}C resonances attributable to

the coordinated CH_3CN ligand in [3.6]$^+$ BF_4^- were not observed in CD_3CN, presumably

due to facile ligand displacement with the deuterated solvent; $^{31}P\{^1H\}$ NMR (CD_3CN): δ

29.5 (s, with Pt satellites $^1J_{PtP}$ = 4562 Hz). ^1H NMR (THF-d_8): δ 7.60 (m, 1H, aryl-CH),

7.49 (m, 1H, aryl-CH), 7.33-7.25 (m, 2H, aryl-CH's), 3.79 (s, 2H, CH_2), 3.19 (s, 6H,

$N(CH_3)_2$), 2.83 (m, 2H, $P(CHCH_3CH_3)_2$), 2.58 (s, 3H, $NCCH_3$), 1.34 (dd, $^3J_{PH}$ = 17.6 Hz,

$^3J_{HH}$ = 7.0 Hz, 6H, $P(CHCH_3CH_3)_2$), 1.24 (dd, $^3J_{PH}$ = 17.2 Hz, $^3J_{HH}$ = 7.0 Hz, 6H,

$P(CHCH_3CH_3)_2$), 0.67 (d, $^3J_{PH}$ = 2.0 Hz, with Pt satellites, $^2J_{PtH}$ = 67.0 Hz, 3H, Pt-CH_3 trans

to N); $^{13}C\{^1H\}$ NMR (THF-d_8): δ 179.1 (d, $^2J_{PC}$ = 11 Hz, C2), 145.9 (d, J_{PC} = 7 Hz, C3a or

C7a), 138.1 (C7a or C3a), 130.5 (d, $^1J_{PC}$ = 47 Hz, C3), 127.7 (aryl-CH), 127.2 (aryl-CH),

126.5 (aryl-CH), 123.3 (aryl-CH), 120.9 (d, $^3J_{PC}$ = 18 Hz, NCCH$_3$), 52.0 ($N(CH_3)_2$), 31.8

(d, $^3J_{PC}$ = 9 Hz, CH_2), 24.8 (d, $^1J_{PC}$ = 39 Hz, P($CHCH_3CH_3)_2$), 19.7 (s, with Pt satellites,

$^3J_{PtC}$ = 36 Hz, $P(CHCH_3CH_3)_2$), 19.2 ($P(CHCH_3CH_3)_2$), 2.9 (NCCH_3), -28.1 (d, $^2J_{PC}$ = 8 Hz,

with Pt satellites, $^1J_{PtC}$ = 594 Hz, Pt-CH$_3$ *trans* to N); ^{31}P{^{1}H} NMR (THF-d_8): δ 28.0 (s, with

Pt satellites $^1J_{PtP}$ = 4600 Hz).

6.3.11 Preparation of [3.7]$^+$ BF$_4$$^-$

To a magnetically stirred solution of **2.2** (0.096 g, 0.18 mmol) in 3 mL of THF was

added solid AgBF$_4$ (0.043 g, 0.22 mmol). The reaction mixture was stirred for 1 h at 24

°C, after which time dimethyl sulfide (0.14 mL, 1.9 mmol) was added and the solution

stirred for an additional 1 h. The solvent and other volatiles were then removed in

vacuo, and 5 mL CH$_2$Cl$_2$ was added to the solid. Insoluble materials were removed by

filtration through a Celite column, from which the filtrate was collected, and the CH$_2$Cl$_2$

and other volatiles were removed in vacuo. This white residue was rinsed with pentane

(2 x 3 mL) to yield a white powder, [3.7]$^+$ BF$_4$$^-$ (0.090 g, 0.14 mmol, 77 %). Crystals

suitable for X-ray diffraction analysis were grown by diffusion of pentane into a

concentrated solution of [3.7]$^+$ BF$_4$$^-$ in CH$_2$Cl$_2$ at 24 °C. Decomposition point 137 – 144 °C

(charring). Anal.(%): calcd. for C$_{20}$H$_{35}$BF$_4$NPPtS: C 37.86, H 5.56, N 2.21, found: C

37.90, H 5.57, N 1.93. ^{1}H NMR (CD$_2$Cl$_2$): δ 7.53-7.46 (m, 2H, aryl-CH's), 7.40-7.32 (m,

2H, aryl-CH's), 3.69 (s, 2H, CH$_2$), 3.08 (s, with Pt satellites, $^3J_{PtH}$ = 12.0 Hz, 6H, N(CH$_3$)$_2$),

2.84 (m, 2H, P(C*H*CH$_3$CH$_3$)$_2$), 2.52 (d, $^4J_{PH}$ = 3.5 Hz, with Pt satellites, $^3J_{PtH}$ = 36.5 Hz,

6H, S(CH$_3$)$_2$), 1.37 (dd, $^3J_{PH}$ = 18.0 Hz, $^3J_{HH}$ = 7.5 Hz, 6H, P(CHC*H*$_3$CH$_3$)$_2$), 1.29 (dd, $^3J_{PH}$

= 17.5 Hz, $^3J_{HH}$ = 7.0 Hz, 6H, P(CHCH$_3$C*H*$_3$)$_2$), 0.78 (d, $^3J_{PH}$ = 2.5 Hz, with Pt satellites,

$^2J_{PtH}$ = 71.0 Hz, 3H, Pt-CH$_3$ *trans* to N); ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): δ 177.6 (d, $^2J_{PC}$ = 13 Hz,

C2), 144.4 (d, J_{PC} = 7 Hz, C3a or C7a), 137.2 (s, C7a or C3a), 131.2 (s, C3), 127.9 (s,

aryl-CH), 127.6 (s, aryl-CH), 126.4 (s, aryl-CH), 123.1 (s, aryl-CH), 51.3 (s, N(CH$_3$)$_2$),

31.6 (d, $^3J_{PC}$ = 9 Hz, CH$_2$), 25.0 (d, $^1J_{PC}$ = 35 Hz, P(*C*HCH$_3$CH$_3$)$_2$), 20.4 (s, S(CH$_3$)$_2$), 19.9

(s, with Pt satellites, $^3J_{PtC}$ = 34 Hz, P(CHCH$_3$*C*H$_3$)$_2$), 19.3 (s, P(CH*C*H$_3$CH$_3$)$_2$), -24.2 (d, $^2J_{PC}$

= 6 Hz, Pt satellites not resolved, Pt-CH$_3$ *trans* to N); ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): δ 39.0 (s, with Pt satellites $^1J_{PtP}$ = 3936 Hz).

6.3.12 Preparation of [3.9]$^+$ BF$_4^-$

To a magnetically stirred solution of **2.2** (0.11 g, 0.21 mmol) in 3 mL of toluene was added a suspension of AgBF$_4$ (0.021 g, 0.11 mmol) in 2 mL toluene. The reaction mixture was stirred for 5 h at 24 °C, after which time the solution was placed in a -35 °C freezer for 16 h to induce precipitation. The cold solution was filtered through Celite; ^{31}P NMR analysis of the filtrate revealed only the presence of **2.2**. The filtrate was discarded, and the solid material remaining on the filter was subsequently isolated by passing 3 mL CH$_2$Cl$_2$ through the filter, and collecting this filtrate. CH$_2$Cl$_2$ and other volatiles were removed in vacuo, and the residue was washed with pentane (2 x 3 mL) to yield an off-white powder, [**3.9**]$^+$ BF$_4^-$ (0.070 g, 0.064 mmol, 61 %). Crystals suitable for X-ray diffraction analysis were grown by slow evaporation of a solution of [**3.9**]$^+$ BF$_4^-$ in THF at 24 °C. Decomposition point 255 – 257 °C (charring, effervescence). Anal.(%): calcd. for C$_{36}$H$_{58}$BClF$_4$N$_2$P$_2$Pt$_2$: C 39.55, H 5.35, N 2.56, found: C 39.44, H 5.30, N 2.64. ^{1}H NMR (CD$_2$Cl$_2$): δ 7.54-7.53 (m, 4H, aryl-CH's), 7.42-7.37 (m, 4H, aryl-CH's), 3.68 (s, 4H, CH$_2$), 3.21 (s, 12H, N(CH$_3$)$_2$), 2.82 (m, 4H, P(C*H*CH$_3$CH$_3$)$_2$), 1.41 (dd, $^3J_{PH}$ = 18.0 Hz, $^3J_{HH}$ = 7.0 Hz, 12H, P(CHC*H$_3$*CH$_3$)$_2$), 1.32 (dd, $^3J_{PH}$ = 17.0 Hz, $^3J_{HH}$ = 7.0 Hz, 12H, P(CHCH$_3$C*H$_3$*)$_2$), 1.04 (s, with Pt satellites, $^2J_{PtH}$ = 63.5 Hz, 3H, Pt-CH$_3$ *trans* to N); ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): δ 176.9 (d, $^2J_{PC}$ = 11 Hz, C2), 144.1 (d, J_{PC} = 7 Hz, C3a or C7a), 137.3 (s, C7a or C3a), 130.5 (d, $^1J_{PC}$ = 46 Hz, C3), 127.5 (s, aryl-CH), 127.0 (s, aryl-CH), 125.9 (s, aryl-CH), 122.8 (s, aryl-CH), 51.0 (s, N(CH$_3$)$_2$), 31.3 (d, $^3J_{PC}$ = 9 Hz, CH$_2$), 25.0 (d, $^1J_{PC}$ = 39 Hz, P(*C*HCH$_3$CH$_3$)$_2$), 19.5 (s, with Pt satellites, $^3J_{PtC}$ = 41 Hz, P(CHCH$_3$*C*H$_3$)$_2$), 18.9 (s,

P(CHCH$_3$CH$_3$)$_2$), -24.5 (d, $^2J_{PC}$ = 7 Hz, Pt satellites not resolved, Pt-CH$_3$ *trans* to N);

^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): δ 32.4 (s, with Pt satellites $^1J_{PtP}$ = 4936 Hz).

6.3.13 Preparation of 4.1

To a magnetically stirred solution of **1.21** (0.077 g, 0.33 mmol), in CH$_2$Cl$_2$ (3 mL) was added a suspension of Me$_2$SAuCl (0.097 g, 0.33 mmol) in CH$_2$Cl$_2$ (2 mL). After 0.25 h at 24 °C, stirring was arrested and residual solvent along with other volatiles were removed in vacuo. The residue was washed with pentane (2 x 3 mL) and crystallized from CH$_2$Cl$_2$/EtOH to yield **4.1** as a white solid (0.014 g, 0.29 mmol, 88%). Crystals suitable for X-ray diffraction were grown from a diffusion of pentane into a CH$_2$Cl$_2$ solution at 24 °C. Melting point 160 – 163 °C. Anal. (%): Calcd for C$_{15}$H$_{21}$AuClP: C, 38.77; H, 4.55. Found: C, 38.79; H, 4.66. ^{1}H NMR (C$_6$D$_6$): δ 7.64 (d, $^3J_{HH}$ = 7.4 Hz, 1H, C7-H), 7.10 (t, $^3J_{HH}$ = 8.8 Hz, 1H, C5-H), 7.06 (t, $^3J_{HH}$ = 8.8 Hz, 1H, C6-H), 6.63 (d, $^2J_{PH}$ = 10.2 Hz, 1H, C2-H), 2.90 (s, 2H, CH$_2$), 1.91 (m, 2H, P(CHCH$_3$CH$_3$)$_2$), 0.86 (dd, 6H, $^3J_{PH}$ = 19.1 Hz, $^3J_{HH}$ = 6.9 Hz, P(CHCH_3CH$_3$)$_2$), 0.64 (dd, 6H, $^3J_{PH}$ = 17.4 Hz, $^3J_{HH}$ = 7.1 Hz, P(CHCH$_3$CH_3)$_2$); ^{13}C{^{1}H} NMR: δ 151.4 (d, $^2J_{PC}$ = 11 Hz, C2), 144.0 (d, J_{PC} = 7 Hz, C7a or C3a), 142.9 (d, J_{PC} = 9 Hz, C3a or C7a), 131.0 (d, $^1J_{PC}$ = 50 Hz, C3), 126.6 (C5), 125.7 (C6), 124.1 (C4), 121.5 (C7), 39.5 (d, $^3J_{PC}$ = 12 Hz, CH$_2$), 24.6 (d, $^1J_{PC}$ = 36 Hz, P(CHCH$_3$CH$_3$)$_2$), 19.6 (d, $^2J_{PC}$ = 5 Hz, P(CHCH$_3$CH$_3$)$_2$), 18.4 (P(CHCH$_3$$CH_3$)$_2$); ^{31}P{^{1}H} NMR: δ 44.4.

6.3.14 Preparation of 4.2

To a magnetically stirred solution of **1.22** (0.31 g, 1.1 mmol) in CH$_2$Cl$_2$ (8 mL) was added a suspension of Me$_2$SAuCl (0.31 g, 1.1 mmol) in CH$_2$Cl$_2$ (4 mL). The reaction mixture was noted to clear almost immediately, and after 0.25 h at 24 °C, stirring was

arrested, and residual solvent along with other volatiles was removed in vacuo. The residue was washed with pentane (2 x 3 mL), and solvent and other volatile materials were removed in vacuo to yield **4.2** as a white solid (0.42 g, 0.79 mmol, 75%). Melting point 155 – 157 °C. Anal. (%): Calcd for $C_{21}H_{17}AuClP$: C, 47.34; H, 3.22. Found: C, 47.44; H, 3.54. ^1H NMR (C_6D_6): δ 7.34 (m, 1H, C7-H), 7.28 – 7.19 (m, 4H, *ortho* Ph-H), 7.16 (m, 1H, C4-H), 7.02 – 6.96 (m, 2H, *para* Ph-H), 6.93 (m, 1H, C5-H), 6.88 – 6.81 (m, 4H, *meta* Ph-H), 6.76 (m, 1H, C6-H), 5.96 (d, 1H, $^3J_{PH}$ = 8.0 Hz, C2-H), 2.93 (s, 2H, CH_2); $^{13}C\{^1H\}$ NMR: δ 148.2 (d, $^2J_{PC}$ = 7 Hz, C2), 143.7 (d, $^3J_{PC}$ = 9 Hz, C7a), 142.2 (d, $^2J_{PC}$ = 15 Hz, C3a), 133.9 (d, $^2J_{PC}$ = 14 Hz, *ortho* Ph-C), 133.8 (d, $^1J_{PC}$ = 61 Hz, *ipso* Ph-C), 133.2 (d, $^1J_{PC}$ = 15 Hz, C3), 131.6 (*para* Ph-C), 129.0 (d, $^3J_{PC}$ = 12 Hz, *meta* Ph-C), 126.9 (C6), 126.0 (C5), 124.0 (C4), 121.5 (C7), 39.9 (d, $^3J_{PC}$ = 12 Hz, CH_2); $^{31}P\{^1H\}$ NMR: δ 15.2.

6.3.15 Preparation of 4.3

To a magnetically stirred solution of Me_2SAuCl (1.1 g, 3.5 mmol) in CH_2Cl_2 (10 mL) was added a solution of **1.19a** (1.0 g, 3.5 mmol) in CH_2Cl_2 (10 mL). After 0.25 h at 24 °C, stirring was arrested and residual solvent along with other volatiles were removed in vacuo. The solid material was crystallized from CH_2Cl_2 to yield **4.3** as light gray needles (1.2 g, 2.3 mmol, 67%). Crystals suitable for X-ray diffraction were grown from a concentrated toluene solution of **4.3** at 24 °C. Melting point 194 – 195 °C. Anal. (%): Calcd for $C_{17}H_{26}AuClNP$: C, 40.21; H, 5.16; N, 2.76. Found: C, 40.17; H, 5.23; N, 2.39. ^1H NMR $(CDCl_3)$: δ 7.29 (d, $^3J_{HH}$ = 7.5 Hz, 1H, C7-H), 7.23 (t, $^3J_{HH}$ = 7.5 Hz, 1H, C6-H), 7.14 (d, $^3J_{HH}$ = 7.5 Hz, 1H, C4-H), 6.96 (t, $^3J_{HH}$ = 7.5 Hz, 1H, C5-H), 5.72 (s, 1H, vinylic CH), 4.30 (d, $^2J_{PH}$ = 10.0 Hz, 1H, allylic CH), 2.90 (s, 6H, $N(CH_3)_2$), 2.59 (m, 1H, P(C*H*CH3aCH3b)), 1.88 (m, 1H, P(C*H*CH3cCH3d)), 1.54 (dd, 3H, $^3J_{PH}$ = 18.0 Hz, $^3J_{HH}$ = 6.5 Hz, P(CHC*H3*aCH3b)), 1.30 (dd, 3H, $^3J_{PH}$ = 18.5 Hz, $^3J_{HH}$ = 6.0 Hz, P(CHCH3aC*H3*b)),

0.98 (dd, 3H, $^3J_{PH}$ = 19.5 Hz, $^3J_{HH}$ = 7.5 Hz, P(CHCH_3cCH$_3$d)), 0.72 (dd, 3H, $^3J_{PH}$ = 15.0

Hz, $^3J_{HH}$ = 7.0 Hz, P(CHCH$_3$cCH_3d)); ^{13}C{^{1}H} NMR: δ 157.8 (d, $^2J_{PC}$ = 3 Hz, C2), 145.6 (d,

$^2J_{PC}$ = 2 Hz, C7a), 135.5 (d, $^2J_{PC}$ = 7 Hz, C3a), 128.4 (C6), 123.5 (C7), 122.0 (C5), 119.4

(C4), 106.6 (allylic C), 44.5 (d, $^1J_{PC}$ = 21 Hz, vinylic C), 43.8 (N(CH$_3$)$_2$), 23.4 (d, $^1J_{PC}$ = 20

Hz, P(CHCH$_3$cCH$_3$d)), 22.9 (d, $^1J_{PC}$ = 20 Hz, P(CHCH$_3$aCH$_3$b)), 22.8 (d, $^2J_{PC}$ = 5 Hz,

P(CHCH$_3$cCH$_3$d)), 20.7 (d, $^2J_{PC}$ = 5 Hz, P(CHCH$_3$aCH$_3$b)), 20.0 (d, $^2J_{PC}$ = 3 Hz,

P(CHCH$_3$aCH$_3$b)), 18.3 (d, $^2J_{PC}$ = 2 Hz, P(CHCH$_3$cCH$_3$d)); ^{31}P{^{1}H} NMR: δ 62.3.

6.3.16 Preparation of 4.4a/4.4b

To a magnetically stirred suspension of Me$_2$SAuCl (0.11 g, 0.36 mmol) in toluene (2 mL) was added a solution of **1.20a** (0.12 g, 0.35 mmol) in toluene (3 mL). After 2 h at 24 °C, stirring was arrested, and residual solvent along with other volatiles were removed in vacuo. The residue was dissolved in minimal THF (2-3 mL) and filtered through Celite to remove black solid material. THF and other volatiles were removed in vacuo, and the resulting solid was washed with pentane (2 x 3 mL). Solvent and other volatiles were removed in vacuo, yielding **4.4a/4.4b** as a yellow/brown solid (0.11 g, 0.20 mmol, 56%). Melting point 169 – 170 °C. Anal. (%): Calcd for C$_{23}$H$_{22}$AuClNP: C, 47.97; H, 3.85; N, 2.43. Found: C, 47.72; H, 3.76; N, 2.39. ^{1}H NMR (CD$_2$Cl$_2$): δ 7.81 – 7.44 (m, 20H, **4.4a** & **4.4b**, Ph-H's), 7.30 (d, $^3J_{HH}$ = 7.5 Hz, 1H, **4.4b**, C4-H or C7-H), 7.18 (t, $^3J_{HH}$ = 7.5 Hz, 1H, **4.4a**, C5-H or C6-H), 7.04 (d, $^3J_{HH}$ = 7.5 Hz, 1H, **4.4a**, C7-H), 6.89 (t, $^3J_{HH}$ = 7.5 Hz, 1H, **4.4b**, C5-H or C6-H), 6.78 (t, $^3J_{HH}$ = 7.5 Hz, 1H, **4.4b**, C5 or C6), 6.72 (t, $^3J_{HH}$ = 7.5 Hz, 1H, **4.4a**, C5 or C6), 6.51 (d, $^3J_{HH}$ = 7.5 Hz, 1H, **4.4a**, C4-H), 6.21 (d, $^3J_{HH}$ = 7.5 Hz, 1H, **4.4b**, C4-H or C7-H), 5.60 (s, 1H, **4.4a**, vinylic C-H), 4.85 (d, $^2J_{PH}$ = 11.5 Hz, 1H, **4.4a**, allylic C-H), 3.79 (s, 2H, **4.4b**, CH$_2$), 3.08 (s, 6H, **4.4b**, N(CH$_3$)$_2$), 2.62 (s, 6H, **4.4a**, N(CH$_3$)$_2$); ^{13}C{^{1}H} NMR: δ 173.2 (**4.4b**, C2), 157.0 (**4.4a**, C2), 146.5 (**4.4a**, C3a or C7a),

135.4 (d, J_{PC} = 14 Hz, **4.4b**, aryl C-H), 134.8 (**4.4a**, 4° C), 133.8 (d, J_{PC} = 13 Hz, aryl C-

H), 133.3 (d, J_{PC} = 14 Hz, aryl C-H), 132.5 (aryl C-H), 131.3 (aryl C-H), 129.0 (d, J_{PC} = 12

Hz, aryl C-H), 128.6 (d, J_{PC} = 21 Hz, aryl C-H), 128.5 (J_{PC} = 22 Hz, aryl C-H), 128.3

(**4.4a**, C5 or C6), 126.0 (**4.4b**, C5 or C6), 124.0 (d, $^4J_{PC}$ = 4 Hz, **4.4a**, C4), 122.7 (**4.4b**,

C4 or C7), 121.4 (2 overlapping s, **4.4a**, C5 or C6, and **4.4b**, C5 or C6), 119.1 (**4.4b**, C4

or C7), 118.8 (**4.4a**, C7), 106.0 (**4.4a**, vinyl CH), 47.5 (d, $^1J_{PC}$ = 25 Hz, **4.4a**, allylic CH),

45.2 (**4.4b**, N(CH$_3$)$_2$), 42.1 (**4.4a**, N(CH$_3$)$_2$), 40.7 (d, $^3J_{PC}$ = 9 Hz, **4.4b**, CH$_2$); ^{31}P{^{1}H} NMR:

δ 47.9 (**4.4a**), 14.8 (**4.4b**).

6.3.17 Preparation of 4.5

To a magnetically stirred solution of **4.1** (0.12 g, 0.26 mmol) in THF (2 mL) was

added a solution of **1.19a** (0.062 g, 0.27 mmol) in THF (1.5 mL). After stirring for 0.1 h at

24 °C, the yellow solution was filtered through Celite, pentane (10 mL) was added and

the solution was placed in a -35 °C freezer. After several days, the supernatant was

decanted, the resulting crystals were washed with pentane (2 x 3 mL), and then solvent

and other volatiles were removed in vacuo to yield light brown crystals, **4.5** (0.13 g, 0.18

mmol, 69%). Crystals suitable for X-ray diffraction were grown from a concentrated

sample of **4.5** in THF at -35 °C. Melting point 160 – 161 °C. Anal. (%): Calcd for

C$_{30}$H$_{42}$AuClP$_2$: C, 51.69; H, 6.07; N, 0. Found: C, 51.73; H, 6.11; N, < 0.3. ^{1}H NMR

(C$_6$D$_6$): δ 7.93 (d, $^3J_{HH}$ = 7.5 Hz, 1H, C4-H or C7-H), 7.19 (d, $^3J_{HH}$ = 7.5 Hz, 1H, C4-H or

C7-H), 7.15 (t, $^3J_{HH}$ = 7.5 Hz, 1H, C5-H or C6-H), 7.08 (t, $^3J_{HH}$ = 7.0 Hz, 1H, C5-H or C6-

H), 6.97 (d, $^3J_{PH}$ = 7.0 Hz, 1H, C2-H), 3.01 (s, 2H, CH$_2$), 2.42 (m, 2H, P(C*H*CH$_3$CH$_3$)$_2$),

1.24 (dd, $^3J_{PH}$ = 17.5 Hz, $^3J_{HH}$ = 10.0 Hz, 6H, P(CHC*H$_3$*CH$_3$)$_2$), 0.96 (dd, $^3J_{PH}$ = 15.5 Hz,

$^3J_{HH}$ = 6.5 Hz, 6H, P(CHCH$_3$C*H$_3$*)$_2$); ^{13}C{^{1}H} NMR: δ 147.9 (C2), 145.1 (d, J_{PC} = 11 Hz,

C3a or C7a), 144.1 (d, J_{PC} = 6 Hz, C3a or C7a), 134.4 (d, J_{PC} = 26 Hz, C3), 126.3 (aryl

CH), 125.3 (aryl CH), 123.8 (aryl CH), 122.1 (aryl CH), 39.6 (d, $^3J_{PC}$ = 9 Hz, CH_2), 24.4

(d, $^1J_{PC}$ = 21 Hz, P(CHCH$_3$CH$_3$)$_2$), 19.8 (d, $^2J_{PC}$ = 8 Hz, P(CHCH$_3$$CH_3$)$_2$), 18.8

(P(CHCH$_3$CH$_3$)$_2$); ^{31}P{^{1}H} NMR: δ 35.2 (broad s, width at ½ height = 950 Hz).

6.3.18 Preparation of [4.6]$^+$ OTf$^-$

To a magnetically stirred solution of **4.5** (0.065 g, 0.093 mmol) in THF (3 mL) was

added a solution of AgOTf (0.024 g, 0.094 mmol) in THF. After 0.75 h at 24 °C, stirring

was arrested, and the light yellow solution was filtered through Celite. The solution was

placed in a -35 °C freezer, and after 2 weeks light yellow cubic crystals formed, which

proved to be suitable for X-ray crystallographic studies. Crystals were isolated and

washed with pentane (2 x 3 mL), and residual solvent and other volatiles were removed

in vacuo to yield [4.6]$^+$ OTf$^-$ (0.054 g, 0.067 mmol, 72%). Melting point 142 °C. Anal.

(%): Calcd for C$_{31}$H$_{42}$AuF$_3$O$_3$P$_2$S: C, 45.93; H, 5.52; N, 0. Found: C, 45.81; H, 5. 34; N, <

0.3. ^{1}H NMR (CD$_2$Cl$_2$): δ 7.85 (d, $^3J_{HH}$ = 7.5 Hz, 1H, C4-H or C7-H), 7.62 (d, $^3J_{HH}$ = 7.5

Hz, 1H, C4-H or C7-H), 7.35 (m, 1H, C5-H or C6-H), 7.31 (t, $^3J_{HH}$ = 7.0 Hz, 1H, C5-H or

C6-H), 7.26 (m, 1H, C2-H), 3.76 (s, 2H, CH_2), 2.96 (virtual t of septets, $^{2/4}J_{PH}$ = 2.5 Hz,

$^3J_{HH}$ = 7.0 Hz, 2H, P(CHCH$_3$CH$_3$)$_2$), 1.43 (virtual t of d, $^{3/5}J_{PH}$ = 10.0 Hz, $^3J_{HH}$ = 7.0 Hz, 6H,

P(CHCH_3CH$_3$)$_2$), 1.28 (virtual t of d, $^{3/5}J_{PH}$ = 8.5 Hz, $^3J_{HH}$ = 7.0 Hz, 6H, P(CHCH$_3$CH_3)$_2$);

^{13}C{^{1}H} NMR: δ 150.8 (C2), 144.1 (C3a or C7a), 143.4 (C3a or C7a), 129.9 (m, C3),

126.7 (C5 or C6), 126.5 (C5 or C6), 124.7 (C4 or C7), 121.1 (C4 or C7), 41.0 (virtual t,

$^{2/4}J_{PC}$ = 6 Hz, CH_2), 25.2 (virtual t, $^{1/3}J_{PC}$ = 16 Hz, P(CHCH$_3$CH$_3$)$_2$), 20.0 (P(CHCH$_3$CH$_3$)$_2$),

19.1 (P(CHCH$_3$$CH_3$)$_2$); ^{31}P{^{1}H} NMR: δ 53.0.

6.4 Summary of Crystallographic Data

Table 6.1 Crystallographic Data for Chapter 2 (**2.1**, **2.3a**, **2.4**, and **2.5**).

	2.1	2.3b	2.4	2.5
empirical formula	$C_{17}H_{26}Cl_2NPPt$	$C_{19}H_{32}NPPt$	$C_{17}H_{26}Cl_2NPPd$	$C_{20}H_{34}NPPtS$
formula weight	541.35	500.52	541.58	546.60
crystal dimensions	0.43 x 0.16 x 0.12	0.35 x 0.17 x 0.16	0.58 x 0.50 x 0.07	0.36 x 0.20 x 0.09
crystal system	orthorhombic	orthorhombic	monoclinic	monoclinic
space group	$P2_12_12_1$	$Pbca$ (No. 61)	$P2_1$ (No. 4)	$P2_1/n$
a (Å)	7.6580 (3)	13.3126 (11)	9.2767 (5)	10.388 (1)
b (Å)	15.2323 (6)	16.7227 (14)	10.7410 (6)	21.813 (2)
c (Å)	16.8331 (7)	18.1608 (15)	9.9877 (6)	10.570 (1)
α (deg)	90	90	90	90
β (deg)	90	90	101.6260 (9)	114.546 (2)
γ (deg)	90	90	90	90
V (Å^3)	1963.6 (1)	4043.0 (6)	974.77 (10)	2178.6 (4)
Z	4	8	2	4
r_{calcd} (g cm^{-3})	1.831	1.645	1.845	1.666
μ (mm^{-1})	7.496	7.018	5.130	6.612
2θ limit (deg)	52.72	52.82	52.70	52.82
	$-9 \le h \le 9$	$-16 \le h \le 16$	$-7 \le h \le 11$	$-12 \le h \le 12$
	$-19 \le k \le 18$	$-20 \le k \le 20$	$-13 \le k \le 13$	$-27 \le k \le 27$
	$-21 \le l \le 20$	$-22 \le l \le 22$	$-12 \le l \le 12$	$-13 \le l \le 13$
total data collected	12801	28838	5613	16628
independent reflections	4011	4144	3826	4466
observed reflections	3968	3349	3588	3792
R_{int}	0.0202	0.0409	0.0244	0.0347
absorption correction	multi-scan (SADABS)	multi-scan (SADABS)	multi-scan (SADABS)	multi-scan (SADABS)
range of transmission	0.4666–0.1409	0.3997–0.1926	0.7153–0.1549	0.5876–0.1994
data/restraints/parameters	4011 / 0 / 200	4144 / 0 / 201	3826 / 0 / 199	4466 / 0 / 219
R_1 [$F_o^2 \ge 2\sigma(F_o^2)$]	0.0155	0.0257	0.0304	0.0275
ωR_2 [$F_o^2 \ge -3\sigma(F_o^2)$]	0.0381	0.0650	0.0744	0.0672
goodness-of-fit	1.085	1.060	1.018	1.076
largest peak, hole (e Å^{-3})	1.433, -0.459	1.724, -0.646	1.238, -0.602	1.923, -0.331

Table 6.2   Crystallographic Data for Chapter 3 (**3.2**, **[3.7]**$^+$ BF$_4^-$, and **[3.9]**$^+$ BF$_4^-$).

	3.1	[3.7]$^+$ BF$_4^-$	[3.9]$^+$ BF$_4^-$
empirical formula	$C_{19}H_{31}AuNP$	$C_{20}H_{35}BF_4NPPtS$	$C_{36}H_{58}BClF_4N_2P_2Pt_2$
formula weight	501.38	634.42	1093.22
crystal dimensions	0.47 x 0.24 x 0.05	0.52 x 0.30 x 0.08	0.36 x 0.22 x 0.10
crystal system	orthorhombic	monoclinic	orthorhombic
space group	$Pbca$ (No. 61)	$P2_1/n$	$Pbca$ (No. 61)
a (Å)	13.2290 (8)	9.4505 (6)	17.2031 (9)
b (Å)	15.9825 (10)	18.1064 (11)	14.2970 (7)
c (Å)	18.6367 (12)	14.4908 (9)	32.2154 (16)
α (deg)	90	90	90
β (deg)	90	92.3590 (10)	90
γ (deg)	90	90	90
V (Å^3)	3940.4 (4)	2477.5 (3)	7923.5 (7)
Z	8	4	8
r_{calcd} (g cm^{-3})	1.690	1.701	1.833
μ (mm^{-1})	7.546	5.849	7.249
2θ limit (deg)	52.78	52.82	52.80
	$-16 \leq h \leq 16$	$-11 \leq h \leq 11$	$-21 \leq h \leq 21$
	$-19 \leq k \leq 18$	$-22 \leq k \leq 22$	$-17 \leq k \leq 17$
	$-23 \leq l \leq 23$	$-18 \leq l \leq 18$	$-40 \leq l \leq 40$
total data collected	25994	18843	50983
independent reflections	4030	5075	8107
observed reflections	3313	4572	7032
R_{int}	0.0378	0.0364	0.0511
absorption correction	multi-scan (SADABS)	multi-scan (SADABS)	multi-scan (SADABS)
range of transmission	0.7041–0.1256	0.6519–0.1509	0.5309–0.1800
data/restraints/parameters	4030 / 0 / 201	5075 / 0 / 263	8107 / 0 / 432
R_1 [$F_o^2 \geq 2\sigma(F_o^2)$]	0.0219	0.0211	0.0492
ωR_2 [$F_o^2 \geq -3\sigma(F_o^2)$]	0.0585	0.0542	0.1198
goodness-of-fit	1.016	1.068	1.298
largest peak, hole (e Å^{-3})	1.266, -0.829	0.838, -0.764	2.541, -1.555

Table 6.3   Crystallographic Data for Chapter 4 (**4.1**, **4.3**, **4.5**, and [**4.6**]⁺ OTf⁻).

	4.1	4.3	4.5	[4.6]⁺ OTf⁻
empirical formula	$C_{15}H_{21}AuClP$	$C_{17}H_{26}AuClNP$	$C_{30}H_{42}AuClP_2$	$C_{31}H_{42}AuF_3O_3P_2S$
formula weight	464.70	507.77	696.99	810.61
crystal dimensions	0.43 x 0.42 x 0.06	0.30 x 0.22 x 0.14	0.39 x 0.32 x 0.22	0.23 x 0.22 x 0.15
crystal system	monoclinic	triclinic	monoclinic	orthorhombic
space group	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)	$Pna2_1$ (No. 33)
a (Å)	15.625 (2)	9.3708 (10)	9.0257 (5)	26.567 (2)
b (Å)	7.3752 (10)	10.1136 (10)	20.3683 (11)	9.2095 (8)
c (Å)	15.269 (2)	10.3753 (11)	16.1902 (9)	13.1111 (12)
α (deg)	90	88.223 (2)	90	90
β (deg)	118.454 (2)	84.120 (2)	94.9747 (8)	90
γ (deg)	90	68.059 (2)	90	90
V (Å³)	1546.9 (4)	907.25 (16)	2965.2 (3)	3207.9 (5)
Z	4	2	4	4
r_{calcd} (g cm⁻³)	1.995	1.859	1.561	1.678
μ (mm⁻¹)	9.767	8.337	5.176	4.799
2θ limit (deg)	52.76	52.74	52.80	52.78
	$-19 \le h \le 19$	$-11 \le h \le 11$	$-11 \le h \le 11$	$-33 \le h \le 33$
	$-9 \le k \le 9$	$-12 \le k \le 12$	$-25 \le k \le 25$	$-11 \le k \le 11$
	$-19 \le l \le 19$	$-12 \le l \le 12$	$-20 \le l \le 20$	$-16 \le l \le 16$
total data collected	11475	6848	23284	24364
independent reflections	3156	3671	6071	6566
observed reflections	3005	3452	5602	5666
R_{int}	0.0313	0.0278	0.0219	0.0376
absorption correction	Gaussian integration (face-indexed)	Gaussian integration (face-indexed)	multi-scan (SADABS)	multi-scan (SADABS)
range of transmission	0.5918–0.1020	0.3882–0.1888	0.3955–0.2374	0.5330–0.4049
data/restraints/ parameters	3156 / 0 / 163	3671 / 0 / 190	6071 / 0 / 307	6566 / 0 / 416
R_1 [$F_o^2 \ge 2\sigma(F_o^2)$]	0.0218	0.0444	0.0160	0.0268
ωR_2 [$F_o^2 \ge -3\sigma(F_o^2)$]	0.0564	0.1373	0.0405	0.0600
goodness-of-fit	1.117	1.222	1.049	1.074
largest peak, hole (e Å⁻³)	0.907, -1.549	5.825, -1.278	0.768, -0.382	2.780, -0.433

6.5   References

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Chapter 7 – Conclusions

7.1   General Conclusions

The substituted indenes (and indenide) **1.19a/1.19b**, **1.20a/1.20b**, **1.21**, **1.22**,

and **1.23** were found to be suitable ligands for Pt(II), Au(III) and Au(I) metal centers. The

complexes resulting from such combinations were prepared and characterized by a

variety of techniques, and ultimately were found to exhibit similar structural features.

While the neutral Pt(II) complexes did not themselves exhibit noteworthy catalytic

activity, the observation of a "bit in" complex, presumably arising from intramolecular C-H

activation suggested that modifications to subsequent ligand generations might promote

intermolecular activation of inert bonds.

Conversely, a study of the closely related Au(III) zwitterionic species **3.1** and

neutral Pt(II) compound **2.3b** revealed that the Au zwitterion was remarkably stable in

the presence of E-H bonds. As such, the head-to-head comparison of electronic factors,

independent of complicating steric and counterion effects could not be conducted as

originally envisioned. A study of neutral and cationic Pt(II) species instead revealed that

while the neutral $(\kappa^2\text{-}P,N)$PtMeCl species **2.2** was a moderately effective catalyst for the

hydrosilylation of styrene, cations derived from AgCl abstraction formed less-competent

species, the identity of which was highly dependant on both solvent and Ag salt

employed. These findings underscored the value of catalysis studies employing

rationally prepared metal complexes, rather than those generated in situ.

Lastly, Au(I) complexes featuring both P,N and P-substituted indene ligands were

shown to serve as catalysts for the hydrosilylation of benzaldehyde, while a combination

of AgOTf and excess trialkylphosphine proved the most effective. This addition of excess

Et$_3$P to a solution of AgOTf was also found to be a suitable catalyst for the hydrosilylation

of benzaldehyde. This last result speaks to the importance of control reactions, as Ag

salts are commonly used activators for many late transition metal catalyst complexes.

These studies are also extremely relevant to the growing field of group 11 homogeneous

catalysis as they represent the first room temperature hydrosilylation by a homogeneous

Au(I) complex, as well as the first hydrosilylation reaction catalyzed by homogenous Ag.

7.2   Future Work

7.2.1   Chapter 2 – Neutral Pt(II) Complexes

It was found that by heating **2.3a** in the presence of an appropriate L donor (such

as Me$_2$S) the cyclometallated complex **2.5** was formed, presumably due to an

intramolecular C-H activation. This was significant because it implied that the amine

donor arm of the P,N ligand **1.19** was capable of decoordinating, as well as that the

resulting Pt fragment was capable of C-H bond activation. As such, the design of a

modified ligand that would be resistant to intramolecular C-H activation, while providing

access to a similar environment might lead to Pt complexes capable of intermolecular C-

H activation, examples of which are shown in Figure 7.1.

Figure 7.1   Three proposed modifications to the P,N ligand **1.19**.

Replacing the N(CH$_3$)$_2$ unit with a N(CF$_3$)$_2$ unit (**7.1**) is a logical modification, as

the C-F bond is stronger than a corresponding C-H bond,[1] and as such the activation of

a C-F bond is more difficult to achieve. A more simple solution would be to replace the

$N(CH_3)_2$ with an NH_2 group (**7.2**). Though N-H bonds are weaker than C-H bonds,[1] the resulting cyclometallated complex would feature a 5-membered ring instead of the 6-membered ring found in **2.6**, potentially resulting in greater steric repulsion of the indene backbone from the metal center. Another option is to employ an amino group derived from piperidine (**7.3a**) or *trans*-3,5-dimethylpiperidine (**7.3b**), where steric bulk prevents the α C-H's from approaching the Pt center, and as such, from intramolecular C-H activation. The use of the trans isomer of 3,5-dimethylpiperidine would be significant, as it would prevent the problematic formation of diastereomers upon complexation to a metal center; it may be prepared in reasonable quantity and yield using literature methods.[2] While it is expected that **7.2** and **7.3** may be readily prepared from 2-indanone,[3-5] it is likely that the electron-withdrawing CF_3 groups in **7.1** will interfere with this condensation, necessitating an alternate route similar to the recently reported Pd-catalyzed coupling of 2-bromoindene and secondary phosphines.[6]

Also of interest is the pronounced difference in reactivity observed between **2.4a** and the related cyclometallated complex **2.6** with E-H bearing substrates. This suggests that a bifunctional ligand featuring phosphine and sulfide donor groups may give rise to desirable metal-centered reactivity. Such a ligand might be constructed using a 2-thioanisylchloroalkylphosphine,[7] as shown in Scheme 7.1. This new ligand (**7.4**) might then serve as either a bifunctional P,S or trifunctional P,S,N ligand, based on the substitution at the 2-position (i.e. X = H, NMe_2). The use of bis(2-thioanisyl)chlorophosphine, prepared following the same methodology,[7] would generate a new, related ligand (**7.5**) that might serve as either a tridentate P,S,S or tetradentate P,S,S,N ligand, based on the substitution at the 2-position.
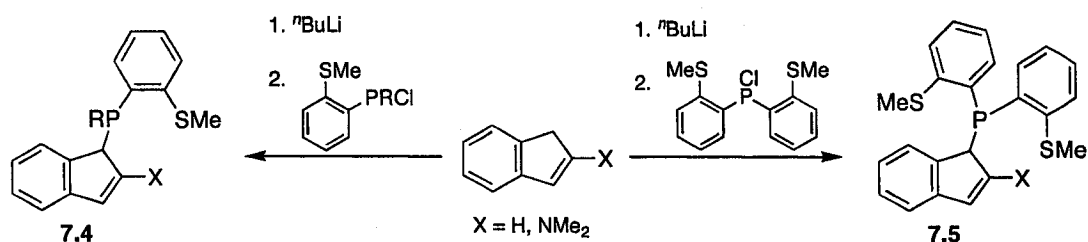
Scheme 7.1 Proposed route to P,S(,N) and P,S,S(,N) ligands related to **1.19**.

Lastly, the successful preparation of the $(\kappa^2\text{-P,N})$Pd complex **2.4** demonstrated the viability of **1.19** as a ligand for Pd(II). Further studies of the scope and reactivity, as well as the catalytic performance of this and related compounds are warranted, especially in light of the importance of Pd-mediated transformations in modern chemistry. Of interest would be the comparison of neutral, cationic and zwitterionic species ligated by **1.19** and **1.23** as catalysts for cross-coupling reactions. A brief survey of the preparation of such compounds starting from the Pd reagents [$(\eta^3\text{-allyl})$PdCl]$_2$, [Pd(OAc)$_2$]$_3$, and Pd$_2$(dba)$_3$ (dba = dibenzylideneacetone) met with limited success, though conditions were not optimized.

7.2.2 Chapter 3 – Cationic Pt(II) and Au(III) Complexes

It was observed that the cationic Pt(II) species employed as catalysts for the hydrosilylation of styrene performed poorer than related neutral species, possibly due to ion-pairing or irreversible coordination of solvent to the cationic metal center. As such, the use of a zwitterionic Pt(II) complex ligated by **1.23** (**7.6**, Figure 7.2) may serve to attenuate the electrophilicity of the metal center, and as such act as a superior catalyst. It would be interesting to examine the stability of **7.6** relative to the Au(III) zwitterion **3.1**, which was noted to be stable at high temperature for extended periods of time (see section 3.2.2).
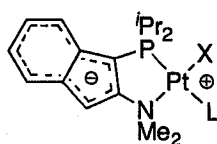
7.6a X = Me
7.6b X = Cl

Figure 7.2   A proposed zwitterionic Pt(II) complex, **7.6**.

Attempts to prepare **7.6a** from a combination of **1.23**[M] (M = Li, Na) and

(COD)PtMeA (A = Cl, BF_4) or **2.3b** and $NaN(SiMe_3)_2$ followed by Ph_3CBF_4 (as a methide-

abstracting agent) were unsuccessful in the presence of L-donors such as $HN(SiMe_3)_2$

and THF, yielding multiple products. Similarly, **7.6b** was not prepared cleanly from a

combination of **1.23**[M] (M = Li, Na) and either $[Cl_2Pt(Me_2S)_2]$ or $PtCl_2$ in the presence of

Me_2S or THF. However, a route that may prove more successful is deprotonation of the

indene framework of cationic complexes such as $[3.6]^+ BF_4^-$ or $[3.7]^+ BF_4^-$ using K_2CO_3 or

$MN(SiMe_3)_2$ (M = Na, K). Deprotonation of the indene ligand using such "gentle" bases

(as opposed to ^nBuLi used in the preparation of **3.1**, see section 3.2.1) has proved

successful for other late transition metal complexes.[5,8,9]

7.2.3   Chapter 4 – Au(I) Complexes

It has been shown that while Au(I) complexes ligated by the κ^1-*P*,N ligands **1.19a**

and **1.20a** exhibited poor activity as catalysts for the hydrosilylation of benzaldehyde,

similar complexes featuring the κ^1-*P* ligands **1.21** and **1.22** performed better under

identical conditions. Moreover, it was seen that an excess of a strongly donating

phosphine such as Et_3P, $^nBu_3P$ and $^tBu_3P$ in combination with a source of "AuCl" was an

active catalyst for the hydrosilylation of various aldehydes at both 70 °C and 24 °C. It is

proposed that other strongly donating phosphines, in the absence of an N-donor

functionality may also serve as efficient ligands for these reactions. As such, electron-

releasing phosphines such as those shown in Figure 7.3, when coupled with a source of

Au(I) (such as Me$_2$SAuCl) may generate suitable catalysts for the efficient hydrosilylation

of carbonyl and other unsaturated functionalities. Complexes of 1.10[10] and 7.7[11] have

proven effective as ligands for Pd-mediated coupling reactions in which alkyl phosphines

were also shown to be effective. Compound 7.8 may be readily prepared as its Li or Na

salt by treating either 1.21 (R = ^{i}Pr) or 1.22 (R = Ph) with ^{n}BuLi or NaN(SiMe$_3$)$_2$,

respectively.
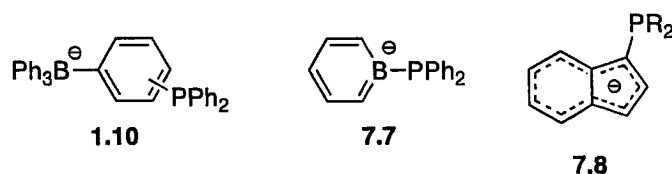
Figure 7.3   Electron releasing phosphines for Au(I) catalysts.

Also of interest would be a more detailed study of the active catalyst in the Au(I)

mediated hydrosilylation of aldehydes, as reported in Chapter 4. An ESI-MS study of a

solution of catalyst (catalyst = 3:20 4.1 and 1.21, or Me$_2$SAuCl and Et$_3$P/^{n}Bu$_3$P/^{t}Bu$_3$P)

should help to clarify coordination number of the most prevalent solution phase species,

and perhaps lead to increased understanding of the mechanism by which this

transformation occurs. Moreover, the gold alkoxide species implicated in the mechanism

presented in Chapter 4 (see Figure 7.4) should in theory serve as a valid entry point into

the catalytic cycle, if the reaction is indeed proceeding in this fashion. As such, a

rationally prepared, monomeric Au(I) alkoxide (7.9) in combination with excess 1.21

might prove to be catalytically active, and as such, lend credence to the proposed

mechanism.
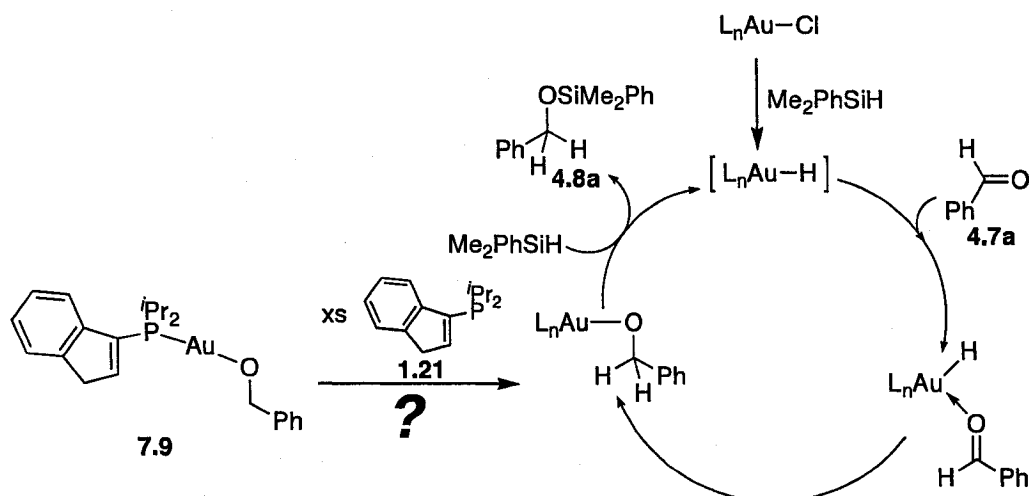
Figure 7.4 Proposed mechanism for the Au(I) catalyzed hydrosilylation of benzaldehyde, showing an alternate potential entry to the catalytic cycle.

Lastly, the $(\kappa^1\text{-}P,N)$Au(I) complexes that did not prove to be viable catalysts for the hydrosilylation of benzaldehyde (**4.3** and **4.4a/4.4b**) may prove to be effective in other reactions. One of the first Au catalyzed reports involving an ancillary ligand is the asymmetric aldol reaction to produce oxazolines, reported by Ito and co-workers.[12] In this report, the presence of a pendant amino group is required to orient and activate the substrate (Scheme 7.2). Moreover, the Cu catalyzed aldol reaction is accelerated by the addition of NEt_3,[13] suggesting that the synergistic benefit of an amino group may not be limited to Au complexes. As such, complexes **4.3** and **4.4a/4.4b** merit study as catalysts for the aldol reaction.
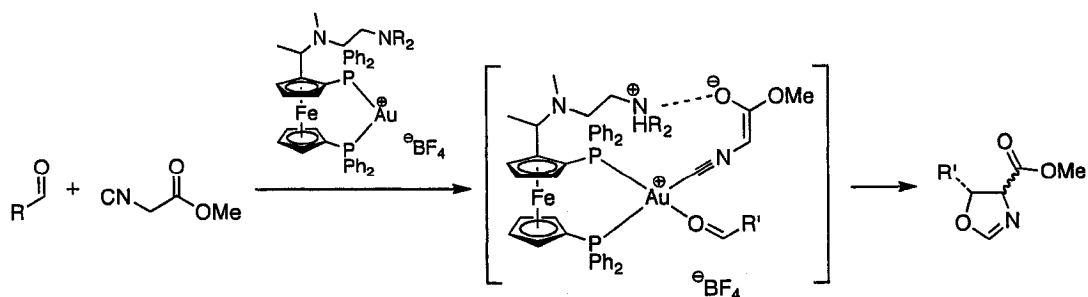
Scheme 7.2 A potential intermediate complex for the asymmetric aldol reaction, as proposed by (and adapted from) Ito and co-workers.[12]

7.2.4 Chapter 5 – Ag(I) Complexes

While a mixture of Et₃P and AgOTf was found to be a suitable catalyst system for the reduction of a variety of aldehydes, it was noted that ketones and alkenes were not reduced under the same conditions (see Chapter 5). This can be rationalized on the basis of the relative reactivity of the unsaturated group to be reduced, as demonstrated in Figure 7.5. As such, one might predict that the R₃P/AgOTf system would be a suitable catalyst for the reduction of imines. Similarly, the reduction of ketones and esters has been accomplished using a combination of CuH and a ligand, when an external base such as NaOᵗBu is added.[14-18] This suggests that ketone or ester reduction with silver might be feasible in the presence of a similar base, potentially permitting the use of prochiral ketones and esters in combination with a chiral phosphine and a cheap and abundant metal reagent (AgOTf) to generate chiral silyl ethers, which are of high synthetic utility.
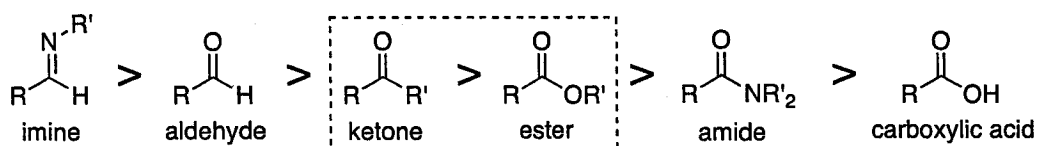
Figure 7.5 Relative ease of reduction (using hydride reducing agents) of carbonyl and related compounds, adapted from *Organic Chemistry*.[19]

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