METAL-LIGAND COOPERATIVITY IN FIRST ROW TRANSITION METALS:
HYDROSILYLATION CATALYSIS AND MECHANISTIC INSIGHTS

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Abstract

The utility of transition metal catalysts has greatly expanded the scope of organic reactions. Historically, homogenous catalysis is dominated by platinum group metals (PGMs) due to their relative high activity and stability to air when compared to the 1st row counterparts of PGMs. However, 1st row late transition metals such as Fe, Co, and Ni offer the advantage of being low cost and earth abundant. This is especially critical when considering that catalyst recycling technologies do not exist for some large scale industrial catalysis, such as the crosslinking of silicone polymers. Recent strive for more sustainable chemical processes has fueled the search for new modes of metal-promoted substrate activation that extend beyond classical organometallic transformation (ie. oxidative addition, reductive elimination, insertion etc.). To this end, metal-ligand cooperative (MLC) activation of small molecules has been implemented in a number of remarkably active 1st row transition metal catalysts. These MLC reactions involve either bond breakage/formation between substrates and ligand, or electronic transformations of the ligands during catalytic reactions.

Hydrosilylation of alkenes is one of the most important reactions in the silicone industry, which is currently dominated by catalysts based on PGMs. 1st row transition metal catalysts for this process typically exhibit low turnover numbers and suffer from severe side reactions, such as dehydrogenative silylation and hydrogenation. However, recent progress has suggested 1st row transition metals employing ligands that assist in MLC activation of hydrosilanes have high potential in promoting PGM-like hydrosilylation activity. Chapter 1 gives an overview of MLC strategies and the classes of metal complexes that exhibit MLC activity, with emphasis on hydrosilylation.

Chapter 2 presents the successful employment of one type of MLC strategy to a diphosphine-dialkoxide iron(II) system, Fe(P₂O₂)(CO)L (L = CO, NCMe, PMe₃, py, acetamide). An unprecedented activation mode of silanes was observed. The iron-alkoxo functionality reacted with silanes to give hydridoiron(II) species with a pendent silyl-ether ligand. Similar activation modes have only been described for a few complexes containing metal-sulfur bonds. The Fe(P₂O₂)(CO)L complexes were also active for catalytic
hydrosilylation of aldehydes, ketones, and styrene. The catalytic activity was observed to be dependent on the binding affinities of L.

Imine ligands have received increased attention in the past decade due to their ability to assist in substrate activation via MLC pathways. Platforms incorporating both imine and phosphines have shown great promise in 1st row transition metal catalyzed hydrofunctionalization reactions. Chapter 3 describes the reactivity of a series of iron complexes containing a phosphine-imine ligand, 2-Ph₂PC₆H₄CH=N(4-ClC₆H₄)(PCH₂ArCl). These complexes show rich redox chemistry that involve the ligand, including redox induced hapticity change and C-imine-C-imine bond coupling reactions.

Chapter 4 expands on the theme of phosphine-imines to incorporate pyridines in a new ligand system. The resulting phosphine-imine-pyridine (PNpy) platform belongs to the large class of α-diimine ligands. The modular synthesis of PNpy provides a convenient system to tune the steric and electron richness of the ligands. Synthesis of several PNpy ligands and the corresponding metal-dihalide complexes are described.

Chapter 5 focuses on Co-(PNpy) complexes obtained by formal 1e reduction of the corresponding Co(II) species. These compounds are active hydrosilylation catalysts, with rates and selectivity dependent on the PNpy ligands employed. In particular, the catalyst system CoCl₂(P₂PC₃Npy)/2NaBEt₃H gave near quantitative anti-Markovnikov hydrosilylation of 1-octene using Ph₂SiH₂ after 15 mins with 1 mol% [Co] loading. DFT studies highlighted the redox non-innocence of PNpy, which is possibly relevant to the high catalytic activity observed. In-situ NMR studies revealed several details related to the mechanism of hydrosilylation: (1) alkene binding is observed in the form Co(SiR₃)(PNpy)(styrene), (2) silanes protonolyze catalyst precursors to give s-silyl complexes, Co(SiR₃)(PNpy)(PPh₃), and (3) ethylene inserts into the Co-Si bond to give Co(CH₂CH₂SiR₃)(PNpy)(PPh₃).

Chapter 6 presents the synthesis, reactivity and electrochemistry of reduced Fe-(PNpy) complexes. Some of these species exhibited high activity for selective anti-Markovnikov hydrosilylation. The electrochemical investigation of Fe(PNpy)(CO)₂ complexes revealed unique redox properties when compared to currently known phosphine-α-diimine platforms.
Chapter 7 describes preliminary studies on Fe, Co, and Ni complexes incorporating phosphine-amide-pyridine and phosphine-amine-pyridine ligands. These ligands were conveniently obtained by reduction of PNpy. The iron(II)-amido complex [Fe(\text{Ph}_2 \text{P} \text{C}_6 \text{H}_4 \text{(amide)py})(\text{CO})_2]^+ reacted with H_2 to form iron(II)-hydrides. This represents a promising strategy for catalytic hydrogenation. The cationic [NiBr(\text{Ph}_2 \text{P} \text{C}_6 \text{H}_4 \text{N} \text{Hpy})]^+ is a pre-catalyst for selective anti-Markovnikov hydrosilylation. It is proposed that the active species is a nickel(II)-hydride that forms by reaction of the precatalyst with HSiR_3 to give BrSiR_3 and [NiH(\text{Ph}_2 \text{P} \text{C}_6 \text{H}_4 \text{N} \text{Hpy})]^+. 
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**Abbreviations**

- **bda**: benzylideneacetone
- **Fe**\(^+\): ferrocenium, \([\text{Fe}(\eta^5\text{-C}_5\text{H}_5)_2]^+\)
- **VPDMS**: vinylpentamethyldisiloxane, \(\text{CH}_2\text{CHSiMe}_2\text{OSiMe}_3\)
- **HMTS**: 1,1,1,3,5,5-heptamethyltrisiloxane, \(\text{HSiMe(OSiMe}_3)^2\)
- **DIP**: diiminopyridine
- **bipy**: 2,2'-bipyridine
- **THF**: tetrahydrofuran
- **BAr\(^4\)**: tetrakis(3,5-bis(trifluoromethyl)phenyl)borate, \([\text{B(C}_6\text{H}_3(\text{CF}_3)_2}_4]\)^-\n- **Cy**: clycohexyl, \(\text{C}_6\text{H}_{11}\)
- **PCHO**: 2-diphenylphosphinobenzaldehyde, 2-(Ph\(_2\)P)C\(_6\)H\(_4\)CHO
- **PGM**: platinum-group metals
- **MLC**: metal-ligand cooperation
- **TON**: turnover number
- **TOF**: turnover frequency
- **OTf**: \((\text{O}_3\text{SCF}_3)^-\)
- **Et**: ethyl, \(\text{C}_2\text{H}_5\)
- **iPr**: isopropyl, \(\text{CH(CH}_3)_2\)
- **Ph**: phenyl, \(\text{C}_6\text{H}_{11}\)
- **Me**: methyl, \(\text{CH}_3\)
- **tBu**: tert-butyl, \(\text{CH(CH}_3)_3\)
- **PCHN\(^{\text{ArCl}}\)**: 2-(Ph\(_2\)P)C\(_6\)H\(_4\)CH=N-(4-ClC\(_6\)H\(_4\))
- **NMR**: nuclear magnetic resonance
- **IR**: infra-red
- **EPR**: electron paramagnetic resonance
- **ESI-MS**: electrospray ionization mass spectrometry
- **1D-NOESY**: 1-dimensional nuclear overhauser effect spectroscopy
- **HMBC**: heteronuclear multiple bond correlation
- **HSQC**: heteronuclear single quantum coherence spectroscopy
- **DFT**: density functional theory
Chapter 1.

First row transition metal catalysis promoted by metal-ligand cooperative activity

Transition metal catalysts have greatly expanded the scope of organic reactions. Classical metal catalysis enable numerous bond transformations facilitated by oxidative addition, reductive elimination, β-hydride elimination, migratory insertion, ligand dissociation/association etc. at the metals. These reactions proceed via 2e processes that are favorable for 2nd and 3rd row transition metals, explaining the widespread adoption of these materials in homogeneous catalysts. In contrast, 1st row transition metals can form stable species by 1e redox reactions that are thermodynamically and kinetically more favorable than 2e changes.\(^1\) In particular, reactions that involve net oxidative addition of substrate to 1st row transition metal complexes typically undergo radical mechanisms that easily fall into thermodynamic traps that terminate catalytic turnover.\(^2\) Consequently, homogeneous 1st row transition metal catalysts are typically significantly less efficient than their 2nd and 3rd row counterparts, exhibiting lower TONs and TOFs.

Homogeneous catalysis is currently dominated by platinum group metals (PGMs) that are expensive and treated as precious commodities. The recent strive for “sustainable” chemistry has fueled tremendous efforts in replacing PGMs with earth-abundant 1st row transition metals for catalysis.\(^3\) New modes of substrate activation by metal complexes have been targeted to facilitate substrate activation, often circumventing unfavorable

Scheme 1.1 Examples of classical organometallic reactions.
electronic transformations at the metal center. To this end, metal-ligand cooperative (MLC) strategies have been remarkably successful in promoting catalytic activity in 1\textsuperscript{st} row transition metal complexes.\textsuperscript{4} Common MLC reactions include heterolytic cleavage by highly polar M-X bonds, activation of H-R bonds by dearomatization/aromatization of pyridine-based metal complexes, and substrate activation promoted by redox-active ligands (Scheme 1.2).

\begin{center}
\textbf{Cooperative activity of M-X bonds}
\[
L_nM{-}X + A{\longrightarrow}B \xrightarrow{\text{L}_nM{-}X} \xrightarrow{\text{A}{\longrightarrow}B} \xrightarrow{\text{L}_nM{-}X} \xrightarrow{\text{A}{\longrightarrow}B} \xrightarrow{\text{L}_nM{-}X}
\]
\end{center}

\begin{center}
\textbf{Cooperative activity of metals with redox-active L}
\[
(L^m)M^n + A{\longrightarrow}B \xrightarrow{\text{(L}^m+x)M^{n+2-x}} B
\]
\end{center}

\begin{center}
\textbf{Cooperative dearomatization/aromatization}
\[
\text{X}
\]
\end{center}

\begin{center}
\textbf{Scheme 1.2} MLC activation of substrates.
\end{center}

Homogeneous hydrosilylation represents one of the largest industrial processes that utilizes PGMs. The high cost and lack of catalyst recovery technologies for these metals motivates the search for low-cost replacements. In particular, recent progress has suggested that 1\textsuperscript{st} row late transition metal complexes that are capable of MLC substrate activation are strong candidates in the campaign of sustainable hydrosilylation catalysts.\textsuperscript{5} These mechanisms are reminiscent of small molecule activation pathways in metal enzymes. Biological systems incorporate earth abundant metals that are easily accessible into metallo-proteins to perform substrate activation by cooperative effects between the metal and surrounding amino-acid residues.\textsuperscript{6} In this thesis, MLC strategies using new base-metal complexes are described, with emphasis on silane activation and hydrosilylation catalysis.
1.1 Late transition metal-alkoxo and metal-amido complexes

Metal-catalyzed organic synthetic reactions involving C-C and C-H bond formation have greatly motivated our interest in metal-carbon and metal-hydrogen bonds, since these catalytic transformations often invoke mechanisms with intermediates containing these bonds. On the other hand, metal-oxygen and metal-nitrogen bonds have been implicated in many metal-catalyzed mechanisms oxidation reactions and biological processes. These reactions propose reactive intermediates containing terminal alkoxo (-OR) or amido (-NR$_2$) ligand.

Important industrial examples of homogenous catalytic reactions invoking intermediates containing metal-oxygen and metal-nitrogen bonds (hereafter abbreviated “M-X”) include hydroamination, and the Wacker olefin oxidatio. One possible pathway for the hydroamination of olefins initiates by oxidative addition of HNR$_2$ to the metal center, giving M-NR$_2$ bonds. The NR$_2$ group transfer takes place through migratory insertion into the olefin, forming the carbon-nitrogen bond. The Wacker process can be thought of as the “mechanistic relative” of hydroamination. In a proposed pathway, H$_2$O reacts with the Pt catalyst to give Pt-OH species. Similar to hydroamination, the OH group transfer proceeds via insertion. These mechanistic proposals underscore the critical roles of M-X bonds in metal-catalyzed reactions of carbon-heteroatom bond formation.

Despite the relative wealth of literature on early and middle transition-metal complexes containing these ligands, simple monomeric late transition metal complexes containing M-X bonds are historically less common. One of the reason is due to the difficulty of synthesis, which is often plagued by facile formation of the multinuclear derivatives bridged by O or N atoms. Nevertheless, synthesis of these complexes generally fall in one of the following categories: (1) salt metathesis, (2) oxidative addition of H-X and (3) $\sigma$-ligand metathesis. Examples of each of these synthetic methods are given in Scheme 1.3.
Compared to metal-carbon and metal-hydrogen bonds, the properties of M-X are more sensitive to the metal center, and reactivity can vary dramatically. Depending on the electronic structure of the metal, lone pair electrons can engage in $\pi$-interactions with metal $d$-orbitals that can either stabilize or weaken the covalent M-X bonding interaction. It is generally believed that early transition metals with high oxidation state and low $d$-electron counts promote strong bonds with alkoxo and amido ligands through ligand-to-metal $\pi$-

Scheme 1.3 Synthesis of metal-alkoxo/amido complexes.
bonding. In this scenario, lone pairs are stabilized by interacting with empty $d_\pi$ orbitals. Consequently, stable monomeric early transition metal species containing M-X bonds are abundant in literature. On the other hand, metals with high $d$-electron count do not allow for these favorable M-X $\pi$-bonds due to filled $d_\pi$ orbitals. Instead, $\pi$-donation from the alkoxo or amido ligands results in occupation of the antibonding orbitals, effectively decreasing the bond order, weakening the M-X bond. This $p_\pi$-$d_\pi$ repulsion model is often proposed for late transition metal complexes with M-X bonds, and has been discussed extensively by Caulton and Mayer.\textsuperscript{14}

\textbf{Scheme 1.4} MO representations of the $p_\pi$-$d_\pi$ repulsion model.

However, extensive work of Bergman and Bryndza revealed that the high reactivity of M-X bonds does not generally correlate with weak bond dissociation energies (BDE).\textsuperscript{15} Instead, the high activity can be attributed to electrostatic interactions of the metal and ligand that promote facile heterolytic cleavage of M-X. Bergman et al. propose using Drago’s Electrostatic-Covalent theory for qualitatively determining M-X bond strengths.\textsuperscript{16} In this model, the BDE comprises of two elements: the ionic bond energy and the covalent bond energy. The low electronegativity of late transition metals, compared to that of the O and N atoms, give rise to highly polar M-X bonds with large ionic character that dominate the BDE calculations in Drago’s model. The result of this polarization is strong M-X bonds (ie. large BDE) in late transition metal complexes.

With the development of general synthetic methods, knowledge regarding M-X bond reactivity has greatly progressed in the past 20 years. There has recently been a surge
of reports on monomeric metal-alkoxo/amido catalysts, with M-X bonds proposed to play vital roles in reactions that extend from the typical nucleophilic and acid/base reactions seen for M-X bonds.

1.2 M-X cooperation for homogenous hydrofunctionalization catalysis

Metalloenzymes have long been known to function through MLC mechanisms. This usually involves bond formation/breakage of substrates with the amino acid residues surrounding the active site. For example, the [Ni-Fe]-hydrogenases are proposed to activate H₂ by heterolytic splitting across the metal-sulfur bond, giving a hydridonickel and protonated cysteine (Scheme 1.5). This mode of heterolytic cleavage of H₂ has inspired development of catalysts containing M-X bonds.

Based on this type of cooperativity seen in enzymes, the concept of MLC have attracted considerable attention in organometallic catalyst designs, especially in the field of hydrofunctionalization reactions with unsaturated bonds. The breakthrough work of Noyori has drastically changed the face of catalytic hydrogenation of C=O functional groups. Incorporation of protic neutral diamino ligands into Ru-H catalysts has yielded several hydrogenation and transfer hydrogenation catalysts with high TON and TOFs. These catalysts are proposed to function through a metal-ligand cooperative H₂ transfer to C=O bonds via a six-member pericyclic transition state (Scheme 1.6, left). Furthermore, chiral diamines can be introduced to the catalyst to effect asymmetric hydrogenation.

Related to hydrofunctionalization of double bonds, the dehydrogenation of alcohols or reduction of aldehydes/ketones catalyzed by the Shvo complex provides another early example of metal-ligand cooperation. While the catalyst was discovered in the 1980s, it wasn’t until some 15 years later that compelling evidence of an MLC outer-sphere
mechanism was provided by Casey et al. for the dehydrogenation of alcohols. In this mechanism the protic \( OH \) of the alcohol substrate is transferred to the cyclopentadienone ligand O atom to form a hydroxycyclopentadienyl ligand, and the acidic \( CH \) is transferred to the metal center giving a Ru-H (Scheme 1.6, right).\(^{20}\)

\[
\text{Scheme 1.6 Examples of MLC catalysts. Left: proposed mechanism of C=O bond hydrogenation using a diamino ruthium hydride catalyst. Right: proposed mechanism of alcohol oxidation catalyzed by Shvo’s complex.}
\]

Following the early examples, new reactivity has been reported for 1\(^{st}\) row late transition metal complexes promoted by MLC over the past decade.\(^{4a}\) Substantial increases in TON and TOFs has been observed for hydrofunctionalization reactions catalyzed by these complexes. Among these examples, the diphosphine amine \( \text{PN}^\text{H} \text{P} \) ligands (\( \text{PN}^\text{H} \text{P} = \text{HN}[(\text{CH}_2)_2\text{PR}_2]_2 \)) are some of the most effective in promoting MLC. The iron(II) carbonyl complex, Fe(\( \text{H} \))\(_2\)\( (\text{PN}^\text{H} \text{P})(\text{CO}) \), reported by Guan’s group, is the first iron-based system for hydrogenation of unactivated esters.\(^{21}\) The complex FeH(\( \text{PNP} \))(\text{CO}), obtained from loss of H\(_2\) from Fe(\( \text{H} \))\(_2\)\( (\text{PN}^\text{H} \text{P})(\text{CO}) \), catalyzes acceptorless dehydrogenation of alcohols under mild and base-free conditions, possibly by concerted \( N \)-protonation and hydride transfer to the metal. The cationic cobalt complex \([\text{Co}(\text{CH}_2\text{SiMe}_3)(\text{PN}^\text{H} \text{P})]^+ \) was reported by Hanson’s group to be active for hydrogenation of C=C, C=O, and C=N bonds. The participation of the NH functional group of \( \text{PN}^\text{H} \text{P} \) was highlighted by showing the dramatically decreased activity of the aprotic derivative, \([\text{Co}(\text{CH}_2\text{SiMe}_3)(\text{PN}^\text{Me} \text{P})]^+ \)
(PN\textsuperscript{Me}P = MeN[(CH\textsubscript{2})\textsubscript{2}PR\textsubscript{2}]\textsubscript{2}).\textsuperscript{22} Cooperative activation of H\textsubscript{2} and hydrosilanes have also been described for the Fe-, Co- and Ni-borane complexes.\textsuperscript{2c,5a,23}

![Diagram of chemical reactions](image)

**Scheme 1.7** Examples of MLC heterolytic H\textsubscript{2} cleavage promoted by base-metals.

Examples of 1\textsuperscript{st} row transition metal catalysis utilizing MLC is still largely focused on nitrogen-containing moieties. High basicity of amido ligands and the low lability of coordinated amines are desirable properties for substrate activation and catalytic turnover. Alkoxo ligands have great potential in MLC activation of hydrosilanes. M-OR impart less steric hindrance compared to M-NR\textsubscript{2}, and the oxygen atoms form stronger bonds with Si. It may be fruitful to integrate these ligands into 1\textsuperscript{st} row transition metal complexes to promote catalytic transformations.
Shuttling of electrons between metal complexes and substrates is an important aspect of catalysis. Redox processes entailing simultaneous 2e transfer are essential to many catalytic reactions and are favorable for PGMs, but significantly less so for 1st row late transition metals due to their ability to form stable species that differ by only 1e.\(^1\)

**Scheme 1.8** Proposed mechanism of alcohol reduction by GO.

### 1.3 Redox non-innocent ligands

Shuttling of electrons between metal complexes and substrates is an important aspect of catalysis. Redox processes entailing simultaneous 2e transfer are essential to many catalytic reactions and are favorable for PGMs, but significantly less so for 1st row late transition metals due to their ability to form stable species that differ by only 1e.\(^1\)
These so-called redox-active ligands can undergo oxidation/reduction reaction by 1 or 2e\(^-\). The term “redox non-innocent” was originally used by Jørgensen to describe the ambiguity of metal oxidation states when it is coordinated by these ligands.\(^{24}\) A simple example is nitric oxide (NO). The “brown ring test” reaction was originally formulated \([\text{Fe(H}_2\text{O)}_6]^{2+} + \text{NO} \rightarrow [\text{Fe(II)(H}_2\text{O)}_5(\text{NO})^+]^{2+}\). It was later found that iron(II) undergoes oxidation instead to give iron(III), whereas NO is reduced by 1e\(^-\) to give \([\text{Fe(III)(H}_2\text{O)}_5(\text{NO})^-]^{2+}\).\(^{25}\) In recent years, redox-active ligands have been implemented in 1\(^{\text{st}}\) row transition metal catalysts.\(^{27\ 28\ 29\ 30}\)

Redox-active ligands are preceded in biological systems. They have been proposed to be crucial in enabling the utilization of earth-abundant metals to activate small molecules.\(^{31}\) For example, galactose oxidase (GO) is a copper-containing metalloenzyme with redox-active tyrosyl ligands coordinated to the metal center. GO exhibits three distinct oxidation states: the fully reduced state (RGO), the intermediate oxidation state (IOGO), and the fully oxidized state (OGO), each separated by 1e\(^-\). The IOGO is an inactive form that can be activated by reduction of 1e\(^-\). This reduction reaction does not change the oxidation state of the Cu metal center, but instead gives the OGO containing a reduced tyrosyl radical ligand (Scheme 1.8).\(^{32}\) Thus, catalytic reduction of alcohols is achieved by the cooperative effects of the Cu center and tyrosyl ligands, avoiding 2e\(^-\) reaction steps that are unfavorable for 1\(^{\text{st}}\) row transition metals.

\[\begin{align*}
\alpha\text{-diimine} & \\
R^1 & \quad R^3 \\
R^2 - N & \quad - N - R^4 \\
\quad + e^- & \quad - e^- \\
\quad - e^- & \quad - e^- \\
\end{align*}\]

\[\begin{align*}
\text{DIP} & \\
R^1 & \quad R^3 \\
R^2 - N & \quad - N - R^4 \\
\quad + e^- & \quad - e^- \\
\quad - e^- & \quad - e^- \\
\end{align*}\]

\textbf{Scheme 1.9} Various oxidation states of \(\alpha\text{-diimine}\) and DIP ligands.

Many synthetic ligands are recognized to exhibit redox-active behavior.\(^{33}\) Among these, ligands containing \(\alpha\text{-diimine}\) functionality have shown great success in promoting
catalytic reactions with base-metals. The conjugated $\pi/\pi^*$ systems in $\alpha$-diimines give rise to low-lying $\pi^*$-orbitals can accept up to 2e to afford ene-diamido ligands (Scheme 1.9).

Within this category, DIP ligands are exceptional. The extended $\pi$-network of DIP can support an open-shell di-radical dianion. The extensive work by Chirik et al. has shown that base metals supported by DIP ligands show PGM-like oxidative addition/reductive elimination reactivity. This behavior was elegantly demonstrated by oxidative addition of biphenylene to $\text{Fe(II)}(\text{DIP}^2)(\text{N}_2)_2$, where both $\text{Fe(II)}$ and $\text{DIP}^2$ undergo 1e oxidation respectively to give the product (Scheme 1.10).$^{27g}$

![Scheme 1.10 Oxidative addition of biphenylene to Fe(DIP)(N2)2.](image)

### 1.4 Reaction of metal complexes with hydrosilanes

Catalytic hydrosilylation is the most important method for making C-Si bonds. Hydrosilanes are frequently used in the reduction of unsaturated bonds.$^{34}$ Pt-catalyzed hydrosilylation (discussed in more detail in section 1.5) is one of the most important reactions in silicone industry. For these reasons, the reactivity of hydrosilanes and metal complexes is the focus of intense research.$^{35}$

Interaction of hydrosilanes with metals can range from weak dative bonds to complete oxidative addition to afford metal-silyl-hydrido complexes (Scheme 1.11).$^{35}$ Si-H bonds can act as $\sigma$-donors when there is significant overlap with an empty metal $d$-orbital of $\sigma$ symmetry. This dative bonding is similar to the agostic interaction of metals with C-H and H-H functionalities, though hydrosilanes are stronger ligands due to the higher basicity and better overlap with metal $d_\sigma$ orbitals.$^{36}$ In addition, higher degree of interaction between Si-H $\sigma^*$ orbitals and metal $d_\pi$ orbitals make them better $\pi$-acceptors compared to C-H and H-H. The metal-to-ligand $\pi$-backdonation results in the decrease of Si-H bond order, which may lead to bond scission and oxidative addition at the metal.
The nature of σ-bonded silyl complexes require coordinatively unsaturated metals centers. As a consequence, ligand dissociation is a common prerequisite in many reactions of complexes with hydrosilanes. Formation of silyl or hydrido metal bonds frequently eliminate small molecules by reductive elimination or σ-bond metathesis (Scheme 1.12). σ-bond metathesis mechanism involve a four-membered ring transition state that requires the orbitals to be of the appropriate symmetry in addition to a vacant metal d-orbital. Consequently, this reaction type is historically characterized as a reaction specific for high oxidation state early transition metal complexes with d⁰ electron counts. In recent years, examples of low-valent late transition metals engaging in σ-bond metathesis reactions have increased significantly, with the most prominent example being Hartwig’s report on reaction of HB(catecholate) with CpRuMe(PPh₃)₂ to form MeB(catecholate) and CpRuH(PPh₃)₂.

Scheme 1.11 Reaction of hydrosilanes with metals.

Scheme 1.12 Silyl-/hydrido-transfer from hydrosilanes to metals.
1.5 Catalytic hydrosilylation of alkenes

Hydrosilylation of alkenes is one of the most important reactions in the silicone industry. It is widely applied in the synthesis of silicone polymers. Crosslinking of polymeric vinylsiloxanes with hydrosiloxanes proceed via homogeneous hydrosilylation to give three-dimensional networks of silicones (Scheme 1.13). Products of this so-called “curing” process include silicone rubbers, liquid injection molded materials, adhesives and paper release coatings.\(^{40}\)

\[
\begin{align*}
\text{Si-O-Si} & \quad + \quad \text{Si-O-Si} \quad \xrightarrow{[\text{Pt}]} \quad \text{Si-O-Si} \\
\end{align*}
\]

Scheme 1.13 Curing of polysilicones.

The net addition of hydrosilanes to C=C is an atom economical route to functionalized organosilanes. The first milestone in hydrosilylation was in the 1950s when Speier reported that isopropanol solutions of chloroplatinic acid were an effective catalyst. However, Speier’s system required long induction periods and activity was insufficient for certain large scale processes. The Karstedt’s catalyst, Pt\(_2\)(O(SiMe\(_2\)CH=CH\(_2\))\(_2\))\(_3\), was developed in the 1970s to improve on Pt-catalyzed hydrosilylations. Its remarkable activity has made it one of the most widely employed hydrosilylation catalysts to date, often operating at ppm concentrations.\(^{41}\) Both Speier’s and Karstedt’s catalysts are proposed to function as the mononuclear Pt(0) species containing labile ligands.\(^{42}\) In addition to high TONs and TOFs, regioselective catalysts are required for curing processes to obtain the desired properties of the crosslinked materials, and production of functional organosilanes demand exquisite chemo-/regio-selectivity. Recent advances in Pt-catalyzed hydrosilylation have been steered towards increased catalyst stability and selectivity. The most notable examples are the NHC-modified (NHC = N-heterocyclic carbenes) versions of Karstedt’s catalyst developed by Markó et al.\(^ {43}\) It is proposed that the NHC ligands remain bound to the Pt-center in the catalytic cycle, which prevents formation of colloidal Pt and offer enhanced selectivity by ligand modification compared to Karstedt’s catalyst.\(^ {44}\)
1\textsuperscript{st} row late transition metal catalysts for hydrosilylation. Given the superior activity compared to other metals, curing of silicones heavily rely on Pt-based catalysts. Some applications are not amenable to recovery of catalysts.\textsuperscript{45} In fact, it is estimated that 4-6 metric tons of Pt is consumed per year in curing processes alone.\textsuperscript{46} Therefore, search for low-cost alternatives remains an important goal in industrial hydrosilylation. 1\textsuperscript{st} row late transition metals such as Fe, Co and Ni are the opposites of Pt in terms of cost and earth abundance, but significant challenges remain in hydrosilylation utilizing these metals. The majority of known base metal catalysts suffer from low selectivity and severe side reactions, such as dehydrogenative silylation and alkene hydrogenation (Scheme 1.14). Though Fe(CO)\textsubscript{5} catalyzes hydrosilylation of 1-hexene, reaction conditions continuous UV-radiation, and are accompanied with significant dehydrogenative silylation.\textsuperscript{47} The related Co\textsubscript{2}(CO)\textsubscript{8} showed similar limitations.\textsuperscript{48}

It wasn’t until almost three decades after the discoveries of Fe- and Co-carbonyl catalysts did base-metals receive serious consideration as viable alternatives to Pt for hydrosilylation, though examples of high turnover catalysts remain rare. The groundbreaking work of Chirik and Bart in 2004 on the highly efficient and selective Fe(DIP)N\textsubscript{2} has encouraged significant efforts in ligand designs for effective base-metal catalysts, often with considerations of electronic structure. Huang et al. reported a chemoselective phosphinite-iminopyridine iron catalyst for hydrosilylation operating at 1 mol\% catalyst loading in 23 °C. It was proposed that the phosphinite-iminopyridine ligand supports an electronic structure similar to that of Fe(DIP)N\textsubscript{2}.\textsuperscript{49}
In terms of Co catalysts, Brookhart reported in 1993 the sigma complex [CoCp*(P(OMe)3)CH2CH2-μ-H]+ that catalyzes the anti-Markovnikov hydrosilylation of 1-hexene and Et3SiH with TONs up to 400.50 However, no notable reports of Co-catalyzed hydrosilylation was seen in the 20 years after. In 2013, Deng’s group showed a new type of Co(II) complex that catalyzes the selective hydrosilylation of 1-octene using PhSiH3 with as low as 0.005 mol% loading.51 Cobalt(II)-arene complexes supported by β-diketiminate ligands were also identified as active hydrosilylation catalysts using (EtO)3SiH, with a high tolerance to a variety of functional groups.52 Related to these reactions, CoR(DIP) (R = H, Me) catalyzes the dehydrogenative silylation of alkenes with little to no hydrosilylation observed.53

Being the first-row counterpart of Pt, complexes containing Ni have also been examined for hydrosilylation. A few cationic phosphine complexes of Ni(II) were found to be active for hydrosilylation of styrene.54 The two-coordinate bis-amido complex Ni(NAr(SiMe3)2) is one of the few examples that catalyzes clean anti-Markovnikov hydrosilylation of unactivated alkenes.55 NiMe(salicylaldiminato)(py) complexes catalyze anti-Markovnikov hydrosilylation of alkenes with notably high activity and mild conditions (0.5 mol% Ni loading at 25 °C).56 However, the substrate scope of these catalysts are still limited. Interestingly, the Ni derivative of Karstedt’s complex, Ni2(O(SiMe2CH=CH2)2)3, catalyzes the reaction of styrene and vinylsilanes to give dehydrogenative silylation products with little to no hydrosilylation observed.57 This highlights the disparate activity of 1st row transition metals with their 2nd and 3rd row counterparts.

So far, iron catalysts have shown the most promising activity for alkene hydrosilylation. However, certain aspects still require significant improvements, such as air stability and undesired coloring of the final products.5c

Hydrosilylation mechanisms. The mechanism that is generally accepted for Pt-catalyzed hydrosilylations was proposed by Chalk and Harrod (Scheme 1.15). The process is initiated by the oxidative addition of hydrosilane to give a “Pt(H)(SiR3)” species, followed by hydride insertion into the alkene and reductive elimination of the silylalkane product.58 In contrast to Pt systems, most base-metal catalyzed reactions show significant production of allyl- and vinyl-silanes. The Chalk-Harrod mechanism fails to account for
the dehydrogenative silylation of Fe- and Co- catalyzed reactions. Sugimoto and coworkers suggested an alternative mechanism for these catalysts, termed the “modified Chalk-Harrod”. The distinction between the Chalk-Harrod and “modified” mechanisms is the migratory insertion step. The modified version proceeds via silyl-insertion rather than hyride-insertion. The resultant cobalt-alkyl can (1) reductively eliminate to afford the hydrosilylation product, or (2) undergo β-hydride elimination to afford the silylalkene. The metal-hydrido species generated in the latter reaction affords the alkane by reaction with alkene. These two mechanisms sufficiently explain the disparate product distributions of Fe-, Co, and Ni- vs. Pt-catalyzed hydrosilylation.

Scheme 1.15 The Chalk-Harrod mechanisms.

Catalytic hydrosilylation using Fe(DIP)(N₂)₂ is proposed to initiate via coordination of olefin. In the absence of alkenes, reaction of Fe(DIP)(N₂)₂ with stoichiometric PhSiH₃ gives the σ-complex Fe(DIP)(η²-H₃SiPh)₂. It was proposed that oxidative addition of H-Si only occurs when it is preceded by coordination of the olefin (Scheme 1.16). The authors suggest that coordination of alkene facilitates electron transfer from the di-radical DIP ligand of “Fe(II)(DIP²-)” to promote oxidative addition, giving
Fe(II)(H)(SiR₃)(DIP)(alkene). The importance of the redox-active ligand was further suggested by the inactivity of Fe(H)(SiR₃)(N₂)(PNP) (PNP = 2,6-bis-(diisopropylphosphinomethylene)pyridine), where the PNP ligand is redox innocent.²⁷b

![Scheme 1.16 Proposed mechanism for hydrosilylation using Fe(DIP)(N₂)₂.](image)

The mechanism of Co₂(CO)₈ catalyzed hydrosilylation has been investigated extensively.⁴⁸,⁶⁰ Strong evidence for a silyl-insertion step in the modified Chalk-Harrod mechanism was first presented by Brookhart et al. for the [CoCp*(P(OMe)₃)CH₂CH₂-μ-H]⁺ system. The authors proposed a σ-bond metathesis reaction of the Co-alkyl bond with Et₃SiH to form [CoCp*(P(OMe)₃)(SiEt₃)]⁺ concomitant with release of ethane. Though involvement of a Co(V) intermediate generated from oxidative addition of Et₃SiH is unlikely, it cannot be ruled out. [CoCp*(P(OMe)₃)(SiEt₃)]⁺ was not observed, but the silyl-insertion product [CoCp*(P(OMe)₃)(CH(C₄H₉)(CH₂SiEt₃)))]⁺ was characterized by NMR spectroscopy (Scheme 1.17).

Beyond Brookhart’s work, detailed mechanistic studies of cobalt-catalyzed hydrosilylation remain rare. Indirect evidence for a silyl-insertion step was presented for Co(SiEt₃)(CO)₃ by Wrighton and coworkers.⁴⁸b Insertion of a silyl group into alkynes was
proposed for the alkyne hydrosilylation catalyst, Co(CH$_2$SiMe$_3$)(IAd)(PPh$_3$) (IAd = 1,3-diadamantylimidazol-2-ylidene).$^{61}$

Scheme 1.17 Proposed mechanism for hydrosilylation catalysis using [CoCp*(P(OMe)$_3$)CH$_2$CH$_2$-$\mu$-H]$^+$. 

1.6 References

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Chapter 2
Metal-ligand cooperative activity and catalysis of Fe(II)-alkoxides†

2.1 Introduction

Monomeric alkoxo iron(II) complexes are rare. The oxygen centers in such complexes are expected to be highly basic owing to the electrostatic interactions between metal and ligand, although the Fe-O bonds themselves remain strong.† The basicity of the alkoxide ligand in these complexes often lead to multinuclear complexes bridging through the O atom. For these reasons, studies on the reactivity of Fe-O bonds are few.

![Figure 2.1](image)

**Figure 2.1** Pincacol-type coupling reactions of PCHO promoted by technetium and tungsten.

† Portions of this chapter are reproduced from the following publication with permission from the authors: Chu, W.-Y.; Zhou, X.; Rauchfuss, T. B. *Organometallics* **2015**, *34*, 1619.
The one-pot synthesis of a monomeric dialkoxo iron(II) complex, Fe\((P_2O_2)(CO)_2\) (\(P_2O_2 = (Ph_2PC_6H_4CHO)_2\)) was previously reported (Eq. 2.1). Reaction of 2 equiv of PCHO with Fe\((bda)(CO)_3\) results in the reductive coupling of the C-C bond of the aldehyde group. This pinacol-type coupling reaction is promoted by the iron(0) center, giving the ferrous complex Fe\((P_2O_2)(CO)_2\). Similar C-C bond forming reactions have been observed using PCHO with low-valent tungsten and technetium. However, the iron-promoted reaction utilizes significantly cheaper materials, are high yielding, and conducted in mild conditions.

While metal-ligand cooperation have been shown for several nitrogen-containing ligands, the reactivity of metal-oxygen bonds is relatively unexplored. This is due to the lower basicity of alkoxo ligands compared to amido ligands, and greater lability of coordinated alcohols compared to amines. A few Ir- and Ru-complexes containing metal-oxygen bonds have been proposed to catalyze alcohol dehydrogenation, dehydrogenative coupling or condensation reactions via MLC mechanisms. For example, an Ir-(PCP) complex was proposed to react with alcohol via the iridium-alkoxide functionality to give an iridium-alkoxide and an pendant alcohol ligand (Scheme 2.1).

![Scheme 2.1 Proposed catalytic cycle of alcohol dehydrogenation by an iridium-alkoxide.](image-url)
We are interested in the reactivity of the unique dialkoxo iron(II) carbonyl Fe(P₂O₂)(CO)₂ since similar complexes have not been described in literature. In particular, our focus is on the reactivity of the Fe-O bonds. Compared to known Ir- and Ru-catalyst containing metal-oxygen bonds, iron provides the benefit of being cheap, environmental friendly and earth-abundent. Moreover, the synthesis of the P₂O₂ ligand is high yielding and utilizes the easily synthesized PCHO. In the previous report, Fe(P₂O₂)(CO)₂ was shown to bind to BF₃ through the O atom, but leaving the Fe-O bond intact (Eq. 2.2). This suggested high basicity of the alkoxo ligand and low lability of the acid-bound oxygen atom. These observations hinted an opportunity for heterolytic cleavage of small molecules by MLC using Fe(P₂O₂)(CO)₂. The following chapter provides new perspectives on the O-centered reactivity of “Fe(P₂O₂)” species. An unprecedented activation mode of Si-H bonds by iron-alkoxo functionalities is shown. The proper modification of Fe(P₂O₂)(CO)₂ to give mono-substituted species led to hydrosilylation catalysts of aldehydes, ketones and even alkenes. The results shown here demonstrate a new strategy for Si-H bond activation promoted by metal-ligand cooperativity that may extend to a broader class of X-H bonds.

\[
\text{Fe(P₂O₂)(CO)₂ + 2 BF₃ → Fe(P₂O₂)(CO)₂.BF₃ \text{BF₃}}
\]  

(2.2)
2.2 Substitution reactions of Fe(P$_2$O$_2$)(CO)$_2$

![Chemical structures and IR spectrum]

**Figure 2.2** IR spectrum of $^{13}\text{CO}$ exchange experiment showing a mixture of Fe(P$_2$O$_2$)(CO)$_2$ (2024, 1965 cm$^{-1}$), Fe(P$_2$O$_2$)(CO)({$^{13}\text{CO}$}) (2008, 1935 cm$^{-1}$) and Fe(P$_2$O$_2$)({$^{13}\text{CO}$})$_2$ (1976, 1923 cm$^{-1}$)

The CO ligands of Fe(P$_2$O$_2$)(CO)$_2$ are labile, as evidenced by monitoring the exchange with $^{13}\text{CO}$ (1 atm) using IR spectroscopy over the course of several hours (Figure 2.2). When a CH$_2$Cl$_2$ solution of Fe(P$_2$O$_2$)(CO)$_2$ was purged with $^{13}\text{CO}$, two sets of new signals appear in the IR spectrum, assigned to Fe(P$_2$O$_2$)({$^{13}\text{CO}$})(CO) ($\nu_{\text{CO}} = 2008$, 1935 cm$^{-1}$) and Fe(P$_2$O$_2$)({$^{13}\text{CO}$})$_2$ ($\nu_{\text{CO}} = 1976$, 1922 cm$^{-1}$). With the goal of promoting activity at the Fe center, synthesis of substitution compounds containing weakly binding ligands was attempted. The mono-substitution complex Fe(P$_2$O$_2$)(CO)(NCMe) was generated by warming an acetonitrile solution of Fe(P$_2$O$_2$)(CO)$_2$ to 80°C for 24 h. Substitution of CO desymmetrizes the complex, as manifested by an AB quartet in the $^{31}\text{P}$ NMR spectrum.
(Figure 2.3). The large coupling value of $J_{P-P} = 289$ Hz is consistent with mutually trans phopshines. Using Eq. 2.3,\textsuperscript{10} the chemical shift of the two sets of signals $\delta_A$ and $\delta_B$ was calculated to be $\delta$ 28.2, 25.5.

\[ \Delta \nu_{AB} = \sqrt{(2D)^2 - (J_{P-P})^2} \]  \hspace{1cm} (2.3)

![Figure 2.3](image) 31P NMR spectrum of Fe(P$_2$O$_2$)(CO)(NCMe) in CD$_2$Cl$_2$. $\nu_A$ and $\nu_B$ are the chemical shifts of the two 31P NMR signals in Hz. D is the difference from the center of the AB quartet to the center of the doublet in Hz.

The structure of Fe(P$_2$O$_2$)(CO)(NCMe) was confirmed by X-ray crystallography (Figure 2.4). The structures of Fe(P$_2$O$_2$)(CO)$_2$ and Fe(P$_2$O$_2$)(CO)(NCMe) differ only slightly when comparing the Fe(P$_2$O$_2$) moiety. The acetonitrile ligand showed a slight contraction of the N≡C bond (1.135(6) Å) in comparison to that of free acetonitrile (1.157 Å). In the absence of added MeCN, CH$_2$Cl$_2$ solutions of Fe(P$_2$O$_2$)(CO)(NCMe) decomposed at room temperature over the course of a few hours. The decomposition reaction was monitored by NMR spectroscopy using a CD$_2$Cl$_2$ solution of Fe(P$_2$O$_2$)(CO)(NCMe) and mesitylene as internal standard in an NMR tube. For every equiv of Fe(P$_2$O$_2$)(CO)(NCMe) decomposed, half equiv of Fe(P$_2$O$_2$)(CO)$_2$ and 1 equiv acetonitrile was observed. The other half equiv of iron was not observable by NMR spectroscopy, suggesting formation of CO-free iron(II) paramagnetic species. This is consistent with the reaction in Eq. 2.4:

\[ 2 \text{Fe(P}_2\text{O}_2\text{)(CO)(NCMe)} \rightarrow \text{Fe(P}_2\text{O}_2\text{(CO)})_2 \ + \ 2 \text{MeCN} \ + \ \text{NMR silent Fe species} \]  \hspace{1cm} (2.4)
An analogous PMe₃ complex, Fe(P₂O₂)(CO)(PMe₃), was obtained in good yield by treating a THF/CH₂Cl₂ solution of Fe(P₂O₂)(CO)₂ with excess PMe₃. Similar to Fe(P₂O₂)(CO)(NCMe), no evidence of disubstitution products of PMe₃ was observed. The ³¹P NMR spectrum of Fe(P₂O₂)(CO)(PMe₃) revealed an ABX spin system with \( J_{P-P} = 44, 44, 280 \) Hz. X-ray crystallography of Fe(P₂O₂)(CO)(PMe₃) confirmed the coordination of PMe₃ in the equatorial position, whereas the diphosphine ligands remained mutually trans (Figure 2.4). Elongation of the Fe(1) – P bonds and a smaller P(1) – Fe(1) – P(2) angle was observed compared to Fe(P₂O₂)(CO₂), reflecting substitution of a π-acidic CO with a bulkier, more electron donating phosphine ligand. The pyridine complex Fe(P₂O₂)(CO)(py) was synthesized by dissolving Fe(P₂O₂)(CO₂) in pyridine. Unlike Fe(P₂O₂)(CO)(NCMe), both PMe₃ and pyridine complexes proved stable as CH₂Cl₂ solutions in room temperature over prolonged periods.

The reaction of Fe(P₂O₂)(CO)₂ with the bidentate ligand 3,4,7,8-tetramethyl-1,10-phenanthroline (phen) was also examined. When 1 equiv of phen was added to a toluene solution of Fe(P₂O₂)(CO)₂ and heated to 80°C for 48 h, a dark blue-green solution was obtained. Slowly cooling the solution gave green crystals with large amounts of red
crystals co-formed. X-ray analysis of the green crystals confirmed the formation of Fe(P₂O₂)(phen) (Figure 2.5). The red crystals were proposed to be cationic [Fe(phen)₃]²⁺, which was supported by ESI-MS spectroscopy of the crude mixture. Further purification of Fe(P₂O₂)(phen) proved difficult due to large amounts of the [Fe(phen)₃]²⁺ byproduct, and further spectroscopic analysis of the phen-substituted complex was not performed.

![Figure 2.5](image)

**Figure 2.5** Solid state representation (50 % thermal ellipsoids) of Fe(P₂O₂)(CO)(phen). Hydrogen atoms and solvent excluded for clarity.

### 2.3 Reactions of Fe(P₂O₂)(CO)₂ with Brønsted Acids

Previous work have established that reaction of Fe(P₂O₂)(CO)₂ with Lewis acids lead to the formation of O-bound adducts. The alkoxo ligands remain bound in these Lewis acid adducts. Here, the reactivity of Fe(P₂O₂)(CO)₂ with Brønsted acids was explored, with the expectation that the alkoxides will react to form labile neutral alcohol ligands, enabling binding of substrates to the iron center.
Titration of a CH$_2$Cl$_2$ solution of Fe(P$_2$O$_2$(CO)$_2$) with HOTf (OTf = CF$_3$SO$_3^-$) resulted in stepwise protonation of the alkoxo ligands to give [Fe(P$_2$O$_2$(CO)$_2$)]H$^+$ and [Fe(P$_2$O$_2$(CO)$_2$)]H$_2^{2+}$. The first protonation occurs independently of the second, suggesting very different basicities for Fe(P$_2$O$_2$(CO)$_2$) and [Fe(P$_2$O$_2$(CO)$_2$)]H$^+$. At ≤1 equiv HOTf, two broad peaks were observed in the $^{31}$P NMR spectrum at $\delta$ 21.1 (unreacted Fe(P$_2$O$_2$(CO)$_2$)) and $\delta$ 26.1, assigned to [Fe(P$_2$O$_2$(CO)$_2$)]H$^+$. Broadening of the signals resulted from intermolecular transfer of protons between Fe(P$_2$O$_2$(CO)$_2$) and [Fe(P$_2$O$_2$(CO)$_2$)]H$^+$. When 1 equiv of acid was added, the signal for [Fe(P$_2$O$_2$(CO)$_2$)]H$^+$ sharpened into an AB quartet with $J_{P-P} = 235$ Hz. Further addition of HOTf gave rise to a broad $^{31}$P NMR resonance at $\delta$ 29.9, corresponding to the doubly protonated species. This signal sharpened to a singlet when ≥2 equiv of HOTf was added. Protonation was also monitored by IR spectroscopy, which also supported the stepwise protonation process (Figure 2.6).

The protonated complexes are rare examples of low-spin Fe(II) complexes containing alcohol ligands. Low-resolution X-ray diffraction data of the mono-protonated [Fe(P$_2$O$_2$(CO)$_2$)]HOTf showed both alkoxides bound to iron. Good diffraction data were obtained for the doubly protonated species, [Fe(P$_2$O$_2$(CO)$_2$)]H$_2$OTf$_2$, and both protons of −OH were located in the electron difference map and refined isotropically. Both alcohol ligands remain bound to the Fe center, retaining the idealized $C_2$ symmetry. This is consistent with its simple $^{31}$P NMR spectrum. In comparison to Fe(P$_2$O$_2$(CO)$_2$), the Fe − O and Fe − P bonds of [Fe(P$_2$O$_2$(CO)$_2$)]H$_2$OTf$_2$ are elongated by 0.03 and 0.05 Å, respectively. The O − H$_{avg}$ is 0.81 Å, indicative of covalent bonding. An H-bonding
interaction was also observed for the alcohol protons with one oxygen of each OTf, with 
H---O_{avg} 1.71 Å.

Figure 2.6 Stepwise protonation of Fe(P_{2}O_{2})(CO)_{2} using HOTf. Top: ^{31}P NMR spectra. 
Bottom: IR spectra.
Titration of Fe(P$_2$O$_2$)(CO)$_2$ using H(Et$_2$O)$_2$BAr$_4^F$ gave similar results by NMR spectroscopy in terms of chemical shifts and number of observed species. Differences in the NMR spectra between protonation with HOTf and H(Et$_2$O)$_2$BAr$_4^F$ are attributed to the weaker hydrogen bonding of H$^+$ with Et$_2$O in comparison to that with OTF$^-$. Thus, faster proton exchange between [Fe(P$_2$O$_2$)(CO)$_2$]HBAr$_4^F$ and Fe(P$_2$O$_2$)(CO)$_2$ is evident. For example, addition of 0.5 equiv of H(Et$_2$O)$_2$BAr$_4^F$ to Fe(P$_2$O$_2$)(CO)$_2$ gave a broad signal in the $^{31}$P NMR spectrum at the average of chemical shifts of [Fe(P$_2$O$_2$)(CO)$_2$]H$^+$ and Fe(P$_2$O$_2$)(CO)$_2$. Under the same conditions but with HOTf, separate signals were observed for the two species.

2.4 Substitution reactions of Fe(P$_2$O$_2$)(CO)$_2$ by H-bonding ligands

The 16e$^-$ entity “Fe(P$_2$O$_2$)(CO)” features adjacent basic alkoxide and coordinatively unsaturated Lewis acidic iron sites. Such a species is suited for binding with ligands that could function both as Lewis bases and H-bond donors. Indeed, under prolonged heating with excess benzamide, Fe(P$_2$O$_2$)(CO)$_2$ converted to new species that featured AB quartets in the $^{31}$P NMR spectra, suggesting formation of desymmetrized Fe(P$_2$O$_2$)(CO)(PhC(O)NH$_2$) complex (Eq. 2.5). The $^1$H NMR spectrum of Fe(P$_2$O$_2$)(CO)(PhC(O)NH$_2$) featured a downfield singlet at $\delta$ 19.1, assigned to the NH group that is H-bonded to the adjacent alkoxide. A similar resonance was observed in the $^1$H NMR spectrum of Fe(P$_2$O$_2$)(CO)(MeC(O)NH$_2$) at $\delta$ 17.9. Curiously, the $^{31}$P NMR spectrum of Fe(P$_2$O$_2$)(CO)(MeC(O)NH$_2$) consisted of a singlet in the presence of excess MeC(O)NH$_2$, suggesting fast exchange between the coordinated and free MeC(O)NH$_2$ ligands.$^{11}$ This symmetrization observed by NMR spectroscopy was not seen for Fe(P$_2$O$_2$)(CO)(NCMe) upon addition of MeCN. After removal of excess MeC(O)NH$_2$ by multiple recrystallizations, the $^{31}$P NMR spectrum of Fe(P$_2$O$_2$)(CO)(MeC(O)NH$_2$) exhibited an AB quartet, as expected for monosubstituted compounds of Fe(P$_2$O$_2$)(CO)$_2$.
(Figure 2.7). The symmetrization process is proposed to proceed via and associative mechanism (Scheme 2.3). When dissolved in CH$_2$Cl$_2$, Fe(P$_2$O$_2$(CO)(MeC(O)NH$_2$) decomposed in the absence of excess MeC(O)NH$_2$ to give FeP$_2$O$_2$(CO)$_2$. This decomposition is proposed to follow a similar mechanism to the decomposition of Fe(P$_2$O$_2$(CO)(NCMe).

To obtain more stable adducts, thioureas were examined. Thioureas are good H-bond donors and are softer Lewis bases than ureas.$^{12}$ Treatment of Fe(P$_2$O$_2$(CO)$_2$ with 1 equiv of thiourea in CH$_2$Cl$_2$ gave the bright green compound Fe(P$_2$O$_2$(CO)(SC(NH$_2$)$_2$) ($\nu_{CO} = 1928$ cm$^{-1}$) in THF). The $^{31}$P NMR spectrum revealed a characteristic AB quartet ($J_{P-P} = 287$ Hz). A signal at $\delta$ 12.4 in the $^1$H NMR spectrum is assigned to the H-bonded NH ($\delta$(NH) 6.58 for free thiourea).

X-ray crystallographic analysis confirmed the structure of Fe(P$_2$O$_2$(CO)(SC(NH$_2$)$_2$) to be a monosubstituted thiourea complex (Figure 2.8). All four hydrogen atoms on the thiourea were located in the electron difference map, and the H-bonding interaction between one alkoxo ligands and one amino group on the thiourea ligand is indicated. The O(2)--H(1)A distance of 1.81(3) Å and the O(2) – H(1)A – N(1) angel of 156(3)$^\circ$ indicate a moderate H-bonding interaction.$^{13}$

![Scheme 2.3 Proposed mechanism for amide exchange in Fe(P$_2$O$_2$(CO)(MeC(O)NH$_2$). The P$_2$O$_2^2-$ ligand is simplified for clarity.](image)
Figure 2.7 $^{31}$P NMR spectra of Fe(P$_2$O$_2$)(CO)(MeC(O)NH)$_2$. Bottom: In the presence of excess acetamide. Top: After multiple recrystallizations.

Figure 2.8 Solid state representation (50 % thermal ellipsoids) of Fe(P$_2$O$_2$)(CO)(SC(NH$_2$)$_2$). Selected hydrogen atoms and solvent excluded for clarity.
2.5 Silane derivatives

The above reactions suggested the feasibility of utilizing the Lewis acid and base pair present in the “Fe(P₂O₂)” system for binding of substrates. This type of interaction is known to promote heterolytic cleavage. In view of the strength of O – H bonds, it was reasoned that Fe(P₂O₂)(CO)L (L = CO, NCMe) complexes would be susceptible to hydrogenation to give a hydrido complex, i.e. HFe[P₂O(OH)](CO)L. Solutions of Fe(P₂O₂)(CO)L were unreactive to H₂. To test the H₂ reactivity with more electron rich derivatives of Fe(P₂O₂)(CO)₂, the dicyclohexylphosphine analogue of complex, Fe(Cy₂P₂O₂)(CO)₂, was synthesized in a manner similar to that of Fe(P₂O₂)(CO)₂ using Cy₂P-2-C₆H₄CHO (Cy = C₆H₁₁) (Eq. 2.6). However, this modification of the Fe(P₂O₂)(CO)₂ complex did not promote any activity with H₂.

Scheme 2.4 Synthesis of HFe[P₂(OSiHPh₂)](CO)₂ and HFe[Cy₂P₂(OSiHPh₂)](CO)₂.

The H-Si bonds of hydrosilanes are polar and more reactive than H₂. Addition of H₂SiPh₂ to a CH₂Cl₂ solution of Fe(P₂O₂)(CO)₂ gave the hydrido complex HFe[P₂(OSiHPh₂)](CO)₂ (Scheme 2.4). Spectroscopic measurements were consistent with the formation of a metal hydride species with an O-silylated diphosphine ligands. The ³¹P NMR spectrum exhibited two doublets at δ 71.2 and 52.8, with large coupling constants (Jₚ₋ₚ = 195 Hz) indicating mutually trans phosphines. The ¹H NMR spectrum featured a
doublet of doublets at δ = 2.97 with $J_{\text{P-H}} = 44.6$ and 76.4 Hz, assigned to FeH. Complex HFe[P$_2$(OSiHPh$_2$)](CO)$_2$ was found to be stable towards additional silanes, no evidence of silylation of the second alkoxo ligand was observed. Similarly, the Si – H bond of HFe[P$_2$(OSiHPh$_2$)](CO)$_2$ was stable toward additional Fe(P$_2$O$_2$)(CO)$_2$. Similar MLC activation of hydrosilanes have been reported for only a few other compounds, mostly containing metal-sulfur bonds (Figure 2.9).$^{9e,15}$

Crystallographic analysis of HFe[P$_2$(OSiHPh$_2$)](CO)$_2$ confirmed the expected endo stereochemistry of the siloxy group, consistent with retention of stereochemistry at carbon (Figure 2.10). The structure exhibited a distorted octahedral geometry with the trans-phosphines canted away from the cis-dicarbonyl groups and a P – Fe – P angle of 157.68(2)$^\circ$. This bending was more prominent than that in the parent compound Fe(P$_2$O$_2$)(CO)$_2$ (P – Fe – P 167.43(4)$^\circ$). The bond distance Fe(1) – C(1) 1.820(2)Å is longer than the Fe-(CO) bond trans to the alkoxo ligand, reflecting the stronger trans influence of the hydride ligand in comparison to that of the alkoxo group. Although alkoxo iron hydrides are rare, the phenolato hydride complex HFe(Ph$_2$PC$_6$H$_4$O)(PMe$_3$)$_3$ and related derivatives have been characterized.$^{16}$
Complex Fe(P$_2$O$_2$)(CO)$_2$ also reacted with Et$_3$SiH (Eq. 2.7), initially affording HFe[P$_2$O(OSiEt$_3$)](CO)$_2$ (A) that is analogous to HFe[P$_2$O(OSiHPh$_2$)](CO)$_2$, albeit at a slower rate of conversion in comparison to the Ph$_2$SiH$_2$ reaction. The $^{31}$P NMR spectrum of HFe[P$_2$O(OSiEt$_3$)](CO)$_2$ was similar to that of HFe[P$_2$O(OSiHPh$_2$)](CO)$_2$, exhibiting two doublets at $\delta$ 70.2 and 52.7 ($J_{P-P} = 197$ Hz). A doublet of doublets at $\delta$ –2.95 ($J_{P-H} = 74.9, 46.5$) in the $^1$H NMR spectrum was assigned to FeH. A second product (B) was observed after several hours of reaction. Similar to A, product B also exhibited a high field resonance at $\delta$ –4.21 (dd, $J_{P-H} = 74, 66$Hz) in the $^1$H NMR spectrum, indicative of a hydrido species. The $^{31}$P NMR spectrum showed an AB quartet at $\delta$ 53.7 and 53.2 ($J_{P-P} = 188$Hz). After 28 h of reaction, the starting material was completely consumed, and the ratio of products A:B was 79:21. Due to the low yield of product B, its identity was not further investigated was proposed to be a structural isomer of A.
The reaction of Ph$_2$SiH$_2$ was tested with the mixed donor alkoxoamidoiron(II) complex Fe(P$_2$O$_2$)(CO)$_2$, which is the unsymmetrical amido analogue of Fe(P$_2$O$_2$)(CO)$_2$. Addition of Ph$_2$SiH$_2$ to a CD$_2$Cl$_2$ solution of Fe(P$_2$O$_2$)(CO)$_2$ initially afforded a hydridoiron(II) complex D, characterized by an AB quartet in the $^{31}$P NMR spectrum ($\delta$ 54, 52) and a doublet-of-doublets in the $^1$H NMR spectrum ($\delta$ –14.8) (Figure 2.12). When heated to 40 °C, a new hydride complex is observed (E), with spectroscopic
characters closely resembling that of HFe[P₂O(SiHPh₂)](CO)₂ (δ (³¹P) 58, 49; δ (¹H) −2.7 for E). Complex E is proposed to be the O-silylated complex, HFe[P₂(OSiHPh₂)NHArCl](CO)₂, with the structure analogous to HFe[P₂O(OSiHPh₂)](CO)₂ due to the high similarities of the spectroscopic characters (Scheme 2.5). After several days of heating, complex D completely converted to E, giving virtually quantitative yield of the hydridoalkoxoiron(II) complex. Though the identity of complex D was not further investigated, it was proposed to be a conformational isomer of E.

Scheme 2.5 Reaction of Fe(P₂ONArCl)(CO)₂ with Ph₂SiH₂.

The complex Fe(CyP₂O₂)(CO)₂ reacted with Ph₂SiH₂ in a similar fashion to give HFe[CyP₂O(OSiHPh₂)](CO)₂, with spectroscopic features closely resembling those of HFe[P₂O(OSiHPh₂)](CO)₂ and HFe[P₂O(OSiEt₃)](CO)₂. However, Fe(CyP₂O₂)(CO)₂ was unreactive toward Et₃SiH even at elevated temperatures (ca. 50°C in CH₂Cl₂). This is attributed to the steric hindrance imposed by the cyclohexyl groups.
Figure 2.12 NMR spectra of reaction of Fe(P$_2$ON$_{Ar}$)(CO)$_2$ with Ph$_2$SiH$_2$ in CD$_2$Cl$_2$ at different time points. Top: $^1$H NMR spectra. Bottom: $^{31}$P NMR spectra.
To clarify aspects of the hydride-forming process, the rate of formation of HFe[P$_2$O(OSiHPh$_2$)](CO)$_2$ from Fe(P$_2$O$_2$)(CO)$_2$ was monitored by $^1$H NMR spectroscopy. At 10 °C in the presence of > 10 equiv of Ph$_2$SiH$_2$, the conversion was first order in Fe.
The rate was also found to depend linearly on the concentration of silane (Figure 2.13). Given that Fe(P₂O₂)(CO)₂ is a coordinatively saturated 18e⁻ complex, it was hypothesized that the labile CO ligand dissociates prior to silane interaction. Interestingly, the rate was unaffected by the presence of CO (2 atm). These results are consistent with the rate law in Eq 2.8. The second-order rate constant (k), determined from the plot \( k_{\text{obs}} \) vs [Ph₂SiH₂], was found to be \( [1.14(6)] \times 10^{-3} \) M⁻¹ s⁻¹.

\[
\text{rate} = k[\text{Ph₂SiH₂}][\text{Fe(P₂O₂)(CO)₂}]
\]

(2.8)

Reactions of iron(II)-alkoxo complexes with organosilanes have not been well reported in literature. For the formation of HFe[P₂O(OSiHPh₂)](CO)₂ from Fe(P₂O₂)(CO)₂ and Ph₂SiH₂, the Lewis basic alkoxo ligand may attack the weakly Lewis acidic silicon atom, weakening the Fe – O bond (see structure of [Fe(P₂O₂)(CO)₂]H₂OTf₂), followed by transfer of hydride to Fe (Scheme 2.6). A related mechanism has been proposed for the addition of silanes to (PPh₃)Re(O)₂I. A pathway involving the dissociation of CO is unlikely, since the rate of HFe[P₂O(OSiHPh₂)](CO)₂ formation is independent of CO pressure.

Scheme 2.6 Proposed mechanism for the formation of HFe[P₂O(OSiHPh₂)](CO)₂. The P₂O₂⁻ ligand has been simplified for clarity.
2.6 Hydrosilylation catalysis using Fe(P$_2$O$_2$)(CO)L

Catalytic activity of Fe(P$_2$O$_2$)(CO)$_2$ and its derivatives were tested for hydrosilylation of C=O. Neither Fe(P$_2$O$_2$)(CO)$_2$ nor HFe[P$_2$O(OSiHPh$_2$)](CO)$_2$ exhibited catalytic activity for hydrosilylation. However, the mono-substituted complexes Fe(P$_2$O$_2$)(CO)L (L = PMe$_3$, NCMe, py) were active catalysts for the hydrosilylation of benzaldehyde using Ph$_2$SiH$_2$. The acetonitrile complex Fe(P$_2$O$_2$)(CO)(NCMe) proved to be the most active, giving 96% conversion of benzaldehyde to the hydrosilylated products after 5 h at 25 °C using 1 mol% catalyst. Two products were observed in the catalytic reactions, PhCH$_2$OSiHPh$_2$ and (PhCH$_2$O)SiPh$_2$ (Eq. 2.9). The 1:1 hydrosilylated product PhCH$_2$OSiHPh$_2$ was consistently higher yielding than (PhCH$_2$O)SiPh$_2$ (Table 2.1). No catalysis was observed when using tertiary silanes Et$_3$SiH and Me$_2$PhSiH. Acetophenone also underwent hydrosilylation with Ph$_2$SiH$_2$, albeit at a slower rate than benzaldehyde. Complexes Fe(P$_2$O$_2$)(CO)(PMe$_3$) and Fe(P$_2$O$_2$)(CO)(py) were also active catalysts with slightly decreased activity compared to Fe(P$_2$O$_2$)(CO)(NCMe), reflecting stronger binding of PMe$_3$ and py to the Fe center. Although Fe(P$_2$O$_2$)(CO)L were unreactive as catalysts for hydrosilylation of 1-octene, Fe(P$_2$O$_2$)(CO)(NCMe) catalyzed the hydrosilylation of styrene using Ph$_2$SiH$_2$. Heating a neat solution of styrene and 1.1 equiv Ph$_2$SiH$_2$ to 60 °C for 15 h gave 18% of the Markovnikov product, PhCH(SiHPh$_2$)Me. Given the high rate of decomposition of the acetamide complex Fe(P$_2$O$_2$)(CO)(MeC(O)NH$_2$), it was proposed that the bound acetamide is more labile compared to the acetonitrile in Fe(P$_2$O$_2$)(CO)(NCMe). Therefore, Fe(P$_2$O$_2$)(CO)(MeC(O)NH$_2$) may serve as a more active catalyst than Fe(P$_2$O$_2$)(CO)(NCMe). Indeed, Fe(P$_2$O$_2$)(CO)(MeC(O)NH$_2$) gave 48% PhCH(SiHPh$_2$)Me under identical catalytic conditions to the Fe(P$_2$O$_2$)(CO)(NCMe) reaction.

\[
\text{[Catalyst]} \quad \begin{array}{c}
\text{Ph} \\
\text{O}
\end{array} + \begin{array}{c}
\text{Ph}_2\text{SiH}_2 \\
\text{Ph}
\end{array} \quad \begin{array}{c}
\text{Ph} \\
\text{O}
\end{array} \quad \begin{array}{c}
\text{Ph} \\
\text{O}
\end{array} + \begin{array}{c}
\text{Ph} \\
\text{O}
\end{array} \quad \begin{array}{c}
\text{Ph} \\
\text{O}
\end{array} \quad \begin{array}{c}
\text{Ph} \\
\text{O}
\end{array} \quad \begin{array}{c}
\text{Ph} \\
\text{O}
\end{array} \quad \begin{array}{c}
\text{Ph} \\
\text{O}
\end{array} \quad \begin{array}{c}
\text{Ph} \\
\text{O}
\end{array}
\]

(2.9)
Table 2.1  Catalytic hydrosilylation using Fe(P$_2$O$_2$)(CO)L as catalysts$^a$.

<table>
<thead>
<tr>
<th>catalyst</th>
<th>substrate</th>
<th>silane</th>
<th>time (h)</th>
<th>Product (%)$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(P$_2$O$_2$)(CO)(NCMe)</td>
<td>PhCHO</td>
<td>Ph$_2$SiH$_2$</td>
<td>3</td>
<td>PhCH$_2$OSiHPPh$_2$ (69)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(PhCH$_2$O)SiPh$_2$ (20)</td>
</tr>
<tr>
<td></td>
<td>PhCHO</td>
<td>Ph$_2$SiH$_2$</td>
<td>5</td>
<td>PhCH$_2$OSiHPPh$_2$ (69)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(PhCH$_2$O)SiPh$_2$ (27)</td>
</tr>
<tr>
<td></td>
<td>PhCHO</td>
<td>PhSiH$_3$</td>
<td>3</td>
<td>(PhCH$_2$O)SiHPPh (18)</td>
</tr>
<tr>
<td></td>
<td>PhCHO</td>
<td>Et$_3$SiH</td>
<td>3</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>PhCHO</td>
<td>PhMe$_2$SiH</td>
<td>3</td>
<td>0</td>
</tr>
<tr>
<td>PhC(O)Me</td>
<td>Ph$_2$SiH$_2$</td>
<td>5</td>
<td>PhCH(OSiHPPh$_2$)Me (26)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>PhC(O)Me</td>
<td>Ph$_2$SiH$_2$</td>
<td>24</td>
<td>PhCH(OSiHPPh$_2$)Me (48)</td>
</tr>
<tr>
<td>PhCH=CH$_2$</td>
<td>Ph$_2$SiH$_2$</td>
<td>15</td>
<td>PhCH(SiHPPh$_2$)Me (18)</td>
<td></td>
</tr>
<tr>
<td>Fe(P$_2$O$_2$)(CO)(PMe$_3$)</td>
<td>PhCHO</td>
<td>Ph$_2$SiH$_2$</td>
<td>24</td>
<td>PhCH$_2$OSiHPPh$_2$ (47)</td>
</tr>
<tr>
<td></td>
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<td></td>
<td>(PhCH$_2$O)SiPh$_2$ (42)</td>
</tr>
<tr>
<td>Fe(P$_2$O$_2$)(CO)(py)</td>
<td>PhCHO</td>
<td>Ph$_2$SiH$_2$</td>
<td>24</td>
<td>PhCH$_2$OSiHPPh$_2$ (18)</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(PhCH$_2$O)SiPh$_2$ (16)</td>
</tr>
<tr>
<td>Fe(P$_2$O$_2$)(CO)(MeC(O)NH$_2$)</td>
<td>PhCH=CH$_2$</td>
<td>15</td>
<td>PhCH(SiHPPh$_2$)Me (48)</td>
<td></td>
</tr>
</tbody>
</table>

$^a$Reaction conditions (unless specified otherwise): substrate (1.0 mmol), silane (1.1 mmol), Fe(P$_2$O$_2$)(CO)L (10 mmol, CH$_2$Cl$_2$ (2 mL), 25 °C. $^b$The percentage yield is according to benzaldehyde and determined by $^1$H NMR spectroscopy with an internal standard. $^c$Conducted at 60 °C, no solvent.

2.7 Mechanism of catalytic hydrosilylation

Catalytic hydrosilylation of ketones and aldehydes is an established process with a well understood mechanism, first proposed by Chalk and Harrod. Historically, precious metals are used for these catalysts due to the high activity.$^{18}$ Due to reports of several highly active base-metal catalysts,$^{19}$ catalytic hydrosilylation has received renewed interest
Illustrative high-activity catalysts feature \(\alpha\)-diimines, \(^{20}\) diiminopyridine, \(^{21}\) N(SiMe\(_3\))\(_2\), \(^{22}\) and \(N\)-phosphinoamidinate\(^{23}\) as ligands.

Stoichiometric reactions of Fe(P\(_2\)O\(_2\))(CO)(NCMe) with silanes were conducted to elucidate mechanistic details of hydrosilylation. When the hydrosilylation of benzaldehyde by Ph\(_2\)SiH\(_2\) was monitored in situ by NMR spectroscopy, only the O-silyl hydride HFe[P\(_2\)O(SiHPh\(_2\))](CO)\(_2\) was detected. As mentioned above, pure Fe(P\(_2\)O\(_2\))(CO)\(_2\) and HFe[P\(_2\)O(SiHPh\(_2\))](CO)\(_2\) are catalytically inactive. The activity of Fe(P\(_2\)O\(_2\))(CO)L correlates qualitatively with the lability of L. This correlation suggests that L dissociation is an important step in the catalytic cycle. The active catalyst is proposed to arise via the sequence of reactions in Eqs 2.10 and 2.11, starting from formation of an O-silylated precatalyst followed by transfer of CO.

\[
\text{Fe(P}_{2}\text{O}_{2})(\text{CO})\text{L} + \text{H}_2\text{SiPh}_2 \rightarrow \text{HFe[P}_{2}\text{O(OSiHPh}_2\text{)](CO)\text{L}}
\]

(2.10)

\[
2\text{HFe[P}_{2}\text{O(OSiHPh}_2\text{)](CO)\text{L}} \rightarrow \text{HFe[P}_{2}\text{O(OSiHPh}_2\text{)](CO)\text{L}}_2 + \text{“HFe[P}_{2}\text{O(OSiHPh}_2\text{)]L_x” (inactive)} + \text{“HFe[P}_{2}\text{O(OSiHPh}_2\text{)]L_x” (active)}
\]

(2.11)

Catalyst activation thus entails accumulating the CO ligands in the thermodynamic sink of HFe[P\(_2\)O(SiHPh\(_2\))](CO)\(_2\). The active species is CO-free and possibly high-spin, which explains the absence of detectable NMR spectroscopy signals. Consistent with this scenario, HFe[P\(_2\)O(SiHPh\(_2\))](CO)\(_2\) was detected in ~ 50% yield after complete conversion of benzaldehyde to the hydrosilylated products. Moreover, when Fe(P\(_2\)O\(_2\))(CO)(NCMe) was treated with 1 equiv of Ph\(_2\)SiH\(_2\), a hydridoiron(II) species was observed after 10 mins. This species was characterized by an AB quartet in the \(^{31}\)P NMR spectrum and a triplet in the high field \(^1\)H NMR spectrum, consistent with HFe[P\(_2\)O(SiHPh\(_2\))](CO)(NCMe) (C) (Figure 2.14).
A mechanism for the hydrosilylation reaction is proposed in Scheme 2.7. After formation of the active species “HFe[P₂O(OSiPh₂)]Lₓ”, the labile L dissociates and substrate binding occurs and the hydride transfers to the electrophilic carbon. The new alkoxo ligand formed from hydride transfer to the substrate can undergo sigma-bonding.

**Figure 2.14** NMR spectra of Fe(P₂O₂)(CO)(NCMe) reaction with Ph₂SiH₂ after 10 mins. Top: ¹H NMR spectrum showing HFe[P₂O(OSiPh₂)](CO)(NCMe) (C). Bottom: ³¹P NMR spectrum showing HFe[P₂O(OSiPh₂)](CO)(NCMe) (C) and unreacted Fe(P₂O₂)(CO)(NCMe).
2.8 Conclusions

The dialkoxodiphosphineiron(II) complex Fe(P₂O₂)(CO)₂ displays rich activity involving CO substitution, reactions at the alkoxo ligands, and the cooperative behavior of these sites. This project established the ligand-substrate cooperativity of alkoxoiron(II) complexes.²⁴

Although Fe(P₂O₂)(CO)₂ was anticipated to activate H₂, the strengths of the O-H and the Fe-H bonds are insufficient to overcome the H-H bond energy of 104 kcal/mol.²⁵ Owing to a much weaker Si-H bond (~75kcal/mol), silanes react with Fe(P₂O₂)(CO)₂ to give hydridoiron(II) complexes. Certainly, the alkoxo functionality is crucial in this transformation, as the strong Si-O bond (~108 kcal/mol) is thermodynamically favored. The addition of silanes is proposed to proceed via alkoxide-assisted activation of the Si-H bond.

The hydrido ligand of the dicarbonyl compounds HFe[P₂O(OSiHPh₂)](CO)₂ and HFe[O₃P₂O(OSiHPh₂)](CO)₂ are unreactive to additional substrates. No reaction was observed when benzaldehyde was added to HFe[P₂O(OSiHPh₂)](CO)₂. When an Et₂O
solution of HFe[P₂O(OSiHPh₂)](CO)₂ was added excess HBF₄·Et₂O, quantitative amount of the O-protonated hydrido complex, HFe[P₂OH(OSiHPh₂)](CO)₂BF₄ formed (Eq. 2.12), and no products were observed that would suggest protonation of the hydrido ligand. This suggests weak hydricity of the hydrido ligand of the dicarbonyl complexes.

When the strongly binding CO was substituted with less strongly binding ligands to give Fe(P₂O₂)(CO)L, catalytic activity was observed. Recently, Li et al. reported hydrosilylation of benzaldehyde and ketones using hydridoiron(II) complexes bearing labile PMe₃ ligands. The authors proposed a mechanism involving hydride insertion into the carbonyl carbon to reduce ketones. Guan et al. also described hydridoiron(II) precatalysts for hydrosilylation. In constrast to Li’s reports, the hydrido ligand in Guan’s precatalyst is a spectator ligand. These and other studies point to intermediates in the catalytic cycle that could not be observed by NMR spectroscopy, which possibly involves high-spin iron(II) complexes.

2.9 Experimental

Materials and Methods. Unless otherwise indicated, reactions were conducted using standard Schlenk techniques under an N₂ or argon atmosphere at room temperature with stirring. Solvents were high-performance liquid chromatography grade, dried and deoxygenated on a Glass Contour System or MBraun solvent purification system, and stored over 4 Å molecular sieves. Fe(bda)(CO)₃, Cy₂P-2-C₆H₄CHO, Fe(P₂ON₄Cl)(CO)₂, and Fe(P₂O₂)(CO)₂ were synthesized according to literature preparations. Silanes (Gelest Inc.), thiourea, acetamide, benzaldehyde, ¹³CO, styrene (Sigma-Aldrich) and PMe₃ (Strem) were used as received. ¹H and ³¹P{¹H} NMR spectra were acquired on Varian Unity Inova 500NB and Unity 500 NB instruments at 20 °C unless otherwise noted. ¹H NMR were referenced to residual solvent relative to
tetramethylsilane.\textsuperscript{32} $^{31}{P^{1H}}$ NMR spectra were referenced to an external 85% H$_3$PO$_4$ standard. The chemical shifts of AB quartets were calculated according to Eq. 2.3. Crystallographic data were collected using either a Siemens SMART diffractometer equipped with a Mo K$a$ source ($\lambda = 0.71073$ Å) and an Apex II detector, or a Bruker D8 Venture diffractometer equipped with a Mo K$a$ microfocus source and a Photon 100 detector. FT-IR spectra were recorded on a Perkin-Elmer 100 FT-IR spectrometer. Elemental analyses were conducted in the School of Chemical Sciences Microanalysis Laboratory utilizing a model CE 440 CHN analyzer.

**Fe(P$_2$O$_2$)(MeCN)(CO).** A suspension of Fe(P$_2$O$_2$)(CO)$_2$ (200 mg, 0.25 mmol) in 500 mL of acetonitrile was heated in a 80 °C oil bath for 24 h. After cooled to room temperature, solvent was removed under reduced pressure. The resulting brown solids were washed with pentane (~15 mL) to afford analytically pure product as a brown powder. Yield: 145 mg (80%). Brown crystals suitable for X-ray diffraction were obtained by slow evaporation of the CH$_2$Cl$_2$ solution. $^1$H NMR (500 MHz, CD$_2$Cl$_2$): $\delta$ 8.01-7.13 (m, 28H, phenyl-$H$), 4.67 (dd, $J = 2.4$, 5.5 Hz, 1H, OCH$_3$), 3.86 (d, $J = 5.9$ Hz, 1H, OCH$_3$), 1.01 (s, 3H, NCC$_{H_3}$). $^{13}$C NMR (126 MHz, CD$_2$Cl$_2$/CD$_3$CN): $\delta$ 218.7 (C≡O), 157.8, 156.6, 137.7, 137.3, 136.8, 135.4, 134.5, 134.2, 134.1, 133.9, 131.0, 130.9, 130.4, 130.2, 129.8, 129.2, 129.0, 128.7, 128.1, 127.9, 127.4, 127.3, 126.5, 126.2, 88.54 (OCH$_3$), 87.66 (OCH). $^{31}{P^{1H}}$ NMR (202 MHz, CD$_2$Cl$_2$): $\delta$ 28.2, 25.5 (AB quartet, $J_{P-P} = 289$ Hz). Anal. Calcd for C$_4$H$_{33}$NO$_3$P$_2$Fe (found): C, 69.8 (69.61); H, 4.71 (4.73); N, 1.99 (2.1) IR spectrum (MeCN): $\nu_{CO} = 1938$ cm$^{-1}$.

**Fe(P$_2$O$_2$)(CO)(PMe$_3$).** A solution of Fe(P$_2$O$_2$)(CO)$_2$ (200 mg, 0.25 mmol) in 150 mL of a THF/CH$_2$Cl$_2$ mixture (4:1) was added PMe$_3$ (3 mL, 29 mmol) and stirred for 3 days. Volatiles were then removed under reduced pressure to yield an orange solid. The residue was recrystallized from a minimum amount of CH$_2$Cl$_2$ by addition of pentane, giving analytically pure orange powder (149 mg, 78%). Red crystals suitable for X-ray diffraction were obtained by vapor diffusion of pentane into a CH$_2$Cl$_2$ solution. $^1$H NMR (500 MHz, CD$_2$Cl$_2$): $\delta$ 8.40 (m, 2H, phenyl-$H$), 7.73 (m, 2H, phenyl-$H$), 7.52-6.85 (m, 26H, phenyl-$H$), 4.54 (m, 1H, OCH$_3$), 3.99 (d, $J = 5.3$ Hz, 1H, OCH$_3$), 0.77 (d, 9H, $J = 8.8$ Hz, PCH$_3$). $^{13}$C NMR (126 MHz, CD$_2$Cl$_2$): $\delta$ 215.9 (C≡O), 158, 155.2, 141.8, 140.2, 137.9,
Fe(P2O2)(CO)(py). A solution of Fe(P2O2)(CO)2 (140 mg, 0.18 mmol) in pyridine (20 mL) was stirred in room temperature for 72 h to afford a greenish-brown solution. Volatiles were removed under reduced pressure, and the resulting solid was washed with pentane (~15 mL) to give analytically pure product as a greenish-brown powder. Yield: 121 mg (83 %). 1H NMR (500 MHz, CD2Cl2): δ 8.47 (d, J = 5.9 Hz, 1H, py-H), 8.22 (d, J = 5.8 Hz, 1H, py-H), 8.03 – 7.98 (m, 2H, phenyl-H), 7.79 – 7.74 (m, 2H, phenyl-H), 7.55 – 6.70 (m , 24H, py-H, phenyl-H), 6.43 – 6.39 (m, 1H, py-H), 5.87 – 5.78 (m, 1H, py-H), 4.83 (dd, J = 5.8, 2.4 Hz, 1H, OC2H), 3.93 (d, J = 5.9 Hz, 1H, OC2H).

31P{1H} NMR (202 MHz, CD2Cl2): δ 29.6, 25.6 (AB quartet, JPP = 283 Hz). IR (CH2Cl2): νCO = 1917 cm⁻¹.

Fe(P2O2)(CO)(MeC(=O)NH2). A solution of Fe(P2O2)(CO)2 (70 mg, 0.1 mmol) in CH2Cl2 (6 mL) was treated with a solution of acetamide (0.36 g, 6.0 mmol) in THF (6 mL). After this solution was stirred for 36 h, solvent was removed under reduced pressure. The green residue was mixed with toluene (5 mL) and filtered. The filtrate was maintained at –30 ºC overnight, filtered, and the filtrate was diluted with pentane (~15 mL) to precipitate the product as a green solid. Yield: 27 mg (38%). 1H NMR (CD2Cl2): δ 17.87 (s, 1H, NH), 4.99 (s, 1H, OCH), 3.78 (d, J = 3.9 Hz, 1H, OCH), 2.86 (s, 1H, NH), 0.65 (s, 3H, CH3). 31P{1H} NMR (202 MHz, CD2Cl2): δ 32.4, 31.7 (AB quartet, JPP = 283 Hz). IR (CH2Cl2): νCO = 1933 cm⁻¹.

Fe(P2O2)(CO)(SC(NH2)2). A mixture of Fe(P2O2)(CO)2 (61 mg, 0.08 mmol) and thiourea (5.4 mg, 0.07 mmol) was dissolved in CH2Cl2 (3 mL) in a capped vial. The initially yellow solution was stirred for 20 h, giving bright green solid precipitate. The suspension was concentrated to 1.5 mL and filtered to obtain fine green powder, which was washed with CH2Cl2 (3 x 0.5 mL) to obtain analytically pure product as bright green powders. Yield: 53 mg (91%). 1H NMR (500 MHz, THF-d8): δ 12.3 (br, 1H, NH), 7.84 (m, 2H, phenyl-H), 7.70 (m, 2H, phenyl-H), 7.38 (m, 1H, phenyl-H), 7.21 – 6.76 (m, 23H, phenyl-H), 5.49 (br, 3H, NH), 4.64 (m, 1H, OCH), 3.42 (m, 1H OCH). 13C NMR (126 MHz, THF-
$d_5$: 186.5 ($S$=C), 157.5, 157.4, 137.8, 137.4, 135.6, 135.0, 134.7, 134.1, 130.2, 129.9, 129.8, 129.54, 128.6, 128.5, 128.3, 127.9, 127.5, 127.4, 126.7, 126.5, 87.4 ($O$CH), 87.2 ($O$CH). ($C$=O carbon not observed due to low solubility). $^{31}$P NMR (202 MHz, THF-$d_8$): 23.2, 21.1 (AB quartet, $J_{PP}$ = 287). Anal. Calcd for C$_{40}$H$_{34}$FeN$_2$O$_3$P$_2$S·THF (found): C, 65.03 (64.93); H, 5.21 (5.31); N, 3.45 (3.67). IR spectrum (THF): $\nu$CO = 1928 cm$^{-1}$.

**Fe(P$_{Cy_2}$O$_2$)(CO)$_2$.** A solution of Fe(bda)(CO)$_3$ (472 mg, 1.65 mmol) and P$_{Cy}$CHO (998 mg, 3.30 mmol) in THF (30 mL) was stirred in a 55°C oil bath for 4 hours. After cooled to room temperature, solvents were removed under reduced pressure. The resulting yellow solid was washed with pentane (4 × 10 mL) to yield analytically pure product as an orange powder. Yield: 782 mg (66%). $^1$H NMR (500 MHz, CD$_2$Cl$_2$): $\delta$ 7.56 (m, 2H, phenyl-H), 7.35-7.24 (m, 4H, phenyl-H), 7.04 (m, 2H, phenyl-H), 3.94 (s, OC$H$), 2.64-0.66 (m, 44H, Cy-H).

$^{31}$P ($^1$H) NMR (202 MHz, CD$_2$Cl$_2$): $\delta$ 25.8 (s). IR spectrum (CH$_2$Cl$_2$): $\nu$CO = 1995, 1930 cm$^{-1}$.

**HFe[P$_2$O(OSiHPh$_2$)](CO)$_2$.** A solution of Fe(P$_2$O$_2$)(CO)$_2$ (832 mg, 1.07 mmol) in CH$_2$Cl$_2$ (60 mL) was added Ph$_2$SiH$_2$ (0.21 mL) and stirred for 8 h. Solvent was removed under reduced pressure, and the resulting yellow solid was washed with pentane (10 mL×3) to obtain analytically pure product. Yellow crystals suitable for X-ray diffraction were obtained by vapor diffusion of pentane into a CH$_2$Cl$_2$ solution. $^1$H NMR (500 MHz, CD$_2$Cl$_2$): $\delta$ 7.97-6.73 (m, 38H, phenyl-H), 5.06 (d, $J_{HH}$ = 3.52 Hz, 1H, OCH), 4.81 (dd, $J_{HH}$ = 3.52 Hz, $J_{PH}$ = 7.50 Hz, 1H, OCH), 3.74 (s, 1H, Si$H$), -2.98 (dd, $J_{PH}$ = 76.3, 44.7 Hz, 1H, FeH).

$^{13}$C (126 MHz, CD$_2$Cl$_2$): $\delta$ 214.9 ($C$=O), 208.8 ($C$=O), 150.4, 147.5, 142.0, 136.9, 136.8, 136.4, 135.1, 134.8, 134.6, 134.4, 133.8, 133.5, 132.8, 132.7, 132.2, 131.9, 130.9, 130.8, 130.7, 130.6, 130.5, 130.3, 130.1, 130.0, 129.7, 129.0, 128.9, 128.2, 128.1, 128.0, 128.0, 127.9, 127.8, 127.6, 125.9, 84.9 (OCH), 77.8 (OCH). $^{31}$P ($^1$H) NMR (202 MHz, CD$_2$Cl$_2$): $\delta$ 71.2 (d, $J_{PP}$ = 194 Hz), 52.7 (d, $J_{PP}$ = 194 Hz). Anal. Calcd for C$_{52}$H$_{42}$FeO$_4$P$_2$Si·(CH$_2$Cl$_2$)$_{0.5}$ (found): C, 68.60 (68.58); H, 4.71 (4.69). IR spectrum (CH$_2$Cl$_2$): $\nu$CO = 2025, 1965 cm$^{-1}$.

**In situ observation of HFe[P$_2$O(OSiEt$_3$)](CO)$_2$.** An NMR tube was charged with a solution of Fe(P$_2$O$_2$)(CO)$_2$ (3 mg, 0.4 μmol) in CD$_2$Cl$_2$ (0.5 mL). The solution was added Et$_3$SiH (1.2 μL, 0.8 μmol) and the reaction was monitored over time by $^1$H NMR and $^{31}$P
NMR spectroscopy. $^1$H NMR (500 MHz, CD$_2$Cl$_2$): $\delta$ 8.01 – 7.88 (m, 4H, phenyl-$H$), 7.13 – 7.03 (m, 1H, phenyl-$H$), 6.86 (dd, $J$ = 11, 7.9 Hz, 1H, phenyl-$H$), 5.21 (d, $J$ = 3.4 Hz, 1H, OCH), 4.93 (dd, $J$ = 7.5, 3.2 Hz, 1H, OCH), 0.37 (t, $J$ = 7.9 Hz, 9H, CH$_3$), 0.04 (dq, $J$ = 16, 7.9 Hz, 3H, CH$_2$), -0.26 (dq, $J$ = 16, 7.9 Hz, 3H, CH$_2$), -2.88 (dd, $J$ = 75, 46 Hz, 1H, FeH).

$^{31}$P NMR (202 MHz, CD$_2$Cl$_2$): $\delta$ 72.1 (d, $J_{P-P}$ = 197 Hz), 54.6 (d, $J_{P-P}$ = 197 Hz). IR spectrum (CH$_2$Cl$_2$): $\nu_{CO}$ = 2000, 1939 cm$^{-1}$

HFe[PCy$_2$O(OSiHPh$_2$)](CO)$_2$. A solution of Fe(PCy$_2$O)(CO)$_2$ (197 mg, 0.27 mmol) in THF was added Ph$_2$SiH$_2$ (55 μL, 0.27 mmol). The resulting mixture was heated in a 55°C oil bath for 1 h. After cooled to room temperature, solvents were removed under reduced pressure. The resulting yellow-green solid was washed with pentane (3 × 5 mL) to obtain analytically pure product as a brown-green powder (157 mg, 63% yield).

$^1$H NMR (500 MHz, CD$_2$Cl$_2$): $\delta$ 7.78 – 6.88 (m, 18H, phenyl-$H$), 5.10 (d, $J$ = 3.6 Hz, 1H, OC$_2$H), 4.93 (s, 1H, SiH), 4.61 (dd, $J$ = 5.7, 3.7 Hz, 1H, OCH), 2.99 – 2.75 (m, 2H, cyclohexyl-$H$), 2.58 – 0.35 (m, 42H, cyclohexyl-$H$), −3.14 (dd, $J$ = 64, 50 Hz, 1H, FeH). $^{31}$P NMR (202 MHz, CD$_2$Cl$_2$): $\delta$ 74.0 (d, $J_{P-P}$ = 179 Hz), 50.9 (d, $J_{P-P}$ = 179 Hz). IR spectrum (CH$_2$Cl$_2$): $\nu_{CO}$ = 1974, 1919 cm$^{-1}$.

Exchange of $^{13}$CO on 1. A J-young NMR tube was charged with a CH$_2$Cl$_2$ solution of 1 (~ 5 μM). The solution was freeze pump thawed three times to remove N$_2$. The NMR tube was then opened to $^{13}$CO (1 atm). An IR spectrum was recorded after letting the solution sit in room temperature for 20 h. IR spectrum (CH$_2$Cl$_2$): $\nu_{CO}$ = 2024, 1965 cm$^{-1}$ (Fe(P$_2$O$_2$)(CO)$_2$), 2008, 1935 cm$^{-1}$ (Fe(P$_2$O$_2$)(CO)(13CO)), 1976, 1923 cm$^{-1}$ (Fe(P$_2$O$_2$)(13CO)$_2$).

Kinetic Study. An NMR tube was charged with 1 (7.8 mg, 10 μmol), hexamethylbenzene (internal standard), and CD$_2$Cl$_2$ (~0.6 mL). After addition of Ph$_2$SiH$_2$, the tube was shaken vigorously and the reaction was monitored over time by $^1$H NMR spectroscopy at 10 °C. Concentrations were determined by integration of the methylene resonances of 1 and 8.

Catalytic Hydrosilylation. A vial was charged with the substrate (1.0 mmol), silane (1.1 mmol), and CH$_2$Cl$_2$ (2 mL), followed by the addition of catalyst (10 μmol). The solution was stirred at room temperature for a desired time period. Mesitylene (0.14 mmol,
20 μL) was added as the internal standard. An aliquot was taken and mixed with C₆D₆. The yield was determined by ¹H NMR spectroscopy.

2.10 Supporting information

**Determination of CO dependence at 25 °C.**

*Determination of k<sub>obs</sub> at 25 °C.* In a J-Young NMR tube was added Fe(P₂O₂)(CO)₂ (8.1 mg, 0.0104 mmol), hexmethylbenzene (~ 2 mg), and CD₂Cl₂ (~ 0.6 mL). A ¹H NMR spectrum was recorded to establish the ratio of Fe(P₂O₂)(CO)₂. To this NMR tube was further added ~ 45 mL of Ph₂SiH₂ to give a total volume of 0.65 mL. This solution was immediately inserted into an NMR instrument that was pre-warmed to 25 °C. Relative concentrations were determined by integration of the signal at δ 4.52 of Fe(P₂O₂)(CO)₂ ([Fe]) and δ –3.14 of FeH(P₂O(OSiHPh₂))(CO)₂ ([FeH]) in the ¹H NMR spectra to the hexmethylbenzene internal standard.

The steady state approximation was used to determine the order dependence of rate on concentration [Fe]. Since [Ph₂SiH₂] > 20[Fe], it was assumed that [Ph₂SiH₂] remained constant during the reaction, then the following equation can be used to determine the dependence of rate on [Fe]:

\[
rate = k_{obs}[Fe]
\]

\[
k_{obs} = k[Ph₂SiH₂]
\]

(2.12)

(2.13)

Since rate was found to depend linearly on [Fe], then the first order rate law was used to determine <i>k</i><sub>obs</sub>:

\[
\ln[Fe] = \ln[Fe]₀ - k_{obs}t
\]

(2.13)

\[ [Fe]₀ = 0.016 \text{ M} \]

\[ [Fe] = \text{concentration at given time} \]

\[ t = \text{time (s)} \]

By plotting ln([Fe]/[Fe]₀) against <i>t</i>, <i>k</i><sub>obs</sub> was determined. For completeness, the appearance of the product FeH(P₂O(OSiHPh₂))(CO)₂ was also monitored, and ln(([Fe]₀+[FeH]₀-[FeH])/[Fe]₀) was plotted against <i>t</i> to determine <i>k</i><sub>obs</sub> (Figure 2.13).  

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Determination of $k_{obs}$ at 25 °C under CO. This sample was prepared in a manner identical to the previous experiment. After addition of Ph$_2$SiH$_2$, the sample was immediately frozen, the head space evacuated and refilled with 2 atm CO. Determination of $k_{obs}$ was performed as above.

**Figure 2.15** Kinetic plots for the reaction of Fe(P$_2$O$_2$)(CO)$_2$ with Ph$_2$SiH$_2$. Conditions: [Fe(P$_2$O$_2$)(CO)$_2$] = 0.016 M, [Ph$_2$SiH$_2$] = 0.37 M, 25 °C in CD$_2$Cl$_2$. $k_{obs}(\text{avg}) = 7.7 \times 10^{-4}$.

**Figure 2.16** Kinetic plots for the reaction of Fe(P$_2$O$_2$)(CO)$_2$ with Ph$_2$SiH$_2$ under CO. Conditions: [Fe(P$_2$O$_2$)(CO)$_2$] = 0.016 M, [Ph$_2$SiH$_2$] = 0.37 M, 2 atm CO, 25 °C in CD$_2$Cl$_2$. $k_{obs}(\text{avg}) = 7.9 \times 10^{-4}$.
Figure 2.17 Proposed reaction pathway for reaction of Ph$_2$SiH$_2$ with Fe(P$_2$O$_2$)(CO)(NCMe) to form HFe[P$_2$O(OSiPh$_2$H)](CO)(NCMe) (C) and decomposition to FeH(P$_2$O(SiPh$_2$))(CO)$_2$. 
Solid state structure of [Fe(P₂(OH)₂)(CO)₂](OTf)₂

Figure 2.18 Front view (top) and top view (bottom) of structure (50% thermal ellipsoids) of [Fe(P₂(OH)₂)(CO)₂](OTf)₂ depicting hydrogen bonding interaction with the OTf. Only one part of the disordered OTf⁻ (including O(10)) is shown.

Table 2.2 Relevant bond distances (Å) and angles (°) for hydrogen bonding interaction in [Fe(P₂(OH)₂)(CO)₂](OTf)₂.

<table>
<thead>
<tr>
<th>Relevant bond distances (Å) and angles (°)</th>
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</tr>
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<td>O(3) – O(10)₂avg</td>
<td>2.52(2)</td>
</tr>
<tr>
<td>O(4) – H(5)</td>
<td>2.52(3)</td>
</tr>
<tr>
<td>H(3) – O(10)₂avg</td>
<td>1.71(4)</td>
</tr>
<tr>
<td>H(4) – O(5)</td>
<td>1.71(3)</td>
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<tr>
<td>O(3) – H(3) – O(10)</td>
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<td>O(4) – H(4) – O(5)</td>
<td>176(4)</td>
</tr>
</tbody>
</table>
2.11 References


(27) Zhao, H.; Sun, H.; Li, X. *Organometallics* **2014**, *33*, 3535.


Chapter 3.

Imino-phosphine complexes of Fe(0), Fe(I), and Fe(II): redox properties and reactions of the imine ligands

3.1 Introduction

Imines are among the most common ligands in coordination chemistry. In the past decade, they have received increased attention due to their ability to assist in activation of substrates by MLC pathways. Promising applications in 1st row transition metal catalysts include hydrogenation catalysis promoted by cooperative effects of the metal-nitrogen bonds,2 Fe and Co alkene hydrofunctionalization catalysts promoted by redox-active ligands,3 and post-metallocene platforms for alkene polymerization.4 These successes indicate that, for first row organometallic compounds, the imine ligand impart reactivity not observed for related phosphine complexes.

In view of the successes with imine ligands, hybrids of imines and phosphines represent attractive ligand platforms that combine the modularity of the imine ligands and the high affinity of soft metal centers for phosphine ligands.5 Phosphine-imines have been extensively developed for application to iron(II) complexes. Systems of phosphine-imines are usually generated by the condensation of diamines with (1) diphenylphosphino-2-benzaldehyde (PCHO)6 or (2) the phosphine-substituted acetaldehydes R₂PCH₂CHO or their equivalent.7 Ligand platforms include tetradequate 6-5-6 diiminodiphosphines,8 tetradequate 5-5-5 diiminodiphosphines,2 and 5-5 diphosphine-imines,9 where the hyphenated numbers refer to the size of the resulting chelate rings. In addition to Morris's work, other phosphine-imine complexes of iron have been described.10 Beyond iron, several hundred complexes of phosphine imines have been described with other metals.
Owing to the versatile application of tridentate and tetradentate phosphine-imines, work on coordination chemistry of these ligands is extensive. In contrast, relatively little work has focused on the redox properties of the phosphine-imine functionality and ligand-based reactions on iron. To probe the redox characteristics of phosphine-imine complexes, the present report focuses on iron derivatives of Fe(0), Fe(I), and Fe(II) oxidation states. We focused our study on the reactivity and redox properties of the complexes derived from the phosphine-imine derived from PCHO and 4-chloroaniline, abbreviated PCHN\textsubscript{ArCl}. Previously, the synthesis of the iron-tricarbonyl complex Fe(PCHN\textsubscript{ArCl})(CO)\textsubscript{3} was reported.\textsuperscript{1} However, the synthetic route presented therein to obtain clean Fe(PCHN\textsubscript{ArCl})(CO)\textsubscript{3} was slow and low yielding. Alternatively, reaction of Fe(bda)(CO)\textsubscript{3} and PCHN\textsubscript{ArCl} also gives Fe(PCHN\textsubscript{ArCl})(CO)\textsubscript{3}, though removal of bda to obtain pure samples was not attempted in the previous report. Nonetheless, samples contaminated with bda was found to react with PCHO to give Fe(P\textsubscript{2}ON\textsubscript{ArCl})(CO)\textsubscript{2} (Eq. 3.1). The coupling of the imine and aldehyde carbons is analogous to the formation of P\textsubscript{2}O\textsubscript{2} (Chapter 2). This chapter focuses on extending the reactivity of phosphine-imines to include an unrecognized and reversible responsiveness of the phosphine-imine platform: N-complexation vs \pi-complexation and C-C coupling vs scission of the imine center.
3.2 Fe(PCHN\textsuperscript{ArCl})(CO)\textsubscript{3}

The tricarbonyl complex Fe(PCHN\textsuperscript{ArCl})(CO)\textsubscript{3} was obtained in high yield by heating Fe(bda)(CO)\textsubscript{3} with 1 equiv of PCHN\textsuperscript{ArCl}. Crude samples of Fe(PCHN\textsuperscript{ArCl})(CO)\textsubscript{3} were always contaminated with a small amount of a phosphine containing complex (\textsuperscript{31}P NMR: δ 25.6) later identified as the C-C bond coupled product, Fe(P\textsubscript{2}N\textsuperscript{ArCl}\textsubscript{2})(CO)\textsubscript{2}. Purification by recrystallization afforded analytically pure samples of Fe(PCHN\textsuperscript{ArCl})(CO)\textsubscript{3}.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure3.1}
\caption{Solid state representation (50% thermal ellipsoids) of Fe(PCHN\textsuperscript{ArCl})(CO)\textsubscript{3}. Selected hydrogen atoms have been omitted for clarity. Selected distances (Å) and angles (°):
Fe(1) – P(1), 2.2510(5); Fe(1) – C(1), 1.809(2); Fe(1) – C(2), 1.804(2); Fe(1) – C(3), 1.791(2); Fe(1) – N(1), 1.981(2); Fe(1) – C(4), 2.066(2); C(4) – N(1), 1.380(3); P(1) – Fe(1) – C(1), 171.54(8).
}
\end{figure}

Crystallographic analysis on yellow crystals of Fe(PCHN\textsuperscript{ArCl})(CO)\textsubscript{3} revealed the κ\textsubscript{1},η\textsubscript{2}-PCHN\textsuperscript{ArCl} coordination mode. The η\textsuperscript{2}-imine was indicated by the bonding Fe(1) – C(4) and Fe(1) – N(1) distances of 2.066(2) and 1.981(2) Å, respectively. The imine carbon-nitrogen distance of 1.380(3) Å is longer than expected for a typical κ\textsubscript{1}-imine (1.25 Å).
suggesting significant π-back donation from the metal center. Although π-bonded aldehyde complexes have been characterized,\(^1\)\(^,\)\(^1\)\(^3\) \(\eta^2\)-imines are more typical for early metals,\(^1\)\(^4\) where the carbon-nitrogen bonds are typically significantly elongated to exhibit single-bond character, often referred to as metallaaziridines.\(^1\)\(^5\) \(\kappa^1N\)-bonded imines are more common for iron, e.g. \([\text{CpFe(CO)}(\text{PCHN}^{\text{CH(Me)Ph}})]^+\).\(^1\)\(^0\)\(^a\)\(^,\)\(^1\)\(^6\) A few other examples of Fe(0) containing π-bound aldimines have been reported.\(^1\)\(^7\) For example, a dimeric \([\text{Fe(DIP)}]_2\) (DIP = \(\text{C}_5\text{H}_3\)-2,6-(CH=NAr)\(_2\), Ar = 2,6-\(\text{C}_6\text{H}_3\)(iPr)\(_2\)) formed through π-bonding interaction between two independent units.\(^1\)\(^8\)

Solutions of \(\text{Fe(PCHN}^{\text{ArCl}}\text{(CO)}_3\) exhibited solvatochromism, giving yellow solutions in alkanes and green solutions in chlorocarbon and aromatic solvents. UV-vis spectra were recorded for solutions of \(\text{Fe(PCHN}^{\text{ArCl}}\text{(CO)}_3\). In pentane, \(\text{Fe(PCHN}^{\text{ArCl}}\text{(CO)}_3\) exhibits an absorption maxima at 395 nm that shifts in \(\text{CH}_2\text{Cl}_2\) to a shoulder ~ 380 nm overlapped with intense UV absorptions (Figure 3.2). Pentane solutions of \(\text{Fe(PCHN}^{\text{ArCl}}\text{(CO)}_3\) were also also thermochromic, changing from yellow to green when cooled in an acetone/dry ice bath.

![Figure 3.2 UV-vis spectra collected in CH\(_2\)Cl\(_2\) and pentane.](image)

One explanation for the observed color differences in different solvents is changes in hapticity of the imine ligand. However, \(^1\)H NMR spectra for both yellow \(d_{12}\)-cyclohexane solutions and green \(\text{CD}_2\text{Cl}_2\) solutions of \(\text{Fe(PCHN}^{\text{ArCl}}\text{(CO)}_3\) are characteristic of \(\eta^2\)-imine species, giving broad resonances at ~ δ5 for the CHN. The signal
expected for a κ¹N species ~ δ 9¹,¹9 is absent for both solutions. Furthermore, IR spectra in the νCO region were very similar for both solutions, showing a single species.

The thermochromism is attributed to changes in the conformation of the p-chloroaryl ring, manifested by the N-C₆H₄Cl resonances between δ 7.35 and 6.78 in the variable temperature ¹H NMR spectra. Two doublets were observed at > 0°C for N-C₆H₄Cl, suggesting fast rotation of the p-chlorophenyl ring along the N–C bond. When the solution was cooled, these signals became broad and eventually split into four separate broad resonances (Figure 3.3). The broadening of CH=N was proposed to be related to the fast rotation of p-chlorophenyl ring at higher temperatures, possibly through CH–π or CH-Cl interactions. ³¹P NMR spectra of Fe(PCHN₄Cl)(CO)₃ remained a singlet at δ 62.8 between −70 to 20°C, and no additional isomers were observed. When Fe(PCHN₄Cl)(CO)₃ was heated in a toluene-d₈ solution, the CH=N resonance remained a singlet at 70°C. It is unclear whether the spectroscopically observed events are related to the solvatochormism.

Figure 3.3 ¹H NMR spectra of Fe(PCHN₄Cl)(CO)₃ in CD₂Cl₂ solution at various temperatures.
3.3 Substitution reactions of \( \text{Fe(PCHN}^{\text{ArCl}})(\text{CO})_3 \).

Treatment of \( \text{Fe(PCHN}^{\text{ArCl}})(\text{CO})_3 \) with excess PMe\(_3\) gave the substituted dicarbonyl \( \text{Fe(PCHN}^{\text{ArCl}})(\text{CO})_2(\text{PMe}_3) \). No evidence of double substitution was observed. Unlike complex \( \text{Fe(PCHN}^{\text{ArCl}})(\text{CO})_3 \), solvatochromism and thermochromism was not exhibited by \( \text{Fe(PCHN}^{\text{ArCl}})(\text{CO})_2(\text{PMe}_3) \), and remains bright orange as a solid and in solution. The \(^{31}\text{P} \) NMR spectrum of \( \text{Fe(PCHN}^{\text{ArCl}})(\text{CO})_2(\text{PMe}_3) \) was indicative of a diphosphine compound, exhibiting two doublets at \( \delta \) 64.1 and 21.4. The large coupling constant of \( J_{\text{P-P}} = 166 \text{ Hz} \) suggested the phosphines were mutually trans.\(^{20}\) The \(^1\text{H} \) NMR spectrum showed similar resonances to complex \( \text{Fe(PCHN}^{\text{ArCl}})(\text{CO})_3 \), with an additional set of doublet-of-doublets at \( \delta \) 1.04 for the PMe\(_3\) resonance. At 20 °C, N-C\(_6\)H\(_4\)Cl resonances at \( \delta \) 6.89 – 6.60 were broad and indistinguishable. Interestingly, the broadening of the \( p \)-chlorophenyl resonances was observed at a much higher temperature than that for \( \text{Fe(PCHN}^{\text{ArCl}})(\text{CO})_3 \). When a toluene-\( d_8 \) solution of \( \text{Fe(PCHN}^{\text{ArCl}})(\text{CO})_2(\text{PMe}_3) \) was cooled to –20 °C, these signals separated to give four distinct. The broadening at 20 °C was attributed to rotation of N-C\(_6\)H\(_4\)Cl, but the rotation barrier is higher for the PMe\(_3\) substituted complex than for \( \text{Fe(PCHN}^{\text{ArCl}})(\text{CO})_3 \), attributable to obstruction of facile rotation of the phenyl ring by the PMe\(_3\) ligand.

Single crystals were obtained by pentane diffusion into a CH\(_2\)Cl\(_2\) solution of \( \text{Fe(PCHN}^{\text{ArCl}})(\text{CO})_2(\text{PMe}_3) \). X-ray diffraction experiments confirmed the structure of the trans-phosphine complex (Figure 3.5). The \( \pi \)-bound C=N is slightly elongated by \( \sim 0.01 \) Å compared to \( \text{Fe(PCHN}^{\text{ArCl}})(\text{CO})_3 \), due to the higher degree of backbonding from the more electron rich metal center of \( \text{Fe(PCHN}^{\text{ArCl}})(\text{CO})_2(\text{PMe}_3) \). The Fe – C\(_{\text{carbonyl}} \) distances of \( \text{Fe(PCHN}^{\text{ArCl}})(\text{CO})_2(\text{PMe}_3) \) exhibited contraction compared to \( \text{Fe(PCHN}^{\text{ArCl}})(\text{CO})_3 \), as expected for the more electron rich diphosphine complex.
Figure 3.4 $^1$H NMR spectra of Fe(PCHN$_{ArCl}$)(CO)$_2$(PMe$_3$) in CD$_2$Cl$_2$ solution at various temperatures.

Figure 3.5 Solid state representation (50% thermal ellipsoids) of Fe(PCHN$_{ArCl}$)(PMe$_3$)(CO)$_3$. Hydrogen atoms have been omitted for clarity. Selected distances (Å) and angles (°): Fe(1) – P(1), 2.2465(5); Fe(1) – C(1), 1.847(1); Fe(1) – C(2), 1.844(1); Fe(1) – C(3), 1.801(1); Fe(1) – N(1), 2.021(1); Fe(1) – C(4), 2.975(1); C(4) – N(1), 1.289(2); P(1) – Fe(1) – C(1), 173.29(5).
When heated with 1 equiv PCHN^ArCl, Fe(PCHN^ArCl)(CO)_3 converts to the dark blue diamido complex Fe(P_2N^ArCl_2)(CO)_2. An analogous pinacol-type coupling reaction is observed for the reaction of 2 equiv PCHO with iron(0) carbonyls. The same diamido Fe(P_2N^ArCl_2)(CO)_2 can be obtained by addition of two equiv of PCHN^ArCl to Fe(bda)(CO)_3 and heated in a toluene solution. The coupling of the imine carbons give rise to two chiral carbon centers.

The above described substitution patterns of Fe(PCHN^ArCl)(CO)_3 point to the following mechanism for formation of Fe(P_2N^ArCl_2)(CO)_2:

$$\text{Fe(κ}_1^1, η^2\text{-PCHN^ArCl})(CO)_3 + PCHN^ArCl \rightarrow \text{Fe(κ}_1^1, η^2\text{-PCHN^ArCl})(κ^1\text{-PCHN^ArCl})(CO)_2 + CO}$$

(3.2)

$$\text{Fe(κ}_1^1, η^2\text{-PCHN^ArCl})(κ^1\text{-PCHN^ArCl})(CO)_2 \rightarrow \text{Fe(P_2N^ArCl_2)(CO)_2}$$

(3.3)

This mechanism is similar to the formation of Fe(P_2O_2)(CO)_2. It was previously reported that PCHO reacts with Fe(PCHN^ArCl)(CO)_3 to give the amido-alkoxo anologue of Fe(P_2N^ArCl_2)(CO)_2, Fe[(Ph_2PC_6H_4)_2CH(O)CH(N(4-ClC_6H_4))](CO)_2 (Fe(P_2ON^ArCl)(CO)_2). These C-C coupling reactions of C=O and C=N bonds all follow the mechanism presented in Eq. 3.2 and 3.3. The donating properties of [P_2O_2]^2-, [P_2O(N^ArCl)]^2-, and [P_2N^ArCl_2]^2- can be ranked by the vCO in the IR spectra: [P_2(N^ArCl_2)]^2- (2022, 1959 cm\(^{-1}\)) > [P_2ON^ArCl]^2- (2025, 1965 cm\(^{-1}\)) > [P_2O_2]^2- (2011, 1954 cm\(^{-1}\)).
Single crystal X-ray diffraction confirmed the structure of this $C_2$-symmetric species (Figure 3.6). Reduction of the imine functionality is evident from the long N(1) – C(16) and N(2) – C(15) bonds, with an average distance of 1.457 Å. Interestingly, the average Fe – N$_{amide}$ distance of 2.039 Å is long compared with the structural relative, Fe(P$_2$ON$_{ArCl}$)(CO)$_2$, which exhibits an Fe – N$_{amide}$ distance of 2.018 Å. This is presumed to be dominated by steric factors, where the sterically hindered N-C$_6$H$_4$Cl results in elongation. Among the series of complexes formed from reductive coupling of PCHO and PCHN$_{ArCl}$, the coupled C-C distance decreases by ~ 0.01 Å each from Fe(P$_2$O$_2$)(CO)$_2$ (1.549(5) Å) > Fe(P$_2$ON$_{ArCl}$)(CO)$_2$ (1.540(3) Å) > Fe(P$_2$N$_{ArCl}$)$_2$(CO)$_2$ (1.530(4) Å).
Figure 3.7 Representation of the solid state structure (50% thermal ellipsoids) of [Fe(PCHNArCl)(CO)₃]⁺. Selected hydrogen atoms, solvent and anion have been omitted for clarity. Selected distances (Å) and angles (°): Fe(1)–P(1), 2.2705(8); Fe(1)–C(1), 1.834(3); Fe(1)–C(2), 1.819(3); Fe(1)–C(3), 1.786(3); Fe(1)–N(1), 2.020(3); Fe(1)–C(4), 2.013(3); C(4)–N(1), 1.427(4); N(1)–H(1), 0.89(5); P(1)–Fe(1)–C(1), 176.8(1).

3.4 Protonation of Fe(PCHNArCl)(CO)₃

Treatment of Fe(PCHNArCl)(CO)₃ with HBarF₄2Et₂O gave the corresponding iminium complex [Fe(PCHNHArCl)(CO)₃]BarF₄. Protonation at the nitrogen atom was supported by ⁱH–¹³C HSQC NMR spectroscopy. ⁱH NMR signals at δ 5.56 and 4.70 integrated to 1:1 ratio, but only the δ 5.56 signal correlated to a ¹³C signal δ at 63.4 and was assigned CH. Having no ¹³C correlation, the other signal at δ 4.7 was assigned to NH. Although both cis- and trans-iminium ligands are possible, only one ⁱH NMR signal was observed for CH. N-protonation induced a ~50 cm⁻¹ increase in νCO vs Fe(PCHNArCl)(CO)₃ (Figure 3.8, left). The protonated [Fe(PCHNHArCl)(CO)₃]⁺ was unreactive toward excess HBarF₄, showing no tendency to form a hydrido complex.
Although [Fe(PCHNArCl)(CO)\textsubscript{3}]BF\textsubscript{4} did not crystallize well, single crystals of [Fe(PCHNArCl)(CO)\textsubscript{3}]BF\textsubscript{4} were obtained by pentane vapor diffusion into a THF/CH\textsubscript{2}Cl\textsubscript{2} solution. The [Fe(PCHNArCl)(CO)\textsubscript{3}]BF\textsubscript{4} salt behaves similarly to [Fe(PCHNArCl)(CO)\textsubscript{3}]BAr\textsuperscript{F},\textsubscript{4}. The crystallographic results were consistent with the structure deduced by NMR spectroscopy for the related BAr\textsuperscript{F},\textsubscript{4} salt (Figure 3.7). The NH center was refined (\textit{r}_{N-H} = 0.89(5) Å), with the imine exhibiting trans geometry. The iminium C(4)–N(1) distance (1.427(4) Å) is elongated by 0.04 Å compared to Fe(PCHNArCl)(CO)\textsubscript{3} but is shorter than typical C-N single bond lengths. Element analysis of the single crystals supported the chemical formula for [Fe(PCHNArCl)(CO)\textsubscript{3}]BF\textsubscript{4} with additional 0.5 molecules of CH\textsubscript{2}Cl\textsubscript{2} per [Fe(PCHNArCl)(CO)\textsubscript{3}]BF\textsubscript{4}. Interestingly, when the single crystals of [Fe(PCHNArCl)(CO)\textsubscript{3}]BF\textsubscript{4} were dissolved in CD\textsubscript{2}Cl\textsubscript{2}, two sets of resonances were observed in the \textsuperscript{1}H and \textsuperscript{31}P NMR spectra, although only one set of resonances were observed for powders of the BAr\textsuperscript{F},\textsubscript{4} salt. This new species is proposed to be the \textit{cis} isomer of [\textit{1H}]BF\textsubscript{4}, and the ratio of \textit{trans}-[\textit{H2}]BF\textsubscript{4}:\textit{cis}-[\textit{H2}]BF\textsubscript{4} was unchanged (93:7) at −20 °C. IR spectrum of [Fe(PCHNArCl)(CO)\textsubscript{3}]BF\textsubscript{4} showed two sets signals, supporting the presence of 2 isomers (Figure 3.8, right). The FT-IR spectrum of [Fe(PCHNArCl)(CO)\textsubscript{3}]BF\textsubscript{4} showed two sets of \textit{\nu}_{CO} signals in the partially resolved high energy region of the spectrum (2087, 2084 vs 2036, 2032) though the band near 2010 was not resolved into two signals, supporting the presence of two isomers. Similar \textit{N}-protonation was observed for [Fe(CO)\textsubscript{2}(PMe\textsubscript{3})(PCHNArCl)]. With BAr\textsuperscript{F},\textsubscript{4} as the anion, only
one isomer was observed, whereas two isomers were present for the BF$_4^-$ salt. This is tentatively attributed to weak electrostatic interactions between the iminium CH and the BF$_4^-$. The average distance between the iminium CH and two of the closest F atoms on BF$_4^-$ was 2.451 Å. $^{21}$ Similar N-protonation patterns were observed for [Fe(PCHNH$_{ArCl}$)(CO)$_2$(PMe$_3$)]$^{2+}$. When BAr$_F^-$ was used as the anion, only one isomer was observed, whereas 2 isomers were present for the BF$_4^-$ salt (Figure 3.9).

![Figure 3.9 IR spectra of [Fe(PCHNH$_{ArCl}$)(CO)$_2$(PMe$_3$)]BAr$_F^-$ (left) and [Fe(PCHNH$_{ArCl}$)(CO)$_2$(PMe$_3$)]BF$_4^-$ (right) in CH$_2$Cl$_2$ solutions.](image)

3.5 Redox properties of Fe(PCHN$_{ArCl}$)(CO)$_3$

The oxidation of Fe(PCHN$_{ArCl}$)(CO)$_3$ was examined. Addition of FcBF$_4$ to CH$_2$Cl$_2$ solutions of Fe(PCHN$_{ArCl}$)(CO)$_3$ gave a green-colored solution of the salt [Fe(PCHN$_{ArCl}$)(CO)$_3$]BF$_4$, which is stable only for a few minutes at room temperature but can be handled at –35 °C. Crystals of [Fe(PCHN$_{ArCl}$)(CO)$_3$]BF$_4$ were obtained by layering pentane over the CH$_2$Cl$_2$ solution and storing at –35 °C for 2 days.

![Chemical structure](image)

\[
\text{Fe(CO)$_3$} + \text{FcBF$_4$} \rightarrow \text{Fe(CO)$_3$}^+ + \text{BF$_4^-$}
\]

(3.2)

X-ray crystallography on green crystals of [Fe(PCHN$_{ArCl}$)(CO)$_3$]BF$_4$ revealed that oxidation induced a change in hapticity of the imine from $\kappa^1,\eta^1$-PCHN$_{ArCl}$ to $\kappa^1,\kappa^1$-
PCHN^ArCl (Eq. 3.4). The Fe(1) – C(4) distance (2.975(1) Å) is considerably elongated compared to Fe(PCHN^ArCl)_3(CO)_3 (2.066(2) Å). The C(4) – N(1) distance (1.289(2) Å) is close to values of N-bound imines without significant π-backdonation.\textsuperscript{17,22} In contrast to the trigonal bipyramidal structure exhibited by Fe(PCHN^ArCl)(CO)_3, the oxidized complex adopts a distorted square pyramid structure, with a CO ligand occupying the apical position (Figure 3.10). In addition, the Fe – C\textsubscript{carbonyl} distances of the oxidized compound are elongated when compared to Fe(PCHN^ArCl)(CO)_3, reflecting the decrease of electron density in iron(I).

**Figure 3.10** Solid state representation (50% thermal ellipsoids) of [Fe(PCHN^ArCl)(CO)_3]BF_4. Hydrogen atoms, solvent, and anion have been omitted for clarity. Selected distances (Å) and angles (°): Fe(1) – P(1), 2.2465(5); Fe(1) – C(1), 1.847(1); Fe(1) – C(2), 1.844(1); Fe(1) – C(3), 1.801(1); Fe(1) – N(1), 2.021(1); Fe(1) – C(4), 2.975(1); C(4) – N(1), 1.289(2); P(1) – Fe(1) – C(1), 173.29(5).

The ν\textsubscript{CO} shifts in the IR spectra are consistent with the hapticity change. Oxidation of Fe(PCHN^ArCl)(CO)_3 induces a shift in ν\textsubscript{CO} by ~ 40 cm\textsuperscript{-1}. For comparison, Δν\textsubscript{CO} of ~80 cm\textsuperscript{-1} is observed for the [Fe(CO)_3(PCy\textsubscript{3})]^{+0} pair.\textsuperscript{23} The smaller value of Δν\textsubscript{CO} for the [Fe(PCHN^ArCl)(CO)_3]^{+0} couple is explicable by a structural change in the donor set concomitant with oxidation: Fe(PCHN^ArCl)(CO)_3 features an η\textsuperscript{2}-imine π-acceptor, whereas [Fe(PCHN^ArCl)(CO)_3]^+ features κ\textsuperscript{1}-imine σ-donor. Consistent with this scenario, the ν\textsubscript{C=N} was observed at 1584 cm\textsuperscript{-1} for CH\textsubscript{2}Cl\textsubscript{2} solutions of Fe(PCHN^ArCl)(CO)_3, whereas ν\textsubscript{C=N} of
[Fe(PCHN\textsuperscript{ArCl})(CO)\textsubscript{3}]BF\textsubscript{4} was assigned at 1599 cm\textsuperscript{-1}. The 15 cm\textsuperscript{-1} shift to higher energy for ν\textsubscript{C=N} upon oxidation of Fe(PCHN\textsuperscript{ArCl})(CO)\textsubscript{3} supports the change from the π-accepting η\textsuperscript{2}-imine to the σ-donating κ\textsuperscript{1}-imine.

The X-band EPR spectrum of [Fe(PCHN\textsuperscript{ArCl})(CO)\textsubscript{3}]BF\textsubscript{4} in fluid solution exhibits a doublet pattern centered at g = 2.047, which arises from coupling to the \textsuperscript{31}P center (Figure 3.11). The hyperfine coupling constant A(\textsuperscript{31}P) is 52.97 MHz. The g-value and hyperfine coupling constant is in parallel to known diphosphine carbonyliron(I) complexes. For example, the EPR of Fe(PPh\textsubscript{3})\textsubscript{2}(CO)\textsubscript{3} exhibits a doublet centered at g = 2.053.\textsuperscript{23-24}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{Figure311.png}
\caption{X-band EPR spectrum of [Fe(PCHN\textsuperscript{ArCl})(CO)\textsubscript{3}]BF\textsubscript{4} in CH\textsubscript{2}Cl\textsubscript{2}/toluene at 10 °C.}
\end{figure}

The cyclic voltammogram of a CH\textsubscript{2}Cl\textsubscript{2} solution of Fe(PCHN\textsuperscript{ArCl})(CO)\textsubscript{3} at 0.02 Vs\textsuperscript{-1} scan rate showed a reversible event at E\textsubscript{1/2} = 0.41 V with i\textsubscript{pa}/i\textsubscript{pc} = 0.915. This process is assigned to the [Fe(PCHN\textsuperscript{ArCl})(CO)\textsubscript{3}]\textsuperscript{0/+} couple. This redox couple is stable in the electrochemical environment at this scan rate, and repeated cycling of the reversible couple up to 3 cycles did not result in observable diminish of the current. When the switching potential was extended to 1 V, a more complicated event was detected at ~ 0.6 V (Figure 3.12). The second oxidation is attributed to the [Fe(PCHN\textsuperscript{ArCl})(CO)\textsubscript{3}]\textsuperscript{+2/+} couple, but the doubly oxidized species is unstable in solution possibly due to loss of CO. Chemical oxidation of Fe(PCHN\textsuperscript{ArCl})(CO)\textsubscript{3} by 2e\textsuperscript{-} will be discussed in the Section 3.6.
The related Fe(PCHNArCl)(CO)2(PMe3) can be oxidized using 1 equiv FcBF4 to give the paramagnetic [Fe(PCHNArCl)(CO)2(PMe3)]BF4. We expect a similar hapticity change from η1,η2-PCHNArCl to η1,η1-PCHNArCl. This is supported by the small shift of the CO frequencies from Fe(PCHNArCl)(CO)2(PMe3) → [Fe(PCHNArCl)(CO)2(PMe3)]+ (ΔνCO(avg) of 22.5 cm⁻¹), and νC=N shift from 1583 cm⁻¹ of Fe(PCHNArCl)(CO)2(PMe3) to a broad signal centered at 1600 cm⁻¹ for [Fe(PCHNArCl)(CO)2(PMe3)]BF4.

3.6 Oxidation of Fe(P2NArCl2)(CO)2

The diamido Fe(P2NArCl2)(CO)2 is rapidly oxidized by ferrocenium salts. With 2 equiv of FcBARF4, Fe(P2NArCl2)(CO)2 afforded a yellow colored compound. This dicationic salt revealed strong signals in the ESI-MS spectrum for dicaticonic species at m/z = 455.05 and 427.3, corresponding to “Fe(PCHNArCl)2(CO)22+” and “Fe(PCHNArCl)22+” respectively. Two signals in the IR spectrum at 2065 and 2030 cm⁻¹ were observed. The 31P NMR spectrum showed a singlet at δ 40.5, and 1H NMR spectrum also suggested a symmetrical species. These spectral characteristics are consistent with C2-symmetric [Fe(PCHNArCl)2(CO)2](BARF4)2. Changing from strongly donating anionic amido ligands to neutral weak π-accepting C=N ligands is consistent with observed Δνavg 65 cm⁻¹ shift to

Figure 3.12 Cyclic voltammogram of Fe(PCHNArCl)(CO)3 in CH2Cl2 at 0.02 Vs⁻¹. Conditions: 0.001 M Fe(PCHNArCl)(CO)3, 0.01 M [Bu4N]PF6 in CH2Cl2 using a glassy carbon working electrode. Potentials are referenced to Fc⁰⁺.
higher energy of the CO ligands in the IR spectrum compared to the parent neutral complex. The same oxidation of Fe(P₂N₃ArCl₂)(CO)₂ can be accomplished using FcBF₄ and FcOTf, though [Fe(PCHN₃ArCl₂)(CO)₂](BF₄)₂ was unstable in solution, even at –35 °C. The decomposed product exhibited a singlet at δ 4.9 in the ³¹P NMR spectrum. It was previously reported that reaction of 2 equiv FcBF₄ with the dialkoxo analogue, Fe(P₂O₂)(CO)₂, gives the BF₃ adduct Fe(P₂(OF₃)₂)(CO)₂ that was isolated in 50 % yield,¹ supposedly via F⁻ abstraction to form iron(II) fluorido species.²⁵

X-ray crystallographic analysis were performed on [Fe(PCHN₃ArCl₂)(CO)₂](OTf)₂, which confirmed the proposed structure (Figure 3.13). The C₂ symmetry was retained. The C-N distances showed significant shortening compared to Fe(P₂N₃ArCl₂)(CO)₂, giving an average length of 1.297 Å. This confirmed oxidation from a diamido ligand to bisimines. The cleaved C-C bond exhibited a non-bonding distance of 3.269(5) Å in [Fe(PCHN₃ArCl₂)(CO)₂](OTf)₂ (C(7) – C(34)). Interestingly, the Fe-P distances (2.321(2) Å) were very long compared to Fe(P₂N₃ArCl₂)(CO)₂ and other related compounds.²²²⁶

![Figure 3.13](image.png)  
**Figure 3.13** Solid state representations (50 % thermal ellipsoids) of [Fe(PCHN₃ArCl₂)(CO)₂](OTf)₂. Anions and hydrogen atoms have been omitted for clarity. Left: side view. Right: view along the C₂ axis. Selected distances (Å) and angles (°): Fe(1) – P(1), 2.321(2); Fe(1) – P(2), 2.321(2); Fe(1) – N(1), 2.092(3); Fe(1) – N(2), 2.061(4); Fe(1) – C(26), 1.797(5); Fe(1) – C(27), 1.787(4); Fe(1) – C(27), 1.787(4); Fe(1) – C(7), 1.787(4); Fe(1) – C(34), 1.298 (7); N(1) – C(7), 1.295(5); N(2) – C(34), 1.298 (7); P(1) – Fe(1) – P(2), 176.77(6).
Studies were conducted to elucidate the mechanism of the oxidation of \( \text{Fe(P}_2\text{N}^\text{ArCl}_2)(\text{CO})_2 \). Upon treatment with 1 equiv of \( \text{FcBAr}^\text{F}_4 \), \( \text{Fe(P}_2\text{N}^\text{ArCl}_2)(\text{CO})_2 \) was completely consumed. IR analysis revealed that the oxidation afforded a complex mixture, with the three most intense signals at 2039, 1988, 1913 cm\(^{-1}\) (Figure 3.13, left, red trace). Alternatively, a similar mixture can be obtained by addition of 1 equiv \( \text{PCHN}^\text{ArCl} \) to \( \text{[Fe(PCHN}^\text{ArCl})(\text{CO})_3]\text{BAr}^\text{F}_4 \) (Figure 3.13, right, red trace). The IR spectrum of the mixture exhibited an intense signal at 1913 cm\(^{-1}\), and two smaller signals with similar intensities at 2039 and 1988 cm\(^{-1}\). Despite the complexity of both solutions, addition of another equiv of \( \text{FcBAr}^\text{F}_4 \) both afforded two sharp signals at 2065 and 2030 cm\(^{-1}\), indicative of \( \text{[Fe(PCHN}^\text{ArCl}_2)(\text{CO})_2]\text{(OTf)}_2 \). (Scheme 3.2).

![Figure 3.14](image-url) Left: IR spectra of stepwise oxidation of \( \text{Fe(P}_2\text{N}^\text{ArCl}_2)(\text{CO})_2 \). Black trace: \( \text{Fe(P}_2\text{N}^\text{ArCl}_2)(\text{CO})_2 \). Red trace: addition of first equiv \( \text{FcBAr}^\text{F}_4 \). Blue trace: addition of a second equiv \( \text{FcBAr}^\text{F}_4 \). Right: stepwise reaction of oxidation of \( \text{[Fe(PCHN}^\text{ArCl})(\text{CO})_3]\text{BAr}^\text{F}_4 \) in the presence of \( \text{PCHN}^\text{ArCl} \). Black trace: \( \text{[Fe(PCHN}^\text{ArCl})(\text{CO})_3]\text{BAr}^\text{F}_4 \). Red trace: addition of \( \text{PCHN}^\text{ArCl} \). Blue trace: addition of \( \text{FeBAr}^\text{F}_4 \).
Conclusions

Iron complexes derived from PCHN$_{\text{ArCl}}$ demonstrate the reactivity and different binding modes of metal-bound imines. Crystallographic studies establish that the couple Fe(PCHN$_{\text{ArCl}}$(CO)$_3$/[Fe(PCHN$_{\text{ArCl}}$(CO)$_3$]$^+$ as an example of a redox-induced hapticity change at an imine ligand. Linkage isomerism of $\kappa^1$- vs $\eta^2$- for ketones, aldehydes, and imines has been invoked or observed in electron-rich metal complexes such as [Ru(NH$_3$)$_5$(Me$_2$CO)]$^{2+/3+}$.\(^{27}\)

Scheme 3.2 Formation of [Fe(PCHN$_{\text{ArCl}}$)$_2$(CO)$_2$]$^{2+}$ via two different routes.

3.7 Conclusions

Iron complexes derived from PCHN$_{\text{ArCl}}$ demonstrate the reactivity and different binding modes of metal-bound imines. Crystallographic studies establish that the couple Fe(PCHN$_{\text{ArCl}}$(CO)$_3$/[Fe(PCHN$_{\text{ArCl}}$(CO)$_3$]$^+$ as an example of a redox-induced hapticity change at an imine ligand. Linkage isomerism of $\kappa^1$- vs $\eta^2$- for ketones, aldehydes, and imines has been invoked or observed in electron-rich metal complexes such as [Ru(NH$_3$)$_5$(Me$_2$CO)]$^{2+/3+}$.\(^{27}\)

New structures reported here provide new insights into the proposed pathway for the coupling reactions that give rise to (P$_2$O$_2$)$_2^-$, (P$_2$ON$_{\text{ArCl}}$)$_2^-$ and [P$_2$(N$_{\text{ArCl}}$)$_2$]$^2$- ligands. We assume the intermediacy of Fe($\kappa^1$,$\eta^2$-PCHN$_{\text{ArCl}}$)(CO)$_2$ in the coupling reaction. This hypothesis is supported by the characterization of the Fe(PCHN$_{\text{ArCl}}$(CO)(PMe$_3$) complex. The imine coupling reaction may proceed via a radical pathway that is analogous to pinacol coupling reactions (Scheme 3.3, top).\(^{28}\) Alternatively, the C–C coupling could proceed via attack of unbound imine with the $\eta^2$-imine (Scheme 3.3, bottom). Ample precedence for such reactivity is provided by studies imine coupling reactions promoted by early transition metal complexes containing $\eta^2$-imines.\(^{29}\) The coupling of imines to give diamido complexes have also been observed in a Mo(IV) system, where a $\pi$-bonded imine complexes is indicated.\(^{30}\)
Reversible bond formation/breakage of the imine carbon bonds represents a case of mild oxidative cleavage of C-C bonds. The unique C(15) – C(16) carbon bond length 1.530(4) Å in Fe(P$_2$N$_2$ArCl$_2$)(CO)$_2$ is actually quite short for a C-C single bond. Thus, the C-C oxidative cleavage under mild conditions is not due to the inherent weakness of this bond, but rather the unique redox properties of Fe(P$_2$N$_2$ArCl$_2$)(CO)$_2$. Complex [Fe(PCHN$_{Ar}$Cl$_2$(CO)$_2$]$_{2+}$ is also a rare example of a dicationic iron(II)-dicarbonyl complex.

**Scheme 3.3** Conceptual pathways for C-C bond coupling leading to Fe(P$_2$N$_2$ArCl$_2$)(CO)$_2$.

3.8 Experimental section

**Materials and methods.** Unless otherwise indicated, reactions were conducted using standard Schlenk techniques under an N$_2$ atmosphere at room temperature with stirring. Solvents were high-performance liquid chromatography grade, dried and deoxygenated on a Glass Contour System or MBraun solvent purification system, and stored over 4 Å molecular sieves. The compounds Fe(bda)(CO)$_3$, FcBF$_4$, FcOTf, HBAr$_3$F·2Et$_2$O, and PCHN$_{Ar}$Cl$_3$ were synthesized according to literature procedures. HBF$_4$·Et$_2$O was used as received from Sigma-Aldrich. PMe$_3$ was used as received from Strem. $^1$H and $^{31}$P{$^1$H} NMR spectra were acquired on Varian Unity Inova 500NB and Unity 500 NB instruments at 20 °C unless otherwise noted. $^1$H NMR were referenced to
residual solvent relative to tetramethylsilane, $^{31}$P($^1$H) NMR spectra were referenced to an external 85% H$_3$PO$_4$ standard. Crystallographic data were collected using either a Siemens SMART diffractometer equipped with a Mo Kα source ($\lambda = 0.71073$ Å) and an Apex II detector, or a Bruker D8 Venture diffractometer equipped with a Mo Kα microfocus source and a Photon 100 detector. EPR spectra were recorded on 1–5 mM solutions in toluene/CH$_2$Cl$_2$ (1:1) solutions at 10 °C. The instrument was a Varian E-line 12” Century Series X-band continuous-wave spectrometer. Fourier transform infrared spectra were recorded on a Perkin-Elmer 100 spectrometer. Cyclic voltammetry experiments were conducted using a 10-mL one-compartment glass cell with a tight-fitting Teflon top inside a N$_2$ filled glove box. The working electrode was a glassy carbon disk (diameter = 3.00 mm). The counter electrode was a Pt wire, and a Ag wire was used as a quasi-reference electrode. Each cyclic voltammogram was referenced to the Fe$^{0/+}$ couple by addition of ferrocene into the sample and collecting 1 scan. Elemental analyses were performed by the School of Chemical Sciences Microanalysis Laboratory utilizing a model CE 440 CHN analyzer. Where co-crystallyzed solvent was located by X-ray crystallography, they were included in the calculated value for elemental analyses.

**Fe(PCHN$_{\text{ArCl}}$(CO)$_3$**. This compound was synthesized using a procedure modified from a previous report.$^1$ A THF solution (15 mL) of Fe(bda)(CO)$_3$ (212 mg, 0.74 mmol) was treated with PCHN$_{\text{ArCl}}$ (297 mg, 0.74 mmol). This orange mixture was stirred in a 55 °C oil bath for 16 h to give a dark green solution. After cooling the solution, solvents were removed under reduced pressure to yield dark green powders. The crude materials was dissolved in a minimal amount of CH$_2$Cl$_2$ (ca. 3 mL), layered with pentane (15 mL) and stored at $-35$ °C for 48 h to obtain the target compound as yellow crystals. Yield: 272 mg (68%). Single crystals suitable for X-ray diffraction were obtained by storing a pentane solution containing the target molecule in $-35$ °C for 24 h. $^1$H NMR (500 MHz, CD$_2$Cl$_2$): $\delta$ 7.94 (br, 2H, aryl-$H$), 7.73 – 7.67 (m, 1H, aryl-$H$), 7.55 – 7.34 (m, 10H, aryl-$H$), 7.31 – 7.21 (m, 1H, aryl-$H$), 7.13 – 7.04 (m, 2H, aryl-$H$), 7.02 – 6.87 (m, 2H, aryl-$H$), 5.12 (br, 1H, N=CH). $^1$H NMR (500 MHz, C$_6$D$_{12}$): $\delta$ 7.94 (br, 2H, aryl-$H$), 7.57 (m, 1H, aryl-$H$), 7.44 – 7.15 (m, 11H, aryl-$H$), 7.08 – 7.01 (m, 1H, aryl-$H$), 6.98 – 6.88 (m, 2H, aryl-$H$), 6.85 – 6.80 (m, 2H, aryl-$H$), 4.94 (br, 1H, N=CH). $^{31}$P NMR (202 MHz, CD$_2$Cl$_2$): $\delta$ 63.3
Fe(PCHN$^{\text{ArCl}}$)(PMe$_3$)(CO)$_2$. A THF solution (5 mL) of Fe(PCHN$^{\text{ArCl}}$)(CO)$_3$ (21.2 mg, 0.039 mmol) was treated with PMe$_3$ (0.2 mL, 1.9 mmol). This mixture was stirred at room temperature for 16 h to give an orange solution. Solvents were then moved under reduced pressure, and the solids were washed with pentane to give the target compound as orange microcrystals. Longer reaction times were required when less PMe$_3$ was used. Single crystals suitable for X-ray diffraction were obtained by slow diffusion of pentane into a CH$_2$Cl$_2$ solution. $^1$H NMR (500 MHz, CD$_2$Cl$_2$): δ 7.95 – 7.86 (m, 2H, aryl-H), 7.64 – 7.58 (m, 1H, aryl-H), 7.44 – 7.27 (m, 11H, aryl-H), 7.13 – 7.07 (m, 1H), 6.88 (d, $J$ = 8.4 Hz, 1H), 6.83 – 6.54 (br, 2H, aryl-H), 4.27 (dd, $J$ = 5.6, 1.9 Hz, 1H, CH$_2$), 1.07 (dd, $J$ = 9.3, 1.6 Hz, 9H, CH$_3$). $^{31}$P [$^1$H] NMR (202 MHz, CD$_2$Cl$_2$): δ 64.10 (d, $J$ = 165 Hz), 21.37 (d, $J$ = 165 Hz). IR spectrum (THF): $\nu_{\text{CO}}$ = 1965, 1900 cm$^{-1}$. Anal. Calcd for C$_{30}$H$_{28}$NClFeO$_2$P$_2$: C, 61.3 (61.31); H, 4.8 (4.64); N, 2.38 (2.65).

[Fe(PCHNH$^{\text{ArCl}}$)(CO)$_3$]X ($X^-$ = BF$_4^-$, BAr$_4^-$). To an Et$_2$O solution (10 mL) of Fe(PCHNH$^{\text{ArCl}}$)(CO)$_3$ (75 mg, 0.139 mmol) was added 5 drops of HBF$_4$·Et$_2$O. A bright yellow solid precipitated immediately. After stirring for 1 h, the slurry was concentrated to ca. 5 mL. Pentane (10 mL) was then added, and the mixture was filtered to obtain the target compound as pale yellow powder. Yield: 75 mg (86%). Single crystals suitable for X-ray diffraction were obtained by vapor diffusion of pentane into THF/CH$_2$Cl$_2$ solution containing [Fe(PCHNH$^{\text{ArCl}}$)(CO)$_3$]BF$_4$. $^1$H NMR (500 MHz, CD$_2$Cl$_2$): δ 8.18 (dd, $J$ = 7.9, 3.5 Hz, 1H, aryl-H), 7.86 – 7.79 (m, 3H, aryl-H), 7.73 – 7.61 (m, 6H, aryl-H), 7.55 – 7.51 (m, 2H, aryl-H), 7.47 (d, $J$ = 8.6 Hz, 2H, aryl$^{\text{Cl-H}}$), 7.40 (d, $J$ = 8.6 Hz, 2H, aryl$^{\text{Cl-H}}$), 5.78 (dd, $J$ = 7.2, 4.3 Hz, 1H)), 5.29 – 5.16 (m, 1H). Anal. Calcd for C$_{28}$H$_{30}$BCIF$_4$FeNO$_3$P·0.5(CH$_2$Cl$_2$): C, 51.09 (51.08); H, 3.16 (3.16); N, 2.09 (2.36). The analogous salt [Fe(PCHNH$^{\text{ArCl}}$)(CO)$_3$]BAR$_4$ was prepared similarly. Combining a CH$_2$Cl$_2$ (3 mL) solution of Fe(PCHNH$^{\text{ArCl}}$)(CO)$_3$ (4.4 mg, 0.0094 mmol) with a CH$_2$Cl$_2$ (2 mL) solution of HBar$_4$·2Et$_2$O (9 mg, 0.088 mmol) converted the green solution immediately to bright orange-yellow. Solvent was then removed under reduced pressure to yield bright yellow solid. $^1$H NMR (500 MHz, CD$_2$Cl$_2$): δ 8.06 (dd, $J$ = 7.8, 3.5 Hz, 1H,
aryl-\(H\)), 7.85 – 7.78 (m, H, aryl-\(H\)), 7.78 – 7.61 (m, H, aryl-\(H\) and BAr\(_{F_4}\)-\(H\)), 7.58 – 7.51 (m, 5H, aryl-\(H\) and BAr\(_{F_4}\)-\(H\)), 7.49 (d, \(J = 8.7\) Hz, 2H, aryl\(_{Cl}\)-\(H\)), 7.39 – 7.31 (m, 2H, aryl-\(H\)), 7.28 (d, \(J = 8.7\) Hz, 2H, aryl\(_{Cl}\)-\(H\)), 5.56 (dd, \(J = 7.1, 4.4\) Hz, 1H, CH), 4.70 (d, \(J = 4.4\) Hz, 1H, NH). \(^{31}\)P NMR (202 MHz, CD\(_2\)Cl\(_2\)): \(\delta \)66.6. IR spectrum (CH\(_2\)Cl\(_2\)): \(\nu_{CO} = 2089,\ 2039,\ 2017\ \text{cm}^{-1}\).

\([\text{Fe(PCHN}\text{ArCl})\text{(CO)}_3]\text{BF}_4\). A solution of [Fe(C\(_5\)H\(_5\)\(_2\)]BF\(_4\) (24.9 mg, mmol) in CH\(_2\)Cl\(_2\) (7 mL) cooled to \(-35\) °C was added to a CH\(_2\)Cl\(_2\) solution (2 mL) of Fe(PCHN\(_{ArCl}\))(CO)\(_3\) (50 mg, mmol) to give a green mixture. Pentane (ca. 15 mL) was immediately layered and the mixture was maintained at \(-35\) °C for a week to afford dark green crystals suitable for X-ray crystallography. IR (CH\(_2\)Cl\(_2\)): \(\nu_{CO} = 2084,\ 2022,\ 1991\ \text{cm}^{-1}\). Anal. Calcd for C\(_{28}\)H\(_9\)NBClF\(_4\)FeO\(_3\)PCH\(_2\)Cl\(_2\) (found): C, 48.96 (48.92); H, 2.97 (2.91); N, 1.97 (2.14).

\([\text{Fe(P}_{2}\text{N}\text{ArCl}_2]\text{(CO)}_2]\text{OTf}_2\)\ ([\text{5}]\text{OTf}_2\). A CH\(_2\)Cl\(_2\) (10 mL) solution of Fe(P\(_2\)N\(_{ArCl}_2\))(CO)\(_2\) (50 mg, 0.055 mmol) was added a CH\(_2\)Cl\(_2\) (5 mL) solution of FeOTf (40 mg, 0.12 mmol). The blue solution gradually turned yellow after 10 mins of stirring. This
solution was concentrated to ca. 1 mL under reduced pressure, and pentane was added to give a dark yellow oil and a yellow solution. The solution was decanted, and the yellow oil was redissolved in a small amount of CH$_2$Cl$_2$. Pentane was added to this solution again to give a bright yellow solid precipitate. This slurry was then stored at –35 °C for 24 h, and the target compound was collected by filtration as a bright yellow powder. Yield: 38 mg (57 %). Single crystals suitable for X-ray diffraction were obtained by vapor diffusion of pentane into a concentrated CH$_2$Cl$_2$ solution. IR spectrum (CH$_2$Cl$_2$): $\nu_{\text{CO}} = 2059, 2023$ cm$^{-1}$. $^{31}$P NMR (202 MHz, CD$_2$Cl$_2$): $\delta$ 40.5.

3.9 Supporting information

![Figure 3.15 ¹H-¹³C HSQC of [Fe(PCHNHArCl)(CO)$_3$]BAr$_4$.](image-url)
3.10 References


Chapter 4.

Synthesis of new phosphine-imine-pyridine ligands
and the corresponding Fe-, Co- and Zn-dihalides†

4.1 Introduction

Coplanar, tri-dentate ligands are extensively applied in homogeneous catalysis.1 Among this category, ligands containing α-diimine functionalities have affinity for diverse oxidation states.2 This redox non-innocence is likely to be relevant to catalytic activity of first-row transition metal catalysts by promoting electronic transformations that are usually unfavorable for these metals (for example oxidative addition).3 This concept was driven by the discovery of especially active Fe-(DIP) catalysts for hydrofunctionalization reactions of unactivated alkenes. Thus, base-metal catalysts incorporating α-diimine tri-dentate ligands have recently demonstrated high activity for hydrosilylation,4 hydroboration5 and hydrogenation6 of alkenes, a field that has been historically dominated by Pt-group metals.7

Within the realm of tri-dentate ligands containing α-diimines, those with P-N-N donors are attractive alternatives to the N-N-N platforms. The incorporation of the relatively softer base phosphorus atom increases the binding affinity to late transition metals, which may prove useful for preventing catalysts decomposition by ligand dissociation. Moreover, it significantly enhances the electron richness of the ligands while preserving the α-diimine functionality. Iron complexes of phosphinite-based P-N-N ligands exhibit high activity for regio- and chemo-selective hydrosilylation of unactivated alkenes, even in the presence of carbonyl functional groups.4c In a related study, a dialkylphosphinomethyl-bipy (P-bipy) platforms supports highly active Fe and Co catalysts for hydroboration.5a,5b

† Portions of this chapter are reproduced from the following publication with permission from the authors: Gilbert-Wilson, R.; Chu, W.-Y.; Rauchfuss, T. B. Inorg. Chem. 2015, 54, 5596.
With the intent of developing a modular synthetic methodology, we were attracted to phosphine-imines. The broad availability of phosphine-amines present a convenient route to obtain permutable phosphine-imine ligands by Schiff-base condensations. Some representative examples of catalysts containing tridentate \(\alpha\)-diimine ligands are presented in Chart 4.1. In recent years, highly active catalysts for the hydrosilylation of carbonyls have been developed with poly-dentate diphosphine-diimine ligands.\(^8\) P-N-N ligands have also been shown to support ethylene polymerization catalysts.\(^9\)

![Chart 4.1 Representative examples of complexes containing phosphine-imine ligands.](image)

To access a wide variety of new \(\alpha\)-diimine containing phosphine ligands, we envisioned a new class of ligands with the general formula \(R^1P^R^2N^R^3py\). The general synthetic route, structure and nomenclature are shown in Scheme 4.1. Synthesis of \(R^1P^R^2N^R^3py\) can be achieved by Schiff-base condensation reactions of pyridine ketones/aldehydes and phosphine amines. These building blocks are available through either commercial vendors or synthesis via established high yielding methods, making them particularly accessible.
Late transition metal complexes with the general formula MCl$_2$L$_3$ are versatile precursors. Reaction of these complexes with alkylating, hydride transfer, or reducing agents give reactive alkyl,$^{10}$ hydrido or low valent complexes.$^{11}$ Synthesis of Fe-, Co-, and Zn-dihalide complexes of R$_1$P$_2$N$_3$py are also reported here for the purpose of serving as starting materials of more reactive species.

### 4.2 Synthesis of R$_1$P$_2$N$_3$py$_4$ ligands

Synthesis of the ligands with the general formula Ph$_2$P$_C$H$_4$N$_3$py was first investigated using o-diphenylphosphinoaniline (Ph$_2$P$_C$H$_4$N$_2$) as the precursor. Incorporation of an aryl linker between the phosphine and imine functionalities provide rigidity to the ligand structure compared to using aliphatic groups. It has been reported by other workers that condensation of 2-pyridinecarboxaldehyde (py-2-CHO) with Ph$_2$P$_C$H$_4$N$_2$ affords phosphine oxides A and B (Scheme 4.2) instead of the desired Ph$_2$P$_C$H$_4$N$_4$py.$^{12}$ The proposed mechanism invokes an azaphospholium intermediate that, under acidic conditions, exists in equilibrium with the Ph$_2$P$_C$H$_4$N$_4$py that is initially formed in the reaction. This intermediate is prone to irreversible hydrolysis by the water generated in the condensation step. We conducted the condensation of (py-2-CHO) with Ph$_2$P$_C$H$_4$N$_2$ in the presence of 4 Å molecular sieves with the goal to suppress the hydrolysis reaction. However, the new product C was observed in this reaction mixture in addition to products A and B. The newly synthesized phosphine oxide C was characterized by X-ray crystallography (Figure 4.1, left).
We assumed that the decreased electrophilicity of ketimines in $\text{Ph}_2\text{P}^\text{C}_6\text{H}_4\text{N}^\text{R}_3\text{py}$ ($\text{R}_3 \neq \text{H}$) ligands would inhibit formation of the undesired azaphospholium cation. Therefore, the condensation reactions of $\text{Ph}_2\text{P}^\text{C}_6\text{H}_4\text{NH}_2$ with pyridine ketones were examined. Heating a toluene solution of $\text{Ph}_2\text{P}^\text{C}_6\text{H}_4\text{NH}_2$ with 2-acetylpyridine (pyAc) to reflux in the presence of 5 mol% $p$-toluenesulfonic acid afforded $\text{Ph}_2\text{P}^\text{C}_6\text{H}_4\text{N}\text{Me}_{\text{py}}$ in 37% conversion after 4 days. The target compound can be purified as a white solid by recrystallization from hexane/Et$_2$O to give 9% isolated yield ($\delta^{(31P)}$ -13.9). Increasing the amount of acid used greatly increased the yield of the phosphine oxide, $\text{Ph}_2\text{P(O)(C}_6\text{H}_4\text{NHCH(CH}_3\text{)}_2\text{py}$, which was identified by a singlet at $\delta$ 36.7 in the $^{31P}$ NMR spectrum, and a doublet-of-quartets at $\delta$ 4.61 in the $^1H$ NMR spectrum assigned to the methyne group. The hydrolyzed $\text{Ph}_2\text{P(O)(C}_6\text{H}_4\text{NHCH(CH}_3\text{)}_2\text{py}$ was obtained in a qualitative reaction of $\text{Ph}_2\text{P}^\text{C}_6\text{H}_4\text{N}\text{Me}_{\text{py}}$ with $\text{H}_2\text{O}$ in the presence of $p$-toluensulfonic acid. This compound was also characterized by X-ray crystallography (Figure 4.1, right).
Heating a toluene solution of $\text{Ph}_2\text{P(C}_6\text{H}_4\text{)NH}_2$ with 2-benzoylpyridine to reflux in the presence of 5 mol% $p$-toluenesulfonic acid for 16 h afforded the desired of $\text{Ph}_2\text{P(C}_6\text{H}_4\text{)}\text{NH}_{\text{Ph}}$ in 65% conversion and 35% of the phosphine oxide A ($R^3 = \text{Ph}$). Recrystallization from CH$_2$Cl$_2$/Et$_2$O afforded analytically pure $\text{Ph}_2\text{P(C}_6\text{H}_4\text{)}\text{NH}_{\text{Ph}}$ in 53% yield as yellow crystals. NMR spectral analysis indicated the existence of two isomers of $\text{Ph}_2\text{P(C}_6\text{H}_4\text{)}\text{NH}_{\text{Ph}}$ in approximately 1:1 ratio. Due to the ease of synthesis, $\text{Ph}_2\text{P(C}_6\text{H}_4\text{)}\text{NH}_{\text{Ph}}$ was used as the ligand in most of our investigations.

**Figure 4.1** Solid state representations (50% thermal ellipsoids) of C (left) and Ph$_3$P(O)(C$_6$H$_4$)NHCH(CH$_3$)py (right). Selected hydrogen atoms omitted for clarity.

**Chart 4.2** Newly synthesized PNpy ligands.
The propensity of $^{\text{Ph2PC6H4N}}_{\text{R3py}}$ to react with water to afford undesirable oxides prompted the investigation of other phosphine amines as precursors. Using less rigid -(CH$_2$)$_n$- linkers between the phosphine and imine could disfavor the formation of the 5-membered ring in the azaphospholium cation. Indeed, Gusev and coworkers have reported the successful synthesis of $^{\text{Ph2PC2NH}}_{\text{py}}$ using Ph$_2$P(CH$_2$)$_2$NH$_2$ and 2-pyridinecarboxaldehyde without formation of phosphine oxides.$^{13}$ Reaction of acrylonitrile with secondary phosphines followed by reduction of phosphine-nitriles is a well-established route to R$_2$P(CH$_2$)$_3$NH$_2$ compounds. This method was used to obtain Ph$_2$P(CH$_2$)$_3$NH$_2$, Cy$_2$P(CH$_2$)$_3$NH$_2$ and 1Pr$_2$P(CH$_2$)$_3$NH$_2$. A new phosphine amine, Ar$^F_2$P(CH$_2$)$_3$NH$_2$ (Ar$^F = 3,5$-(CF$_3$)$_2$C$_6$H$_3$), was synthesized analogously starting with Ar$^F_2$PH. The reaction of R$_2$P(CH$_2$)$_3$NH$_2$ with 2-pyridinecarboxaldehyde proceeded in THF at room temperature and gave the corresponding R$_1$P$^\text{C3N}$H$_2$py ligands. These ligands were which were stable to hydrolysis. Reaction of Ph$_2$P(CH$_2$)$_3$NH$_2$ with 2-benzoylpyridine to give Ph$_2$PC$_3$NH$_2$py required more forcing conditions involving higher temperatures and addition of 5 mol% acid. A summary of the newly synthesized R$_1$P$^\text{R2N}$R$_3$py ligands is given in Chart 4.2.

4.3 Synthesis and characterization of FeX$_2$(PNpy) (X = Cl, Br)

Attempted synthesis of FeCl$_2$(Ph$_2$PC$_6$H$_4$NMe$_2$py) by addition of Ph$_2$PC$_6$H$_4$NMe$_2$py to a THF solution of FeCl$_2$ resulted in precipitation of a blue solid. Extraction of this solid into CH$_2$Cl$_2$ afforded a blue solution. The $^1$H NMR of the blue solution in CD$_2$Cl$_2$ showed one major paramagnetic product, proposed to be FeCl$_2$(Ph$_2$PC$_6$H$_4$NMe$_2$py) (Figure 4.2). After ca. 10 mins, this solution decomposed to give the insoluble purple solid precipitate, proposed to be [Fe(Ph$_2$PC$_6$H$_4$NMe$_2$py)](FeCl$_4$) or [Fe(Ph$_2$PC$_6$H$_4$NMe$_2$py)](Fe$_2$Cl$_6$).
Figure 4.2 $^1$H NMR spectrum of freshly prepared FeCl$_2$($^{Ph_2}p^{C_6H_4}N^Me$py) in CD$_2$Cl$_2$ solution.

Figure 4.3 Solid state representation (50% thermal ellipsoids) of FeCl$_2$($^{Ph_2}p^{C_6H_4}N^{Ph}$py). Hydrogen atoms omitted for clarity.
Formation of [Fe(tridentate)2]^{2+} "1:2" complexes by ligand redistribution reactions of FeX_2(tridentate) 1:1 complexes has been observed by other researchers. Decomposition to coordinatively saturated 1:2 complexes is a challenge commonly associated with compact tridentate ligands that can allow for the accommodation of two ligands on a single metal center. Reaction of the more sterically bulky Ph2P(C6H4)NPh py with THF solutions of FeCl_2 or FeBr_2 afforded the 1:1 complexes FeCl_2(Ph2P(C6H4)NPh py) and FeBr_2(Ph2P(C6H4)NPh py) in good yield. Slow evaporation of a CH_2Cl_2 solution of FeCl_2(Ph2P(C6H4)NPh py) at -35°C afforded single crystals that were analyzed by X-ray diffraction (Figure 4.3). The geometry is best described as square pyramidal with \( \tau = 0.36 \) (\( \tau \) is a geometrical parameter for five-coordinate complexes, where \( \tau = 0 \) indicates a perfect square pyramidal geometry and \( \tau = 1 \) indicates a perfect trigonal bipyramidal geometry). The Ph2P(C6H4)NPh py ligand exhibited distortion from planarity in the solid state structure.

NMR spectroscopy studies were carried out in CD_2Cl_2 using FeBr_2(Ph2P(C6H4)NPh py) due to its favorable solubility and relative stability. The \( ^1 \)H NMR spectrum exhibited resonances between \( \delta \) 177 to -3.70 (Figure 4.5, top). Out of the 14 predicted signals, 13 were unambiguously identified in the \( ^1 \)H NMR spectrum. No \( ^3 \)P NMR spectral resonances were observed. The magnetic moment determined by Evan’s method (5.1 \( \mu_B \)) was in agreement with \( S = 2 \) spin state, suggesting a high-spin Fe(II) complex.

Solutions of FeCl_2(Ph2P(C6H4)NPh py) in CH_2Cl_2 exhibited significantly slower rates of redistribution compared to FeCl_2(Ph2P(C6H4)NMe py), giving purple crystals of the 1:2 complex after \( > 1 \) day in CH_2Cl_2. The 1:2 complex was isolated as [Fe(PNpy)_2](FeCl_6) and characterized by X-ray crystallography (Figure 4.4). In contrast to the distorted Ph2P(C6H4)NPh py ligand exhibited in the 1:1 complex, planar Ph2P(C6H4)NPh py ligands were observed for [Fe(PNpy)_2](FeCl_6). Reorganization of FeX_2(PNpy) may occur via one of the following reactions:

\[
2\text{FeCl}_2(\text{PNpy}) \rightarrow [\text{Fe}(\text{PNpy})_2](\text{FeCl}_4) \quad (4.1)
\]
\[
3\text{FeCl}_2(\text{PNpy}) \rightarrow [\text{Fe}(\text{PNpy})_2](\text{Fe}_2\text{Cl}_6) + \text{PNpy} \quad (4.2)
\]
The isolation of [Fe(Ph2pC6H4NPhpy)](Fe2Cl6) is consistent with Eq. 4.2. The cyclohexylphosphine substituted Cy2pC3NHpy ligand also reacted with THF solutions of FeBr2 to give FeBr2(Cy2pC3NHpy), which were stable to redistribution in both THF and CH2Cl2.

Figure 4.4 Solid state representation (50% thermal ellipsoids) of [Fe(Ph2pC6H4NPhpy)2](Fe2Cl6). Hydrogen atoms and solvent omitted for clarity.

4.4 Synthesis and characterization of CoCl2(PNpy)

Synthesis of CoCl2(PNpy) complexes were carried out in a manner similar to the Fe(II) analogues. The newly synthesized ligands Ph2pC6H4NPhpy, Ph2pC6H4NMe2py, Ph2pC3NPhpy and iPr2pC3NHpy react with THF solutions of CoCl2 to give red-brown or red-purple CoCl2(PNpy) complexes in high yields. In contrast to the Fe(II) analogues,
CoCl$_2$(Ph$_2$P$_2$C$_6$H$_4$N$_{Me}$py) and CoCl$_2$(Ph$_2$P$_2$C$_6$H$_4$N$_{Ph}$py) were stable as CH$_2$Cl$_2$ solutions. However, when Ph$_2$P$_2$C$_2$N$_{H}$py was used in the synthesis, [Co(Ph$_2$P$_2$C$_2$N$_{H}$py)$_2$]$^{2+}$ was obtained.

Solid state structural analysis were carried out on CoCl$_2$(Ph$_2$P$_2$C$_6$H$_4$N$_{Me}$py), CoCl$_2$(Ph$_2$P$_2$C$_6$H$_4$N$_{Ph}$py) and CoCl$_2$(Ph$_2$P$_2$C$_3$N$_{Ph}$py) (Figure 4.5). These complexes adopt geometries similar to that of FeBr$_2$(Ph$_2$P$_2$C$_6$H$_4$N$_{Ph}$py), exhibiting distortions from planarity that arise from the phosphine nitrogen linkers bending out of the plane of the iminepyridine moiety. $^1$H NMR spectra of CoCl$_2$(PNpy) exhibited resonances over a wide range (δ 203 to -15). By comparing the $^1$H NMR spectra of all newly synthesized MX$_2$(PNpy), some characteristic resonances were tentatively assigned. The single broad low field resonance observed for all complexes (δ 200 to 170) was assigned to the 6-pyridyl proton. Two sharper signals in the δ 70 to 45 range were also assigned as pyridine resonances. Complexes containing PNpy ligands with -(CH$_2$)$_3$- linkers exhibited two additional
resonances between δ 146 and 76 (Figure 4.6). The magnetic moment ($\mu_{\text{eff}}$) was determined to be 4.71 by Evan’s method for \(\text{CoCl}_2^{\text{(Ph}_2\text{P})\text{C}_6\text{H}_4\text{N}^\text{Ph}_\text{py}}\), indicative of \(S = \frac{3}{2}\) spin state. This suggests high-spin \(d^7\) ground state with spin-orbit coupling, as is typical for Co(II) phosphine complexes.\(^{19}\)

Figure 4.6 Top: \(^1\)H NMR spectrum of \(\text{FeBr}_2^{\text{(Ph}_2\text{P})\text{C}_6\text{H}_4\text{N}^\text{Ph}_\text{py}}\) in \(\text{CD}_2\text{Cl}_2\). Bottom: \(^1\)H NMR spectrum of \(\text{CoCl}_2^{\text{(Ph}_2\text{P})\text{C}_3\text{N}^\text{Ph}_\text{py}}\) in \(\text{CD}_2\text{Cl}_2\).
A summary of the reactions of CoX₂ and FeX₂ with PNpy ligands is given in Table 4.2. In general, FeX₂(PNpy) is significantly less stable to redistribution compared to the Co(II) analogues. This is possibly due to the favorable transition from high-spin to low-spin $d^6$ iron(II) upon redistribution of the 1:1 complex to 1:2 complex, whereas 1:2 complexes of $d^7$ cobalt (II) containing neutral coplanar tri-dentate ligands usually exhibits high-spin ground states. However, when compact tridentate ligands such as Ph₂P₂C₂NHpy are used, redistribution to the 1:2 complex still occurred. It has been shown by Milstein and coworkers that even though the 1:1 complex FeCl₂(Pr-PNN) (Pr-PNN = 6-((di-isopropylphosphino)methyl)-2,2'-bipyridine) can be isolated, reaction of additional Pr-PNN with FeCl₂(Pr-PNN) leads to the formation of [Fe(Pr-PNN)]Cl₂, driven by the formation of the insoluble 1:2 complex.

Increasing the steric bulk of the PNpy ligands disfavors formation of the 1:2 complexes, underscoring the. Phosphine-aldimines Ph₂P₂C₂NHpy, Ph₂P₂C₆H₄NHpy and Ph₂P₂C₃NHpy are less sterically encumbered than phosphine-ketimines and gives the 1:2 Fe complexes. The -(CH₂)₃- linkage in Ph₂P₂C₃NHpy provided increased stability compared to Ph₂P₂C₆H₄NHpy, giving the stable 1:1 FeCl₃(Ph₂P₂C₃NHpy) without redistribution observed. Using bulky alkylphosphines also increases the stability of the dihalide complexes, as seen for CoCl₂(Ph₂P₂C₃NHpy) and FeBr₂(C₆P₂C₃NHpy). According to the reactivity of MX₂ with various PNpy ligands, we proposed the following guidelines to synthesize stable MX₂(PNpy) species: (1) use large substituents on the ketamine carbon, (2) use longer linkages between the phosphine and imine, and (3) use bulkier phosphine substituents.
Table 4.1 Results of the reactions of CoX₂ and FeX₂ (X = Cl, Br) with PNpy ligands. 1:1 complex denotes MX₂(PNpy) and 1:2 complex [M(PNpy)₂]^2⁺.

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<th>Co(II)</th>
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<td></td>
<td>1:2 complex</td>
<td>1:2 complex</td>
</tr>
<tr>
<td>N</td>
<td>1:1 complex</td>
<td>1:2 complex</td>
</tr>
<tr>
<td>PPh₂</td>
<td>by template synthesis</td>
<td>by template synthesis</td>
</tr>
<tr>
<td>N</td>
<td>1:1 complex</td>
<td>1:2 complex</td>
</tr>
<tr>
<td>PPh₂</td>
<td>by redistribution</td>
<td>by slow redistribution</td>
</tr>
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<td>N</td>
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<td>1:1 complex</td>
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<tr>
<td>N</td>
<td>1:1 complex</td>
<td>1:2 complex</td>
</tr>
<tr>
<td>PPh₂</td>
<td>by redistribution</td>
<td>by redistribution</td>
</tr>
<tr>
<td>N</td>
<td>1:1 complex</td>
<td>1:1 complex</td>
</tr>
<tr>
<td>PPh₂</td>
<td>(R = 'Pr, Ar^f)</td>
<td>(R = Cy)</td>
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4.5 Comparison of the bond distances of imine-pyridine in Ph₂P₂C₆H₄NPhpy

Coordinated α-diimine ligands are viewed as redox non-innocent and often coordinate to metals in reduced states (i.e. (α-diimine)⁻ or (α-diimine)₂⁻),²¹ which can complicate analysis of the oxidation states of metal centers. In addition to magnetic moment measurements that were carried out above, the solid state bond lengths of the α-
diimine ligands of MX$_2$(PNpy) were also carefully examined to establish the oxidation states of both PNpy and the metal centers. Since Zn(II) is generally viewed as inert to redox, the complexes ZnX$_2$(Ph$_2$P$_{C6H4}$N$_{Ph}$py) were synthesized for reference. Addition of Ph$_2$P$_{C6H4}$N$_{Ph}$py to a THF solution of ZnCl$_2$ and ZnI$_2$ afforded ZnCl$_2$(Ph$_2$P$_{C6H4}$N$_{Ph}$py) and ZnI$_2$(Ph$_2$P$_{C6H4}$N$_{Ph}$py), respectively, of which the chloride analogue was characterized by X-ray crystallography. Comparison of the α-diimine moiety bond lengths of MCl$_2$(Ph$_2$P$_{C6H4}$N$_{Ph}$py) (M = Fe, Co, Zn) showed little variance between the three complexes (Table 4.1). Since we assume ZnCl$_2$(Ph$_2$P$_{C6H4}$N$_{Ph}$py) contains a strictly neutral Ph$_2$P$_{C6H4}$N$_{Ph}$py, the Fe and Co analogues appear to also contain strictly neutral Ph$_2$P$_{C6H4}$N$_{Ph}$py ligands by comparison of bond metrics. The crystallographic results are consistent with the magnetic moment measurements of FeCl$_2$(Ph$_2$P$_{C6H4}$N$_{Ph}$py) and CoCl$_2$(Ph$_2$P$_{C6H4}$N$_{Ph}$py), which suggested both complexes in high-spin M(II) states.

Table 4.2 Selected bond distances of MCl$_2$(Ph$_2$P$_{C6H4}$N$_{Ph}$py)

<table>
<thead>
<tr>
<th></th>
<th>FeCl$<em>2$(Ph$<em>2$P$</em>{C6H4}$N$</em>{Ph}$py)</th>
<th>CoCl$<em>2$(Ph$<em>2$P$</em>{C6H4}$N$</em>{Ph}$py)</th>
<th>ZnCl$<em>2$(Ph$<em>2$P$</em>{C6H4}$N$</em>{Ph}$py)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M – N(1)</td>
<td>2.128(3)</td>
<td>2.076(2)</td>
<td>2.101(1)</td>
</tr>
<tr>
<td>M – N(2)</td>
<td>2.214(3)</td>
<td>2.255(2)</td>
<td>2.366(1)</td>
</tr>
<tr>
<td>N(1) – C(1)</td>
<td>1.339(4)</td>
<td>1.344(4)</td>
<td>1.336(2)</td>
</tr>
<tr>
<td>C(1) – C(2)</td>
<td>1.375(5)</td>
<td>1.354(4)</td>
<td>1.381(3)</td>
</tr>
<tr>
<td>C(2) – C(3)</td>
<td>1.371(5)</td>
<td>1.383(4)</td>
<td>1.377(3)</td>
</tr>
<tr>
<td>C(3) – C(4)</td>
<td>1.376(5)</td>
<td>1.382(4)</td>
<td>1.391(3)</td>
</tr>
<tr>
<td>C(4) – C(5)</td>
<td>1.371(4)</td>
<td>1.381(4)</td>
<td>1.385(2)</td>
</tr>
<tr>
<td>C(5) – C(6)</td>
<td>1.480(4)</td>
<td>1.484(3)</td>
<td>1.495(2)</td>
</tr>
<tr>
<td>C(6) – N(2)</td>
<td>1.296(4)</td>
<td>1.287(3)</td>
<td>1.285(2)</td>
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</table>
4.6 Template synthesis of MX$_2$(PNpy) complexes

The isolation of Ph$_2$P($\text{C}_6\text{H}_4$NHpy was prevented by facile reaction with H$_2$O present in the reaction mixtures. However, synthesis of [Ni(Ph$_2$P($\text{C}_6\text{H}_4$NHpy)$_2$]$^{2+}$ has been achieved by condensing Ph$_2$P($\text{C}_6\text{H}_4$NH$_2$ with 2-pyridinecarboxaldehyde in the presence of a Ni(II) precursor.$^{12}$ In this work, analogous Fe(II) complexes were synthesized in a similar “template” manner. Mixing FeBr$_2$ with Ph$_2$P($\text{C}_6\text{H}_4$NH$_2$ in THF, followed by slow addition of py-2-CHO, afforded a blue solid precipitate that was poorly soluble in CH$_2$Cl$_2$ but highly soluble in MeOH and H$_2$O. ESI-MS of the solubilized blue compound in MeOH indicated the formation of the dication [Fe(Ph$_2$P($\text{C}_6\text{H}_4$NHpy)$_2$]$^{2+}$ ($m/z = 308$). This complex can be purified by conversion to [Fe(Ph$_2$P($\text{C}_6\text{H}_4$NHpy)$_2$](BPh$_4$)$_2$. The analogous [Fe(Ph$_2$P($\text{C}_6\text{H}_4$NHpyMe)](BPh$_4$)$_2$ can be prepared in a similar manner using 6-Me-2-pyridinecarboxaldehyde (Eq. 4.3). X-ray crystallography revealed [Fe(Ph$_2$P($\text{C}_6\text{H}_4$NHpyMe)$_2$](BPh$_4$)$_2$ to exhibit a structure highly similar to [Fe(Ph$_2$P($\text{C}_6\text{H}_4$NHpy)$_2$](Fe$_2$Cl$_6$). The template synthesis was also successfully applied to ketimines. Mixing FeBr$_2$ and 2 equiv pyAc in THF afforded the known octahedral high-spin complex FeBr$_2$(pyAc)$_2$. Addition of 2 equiv Ph$_2$P($\text{C}_6\text{H}_4$NH$_2$ to FeBr$_2$(pyAc)$_2$ in MeOH, followed by addition of NaBPh$_4$, afforded [Fe(Ph$_2$P($\text{C}_6\text{H}_4$NMe$_2$py)$_2$](BPh$_4$)$_2$. NMR spectral analysis of [Fe(PNpy)$_2$](BPh$_4$)$_2$ indicated diamagnetism (Figure 4.7).
Figure 4.7  Top: $^1$H NMR spectrum of of [Fe(Ph$_2$P$_{C6H4}$N$_{pyMe}$)$_2$(BPh$_4$)$_2$] in CD$_3$CN. Bottom: $^{31}$P NMR spectrum of [Fe(Ph$_2$P$_{C6H4}$N$_{pyMe}$)$_2$(BPh$_4$)$_2$] in CD$_3$CN.
In contrast to iron, 1:1 complexes of cobalt dihalide can be easily obtained by the template synthesis route. For example, addition of 2-pyridinecarboxaldehyde to a mixture containing equimolar PNH₂ and CoCl₂ in THF gave a red-brown precipitate of CoCl₂(\text{Ph}_2\text{P}C_6\text{H}_4\text{N}^{\text{H}}\text{py}). Similarly, the reaction of 2-acetylpyridine, PNH₂, and CoCl₂ in refluxing THF gave CoCl₂(\text{Ph}_2\text{P}C_6\text{H}_4\text{N}^{\text{Me}}\text{py}). Though \text{Ph}_2\text{P}C_6\text{H}_4\text{N}^{\text{Ph}}\text{py} can be prepared and isolated in moderate yields, the template reaction of PNH₂, 2-benzoypyrindine, and CoCl₂ gave quantitative yields of CoCl₂(\text{Ph}_2\text{P}C_6\text{H}_4\text{N}^{\text{Ph}}\text{py}). The template method also allowed the synthesis of a new ligand derived from 2-benzoyl-4-diaminopyridine\textsuperscript{22} and \text{Ph}_2\text{P}C_6\text{H}_4\text{NH}_2 (Eq. 4.4).

![Chemical Structure]

(4.4)

4.7 Conclusions

A new family of tridentate ligands have been synthesized. The herein reported synthetic method for PNpy provides a modular route to obtain phosphine ligands that also incorporate a redox-active \(\alpha\)-diimine functionality. The present work addresses the vulnerability of phosphine-imines to acid-catalyzed hydrolysis, therefore caution must be used in the choice of condensation components. In cases where isolation is difficult, synthesis of PNpy can be achieved by “templating” on a metal center. Template reactions to give M-(PNpy) complexes is especially efficient using \text{Ph}_2\text{P}C_6\text{H}_4\text{NH}_2, possibly due to the favorably chelation of \text{Ph}_2\text{P}C_6\text{H}_4\text{NH}_2 to the metal center to form a 5-membered ring.

Metal-dihalide complexes of PNpy were synthesized by mixing MX₂ with PNpy or via a templated route. MX₂(PNpy) can be easily transformed into more reactive halide-free species, which will be discussed extensively in Chapters 5 and 6. Bond metrics of the solid state structures of the Fe-, Co-, Zn-dihalide complexes were closely examined to determine the neutral character of \text{Ph}_2\text{P}C_6\text{H}_4\text{N}^{\text{Ph}}\text{py} in these complexes. These parameters will serve as references for analysis of the electronic structures of reduced complexes derived from MX₂(PNpy),
The iron-dihalide complexes were found to be highly unstable to redistribution to give [Fe(PNpy)]$^{2+}$. The coordinatively saturated nature of the redistribution products renders further modification of the complexes difficult. They are also expected to be catalytically inert due to inability to react with substrates through inner-sphere mechanisms. By increasing the steric bulk of the PNpy ligands using the guidelines provided in Section 4.3, isolation of FeX$_2$(PNpy) can be achieved.

4.8 Experimental section

Materials and methods. Unless otherwise indicated, reactions were conducted using standard Schlenk techniques or in a glovebox under an N$_2$ atmosphere at room temperature with stirring. Solvents were high-performance liquid chromatography grade, dried and deoxygenated on a Glass Contour System or MBraun solvent purification system, and stored over 4 Å molecular sieves. The compounds Ph$_2$P(C$_6$H$_4$)NH$_2$,$^{23}$ Ph$_2$P(CH$_2$)$_3$NH$_2$,$^{14}$ Ph$_2$P(3,5-(CF$_3$)$_2$C$_6$H$_3$)$_2$,$^{24}$ HPPh$_2$,$^{25}$ and 2-benzoyl-4-diaminopyridine$^{22}$ were prepared according to literature procedures. The following materials were purchased from Sigma-Aldrich and used as received: $p$-toluenesulfonic acid monohydrate, FeBr$_2$, FeCl$_2$, CoCl$_2$, ZnCl$_2$, ZnI$_2$, CF$_3$CO$_2$H, NaBPh$_4$, 4 Å molecular sieves, 2-benzoylpyridine, LiAlH$_4$, 2,2’-azobis(2-methylpropionitrile) (AIBN). The following materials were purchased from Sigma-Aldrich, deoxygenated and stored with 4 Å molecular sieved for 48 h prior to use: 2-pyridinecarboxaldehyde, pyAc, 6-methylpyridine-2-carboxaldehyde. The following materials were purchased from Strem and used as received: HP($i$Pr)$_2$, PPh$_3$. $^1$H and $^{31}$P{$^1$H} NMR spectra were acquired on Varian Unity Inova 500NB and Unity 500 NB instruments at 20 °C unless otherwise noted. $^1$H NMR were referenced to residual solvent relative to tetramethyldisilane, $^{31}$P{$^1$H} NMR spectra were referenced to an external 85% H$_3$PO$_4$ standard. Magnetic moment measurements were carried out using the Evan’s method by collection of the $^{19}$F NMR spectra using trifluorotoluene as the standard.$^{26}$ Crystallographic data were collected using either a Siemens SMART diffractometer equipped with a Mo Kα source ($\lambda = 0.71073$ Å) and an Apex II detector, or a Bruker D8 Venture diffractometer equipped with a Mo Kα microfocus source and a Photon 100 detector. Elemental analyses were performed by the School of Chemical Sciences Microanalysis Laboratory utilizing a model CE 440 CHN analyzer.
Ph₂P(C₆H₄)NPh₂PY. 2-Benzoylpyridine (2.17 g, 11.8 mmol), Ph₂P(C₆H₄)NH₂ (1.80 g, 7.90 mmol), and p-toluenesulfonic acid monohydrate (75 mg, 0.39 mmol) were combined in 50 mL of toluene in a Schlenk flask. The flask was fitted with a Dean–Stark trap, and the mixture was heated at reflux for 22 h. The solution was then cooled and washed with aqueous NaHCO₃. The organic layer was dried with MgSO₄, and volatiles were removed under reduced pressure. The resulting yellow oil was extracted into a small amount of CH₂Cl₂ and recrystallized by layering Et₂O and storing at −10 °C for 16 h to afford the target compound as large yellow crystals. Yield: 53% (1.87 g).

1H NMR (CDCl₃) Isomer A: δ 8.57 (d, 3.6 Hz, 1H), 8.05 (d, 7.9 Hz, 1H), 7.77–7.68 (m, 1H), 7.65–7.56 (m, 1H), 7.46–6.83 (m, 17H), 7.29–7.27 (m, 1H), 6.47–6.42 (m, 1H).

1H NMR (500 MHz, CDCl₃) Isomer B: δ 8.64 (d, 4.4 Hz, 1H), 7.65–7.56 (m, 1H), 7.46–6.83 (m, 17H), 7.39–7.34 (m, 1H), 7.16–7.12 (m, 1H), 6.47–6.42 (m, 1H), 6.29 (d, 7.8 Hz, 1H).

31P{¹H} NMR (CDCl₃): δ −13.6 (s, 1P, single isomer), −13.7 (s, 1P, single isomer). Anal. Calcd (found) for C₃₀H₂₃NP·H₂O: C, 78.24 (78.25); H, 5.47 (5.39); N, 6.08 (6.09).

Ph₂P(C₆H₄)Me₂PY. 2-Acetylpyridine (998 mg, 8.23 mmol), PNH₂ (906 mg, 3.98 mmol), and 4Å molecular sieves (50 mg) were combined in 50 mL of toluene in a Schlenk flask. The flask was fitted with a Dean–Stark trap, and the mixture was heated at reflux for 72 h. The solution was then cooled and washed with aqueous NaHCO₃. The organic layer was dried with MgSO₄, and volatiles were removed under reduced pressure. The resulting yellow oil was extracted into a small amount of Et₂O and recrystallized by layering pentane and storing at −10 °C for 16 h to afford the target compound as white powders. Yield: 102 mg (6.5%).

1H NMR (500 MHz, CDCl₃): δ 8.54 (ddd, J = 4.7, 1.7, 0.7 Hz, 1H), 8.03 (ddd, J = 8.0, 0.7, 0.7 Hz, 1H), 7.71 (ddd, J = 7.8, 7.7, 1.8 Hz, 1H), 7.37–7.26 (m, 12H), 7.04 (ddd, J = 7.7, 7.4, 1.0, 0.7 Hz, 1H), 6.89 (ddd, J = 7.6, 4.4, 1.3 Hz, 1H), 6.74 (ddd, J = 7.7, 4.5, 0.9 Hz, 1H), 1.97 (d, J = 0.7 Hz, 3H). 3¹P{¹H} NMR (202.4 MHz, CDCl₃): δ −13.9 (s, 1P).

Ph₂P(O)(C₆H₄)NHCH(CH₃)₂PY. 2-acetylpyridine (1.06 g, 8.75 mmol), PNH₂ (1 g, 3.61 mmol), and 4Å molecular sieves (ca. 50 mg) were combined with 50 mL toluene in a screw cap round bottom flask. To the mixture was added 1 mL of CF₃CO₂H, and the flask was sealed. The mixture was heated in a 115 °C oil bath. After 48 h, the mixture was
allowed to cool, and the suspension was filtered. Volatiles were removed from the filtrate under reduced pressure. The resulting yellow oil was extracted into a small amount of Et$_2$O and recrystallized by layering pentane and storing at –10 °C for 16 h to afford the target compound as off-white powders. Yield: 1.53 g (43%). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.54 – 8.47 (m, 1H), 7.76 – 7.37 (m, 21H), 7.19 – 7.13 (m, 1H), 7.09 – 7.05 (m, 1H), 6.79 (ddd, $J = 14.7$, 7.7, 1.6 Hz, 1H), 6.50 (dt, $J = 7.5$, 3.8 Hz, 1H), 6.42 (dd, $J = 8.4$, 5.0 Hz, 1H), 4.59 (dq, $J = 12.1$, 6.8 Hz, 1H), 1.48 (d, $J = 6.8$ Hz, 3H). $^{31}$P$^1$H NMR (202 MHz, CDCl$_3$): $\delta$ 36.7 (s, 1P).

$\text{Ph}_2\text{P(O)}\text{C}_6\text{H}_4\text{NH}(\text{py})=\text{CHpy}$. 2-pyridine carboxaldehyde (80 mg, 0.75 mmol) and $\text{Ph}_2\text{P(C}_6\text{H}_4\text{)}\text{NH}_2$ (116 mg, 0.42 mmol), 4 Å molecular sieves (50 mg) were added to THF (5 mL) in a 20 mL scintillation vial and stirred for 2 hours. The solution was then filtered and the filtrate allowed to stand overnight, whereupon X-ray diffraction quality crystals grew from the solution.

**Preparation of Ph$_2$P(CH$_2$)$_3$NH$_2$.** The following procedure was modified from a literature method.$^{27}$ *Step 1: synthesis of Ph$_2$P(CH$_2$)$_2$CN.* To a stirring mixture containing diphenylphosphine (3 mL, 17.2 mmol), 50% NaOH(aq) (0.2 mL), and acetonitrile (ca. 15 mL) was added acrylonitrile (1.75 mL, 26.7 mmol) via syringe. This mixture was heated in a 58 °C oil bath for 1 h, during this time an orange color evolved. After cooling to room temperature, water (ca. 10 mL) was added and the solution was extracted with benzene (3×10 mL). The organic layer was separated and dried over Na$_2$SO$_4$, and solvent was removed under reduced pressure. The resulting yellow oil was extracted using boiling Et$_2$O. After removal of Et$_2$O under reduced pressure a pale yellow oil was obtained. This crude oil containing Ph$_2$P(CH$_2$)$_2$CN was used in subsequent reactions without further purification.

*Step 2: reduction of Ph$_2$P(CH$_2$)$_2$CN.* LiAlH$_4$ (800 mg, 21 mmol) was added Et$_2$O (50 mL) and cooled to 0°C. To this white suspension was added dropwise a solution of the crude Ph$_2$P(CH$_2$)$_2$CN from the previous preparation in Et$_2$O (ca. 10 mL). After the addition was completed, the mixture was heated to reflux for 1.5 h. The mixture was then cooled to room temperature and added water (ca. 40 mL) dropwise. The organic layer was separated and dried over Na$_2$SO$_4$. Solvent was evaporated under reduced pressure to give
the target compound \( \text{Ph}_2 \text{PCl}_3 \text{NH}_2 \) as a colorless liquid. Yield: 2.1 g (50 %). \(^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta 7.44 - 7.30 \) (m, 10H, aryl-H), 2.78 (t, \( J = 7.0 \) Hz, 2H, \( CH_2 \)), 2.09 – 2.03 (m, 2H, \( CH_2 \)), 1.60 – 1.53 (m, 2H, \( CH_2 \)), 1.07 (br, 2H, \( NH_2 \)). \(^{31}\)P\{\(^1\)H\} NMR (202.4 MHz, CDCl\(_3\)): \( \delta -15.06 \) (s, 1P).

Preparation of \( \text{iPr}_2 \text{P(CH}_2\text{)}_3\text{NH}_2 \). Step 1: synthesis of \( \text{iPr}_2 \text{P(CH}_2\text{)}_2\text{CN} \). This compound was synthesized using a modified literature procedure.\(^{15}\) In a screw cap round bottom flask was combined \( \text{iPr}_2 \text{PH} \) (820 mg, 6.9 mmol), acrylonitrile (0.6 mL, 9 mmol) and AIBN (35 mg, 0.2 mmol). The mixture was heated in a 135 °C oil bath for 16 h. According to the \(^{31}\)P NMR spectrum of the dark red reaction mixture recorded at this time, the conversion was determined to be 55% by relative integration of \( \text{iPr}_2 \text{PH} \): \( \text{iPr}_2 \text{P(CH}_2\text{)}_2\text{CN} \). Additional acrylonitrile (0.6 mL, 9 mmol) and AIBN (35 mg, 0.2 mmol) was added, and heating was continued in a 135°C oil bath for another 16 h. After cooling the mixture, volatiles were removed under reduced pressure to give a dark red oil. The product \( \text{iPr}_2 \text{P(CH}_2\text{)}_2\text{CN} \) was obtained by distillation at 95°C using a Kugelrohr device as a colorless liquid, and was used in subsequent reactions without further purification.

Step 2: reduction of \( \text{iPr}_2 \text{P(CH}_2\text{)}_2\text{CN} \). An Et\(_2\)O (100 mL) suspension containing LiAlH\(_4\) (300 mg, 7.9 mmol) was added dropwise a 20 mL Et\(_2\)O solution of \( \text{iPr}_2 \text{P(CH}_2\text{)}_2\text{CN} \) obtained from the previous step. After the addition was complete, the mixture was heated in a 40 °C oil bath for 1 h. Water (100 mL) was then added to the mixture. The Et\(_2\)O layer was separated, dried over Na\(_2\)SO\(_4\) and dried under reduced pressure to yield the target compound \( \text{iPr}_2 \text{P}^{\text{C}_3} \text{NH}_2 \) as a colorless liquid. Yield: 352 mg (41.8%). \(^1\)H NMR (500 MHz, C\(_6\)D\(_6\)): \( \delta 2.55 \) (p, \( J = 6.7 \) Hz, 2H, \( CH \)), 1.63 – 1.45 (m, 4H, \( CH_2 \)), 1.28 – 1.24 (m, 2H, \( CH_2 \)), 1.07 – 0.98 (m, 12H, \( CH_3 \)), 0.48 (s, 2H, \( NH_2 \)). \(^{31}\)P\{\(^1\)H\} NMR (202.4 MHz, C\(_6\)D\(_6\)): \( \delta 3.64 \) (s, 1P).

Preparation of \( (\text{3,5-(CF}_3\text{)}_2\text{C}_6\text{H}_3)_2\text{P(CH}_2\text{)}_3\text{NH}_2 \). Step 1: synthesis of \( (\text{3,5-(CF}_3\text{)}_2\text{C}_6\text{H}_3)_2\text{P(CH}_2\text{)}_2\text{CN} \). In a Schlenk flask was loaded \( (\text{3,5-(CF}_3\text{)}_2\text{C}_6\text{H}_3)_2\text{PH} \) (917 mg, 2.00 mmol) and dissolved in MeCN (20 mL). To this colorless solution was added NaOH\(_{\text{aq}}\) (5 mL) to give a bright orange mixture. Acrylonitrile (0.3 mL) was then added via syringe, and the orange solution was heated in a 55 °C oil bath for 1 h. After cooling to room temperature, degassed H\(_2\)O (10 mL) was added, followed by extraction of the organic layer.
by benzene (25 mL×3). The benzene extract was dried over Na₂SO₄ and evaporated under vacuum to obtain the target compound as white solids. Yield: 770 mg (75%). ¹H NMR (499 MHz, C₆D₆): δ 7.62 (s, 2H), 7.43 (d,  J = 6.5 Hz, 4H), 1.29 – 1.18 (m, 2H), 1.06 – 0.99 (m, 2H). ¹⁹F NMR (470 MHz, C₆D₆): δ –63.20 (s, 6F). ³¹P NMR (202 MHz, C₆D₆): δ –13.38 (s, 1P).

Step 2: reduction of (3,5-(CF₃)₂C₆H₃)₂P(CH₂)₂CN. To a schlenk flask was loaded an Et₂O (15 mL) suspension of LiAlH₄ (90mg, 2.37 mmol). This flask was equipped with an addition funnel, and the LiAlH₄ suspension cooled to –78 °C. In a separate flask was prepared an Et₂O (50 mL) solution containing (3,5-(CF₃)₂C₆H₃)₂P(CH₂)₂CN (770 mg, 1.51 mmol), and was cannula transferred into the addition funnel under a positive N₂ atmosphere. The phosphine solution was slowly added to the LiAlH₄ suspension (ca. 1 h). After addition was complete, the solution was slowly warmed to reflux and stirred for 1 h. After cooling to room temperature, the reaction was quenched with degassed H₂O (10 mL). The organic phase was separated, dried over Na₂SO₄, and evaporated under reduced pressure to afford a lightly colored oil that is the target compound (3,5-(CF₃)₂C₆H₃)₂P(CH₂)₂NH₂. Yield: 395 mg (51 %). Further purification can be achieved by recrystallization from hexane. ¹H NMR (499 MHz, C₆D₆): δ 7.70 (ddd,  J = 5.8, 1.8, 1.0 Hz, 4H), 7.64 (dd,  J = 1.9, 1.0 Hz, 2H), 2.37 – 2.15 (m, 2H), 1.66 – 1.57 (m, 2H), 1.10 – 0.98 (m, 2H). ¹⁹F NMR (470 MHz, C₆D₆): δ –63.22 (s, 1F). ³¹P NMR (202 MHz, C₆D₆) δ –12.07 (s, 1P).

R₂PC₃NH₃py⁻ ligands. R₂pC₃NH₂ (R = Ph, iPr) and 1 equiv of the corresponding pyridine was combined in THF and stirred in room temperature. After 1 hour, volatiles were removed under reduced pressure to afford the ligands in >99% yield. Ligands obtained from this procedure was used for synthesis of CoCl₂(PNpy) without further purification.

²⁻Pr₂PC₃NH₃py. ¹H NMR (500 MHz, C₆D₆): δ 8.59 (s, 1H, C=NH), 8.52 – 8.42 (m, 1H, py-H), 8.18 (m, 1H, pyH), 7.04 (td,  J = 7.6, 1.8 Hz, 1H, pyH), 6.61 (ddd,  J = 7.4, 4.8, 1.3 Hz, 1H, pyH), 3.57 (td,  J = 6.7, 1.5 Hz, 2H, CH₂), 1.97 – 1.86 (m, 2H, CH₂), 1.59 – 1.52 (m, 2H, methine-H), 1.39 – 1.35 (m, 2H, CH₂), 1.05 – 0.97 (m, 12H, CH₃). ³¹P{¹H} NMR (202.4 MHz, C₆D₆): δ 2.66 (s, 1P)
Ph2P<sub>C3</sub>N<sub>2</sub>py. 1H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.66 – 8.62 (m, 1H, py-H), 8.37 (s, 1H, N=C-H), 7.97 (d, J = 7.9, 1H, py-H), 7.74 (td, J = 7.7, 1.8 Hz, 1H, py-H), 7.46 – 7.28 (m, 11H), 3.76 (t, J = 6.8 Hz, 2H, C-CH), 2.18 – 2.10 (m, 2H, CH), 1.92 – 1.83 (m, 2H, CH).

31P{1H} NMR (202.4 MHz, CDCl<sub>3</sub>): δ −15.5 (s, 1P).

Ph2P<sub>C3</sub>N<sub>2</sub>Ph<sub>2</sub>py. A mixture of Ph2P<sub>C3</sub>NH<sub>2</sub> (1.40 g, 6.12 mmol), benzoylpyridine (1.12 g, 6.12 mmol) and p-toluenesulfonic acid monohydrate (52 mg, 0.306 mmol) was dissolved in toluene (100 mL) in a schlenk flask. The flask was equipped with a Dean-Stark trap and the mixture was heated to reflux for 18 hours. The solution was then washed with saturated NaHCO<sub>3</sub>(aq) and dried with anhydrous MgSO<sub>4</sub>. Volatiles were removed under reduced pressure to yield the desired compound as yellow oil containing 2 isomers in approximately 1:1.3 ratio. Yield: 2.324 g (93%). 1H NMR (500 MHz, CDCl<sub>2</sub>): δ 8.74 (d, J = 4.82 Hz, 1H, isomer A), 8.59 (d, J = 4.77 Hz, 1H, isomer B), 8.16 (dt, J = 8.0, 1.1 Hz, 2H, isomer A), 7.80 – 7.73 (m, 4H, isomer A+B), 7.56 – 7.24 (m, 24H, isomer A+B), 7.17 (dt, J = 7.7, 1.2 Hz, 2H, isomer A+B), 7.14 – 7.11 (m, 4H, isomer A+B), δ 3.49 (t, J = 6.8 Hz, 2H, isomer B), 3.41 (t, J = 6.7 Hz, 2H, isomer A), 2.17 – 2.04 (m, 4H, isomer A+B), 1.87 – 1.69 (m, 4H, isomer A+B). 31P{1H} NMR (202.4 MHz, CDCl<sub>2</sub>): δ −15.09 (s, 1P, single isomer), −15.08 (s, 1P, single isomer).

[Fe(Ph2P<sub>C6H4</sub>NH<sub>py</sub>Me<sub>2</sub>)(BPh<sub>4</sub>)<sub>2</sub>]. A mixture of FeBr<sub>2</sub> (190 mg, 0.88 mmol) and Ph2P<sub>C6H4</sub>NH<sub>2</sub> (244 mg, 0.88 mmol) were combined in THF (6 mL) to give a yellow solution. To this solution was added 6-methylpyridine-2-carboxaldehyde (110 mg, 0.91 mmol) in THF solution (3 mL) dropwise, leading to an immediate color change to dark blue. The mixture was then stirred for 1 h, affording a blue solid precipitate that was collected and washed with THF (3 mL). This solid was then dissolved in MeOH (5 mL) followed by the slow addition of a MeOH solution (3 mL) of sodium tetraphenylborate (310 mg, 0.91 mmol), leading to the precipitation of a dark blue solid. This blue solid was collected by filtration and washed with MeOH (2 × 2 mL) and Et<sub>2</sub>O (2 × 3 mL). Yield: 236 mg (36%). The salt [Fe(PN<sub>2</sub>H<sub>py</sub>M<sub>e</sub>)<sub>2</sub>](BPh<sub>4</sub>)<sub>2</sub> is insoluble in THF, sparingly soluble in CH<sub>2</sub>Cl<sub>2</sub>, and highly soluble in MeCN. 1H NMR (500 MHz, CD<sub>3</sub>CN): δ 9.86 (s, 2H), 8.71 (d, 8.2 Hz, 2H), 8.14 (t, 7.8 Hz, 2H), 7.84 (t, 7.5 Hz, 2H), 7.61 (m, 2H), 7.56 (t, 7.8 Hz, 2H), 7.48 (d, 7.5, 2H), 7.26 (m, 16H), 7.17 (t, 7.4 Hz, 2H), 7.14 (t, 7.4 Hz, 2H), 6.98 (m, 16H), 6.88 (t,
7.6 Hz, 4H), 6.83 (t, 7.1 Hz, 8H), 6.78 (t, 7.4 Hz, 4H), 6.52 (m, 8H), 1.74 (s, 6H); *a resonance at 5.33, assigned to CH$_2$Cl$_2$, was observed even after extended drying under vacuum. $^{31}$P{¹H} NMR (202.4 MHz, CD$_2$CN): δ 60.1 (s, 2P). Anal. Calcd (found) for FeP$_2$N$_4$B$_2$C$_9$H$_8$: C, 79.26 (79.00); H, 5.51 (5.59); N, 3.98 (3.74).

**FeBr$_2$(Ph$_2$P$_2$C$_6$H$_4$NPh$_2$).** A suspension of FeBr$_2$ (80 mg, 0.37 mmol) in THF (3 mL) was treated with a THF solution of Ph$_2$P$_2$C$_6$H$_4$NPh$_2$ (156 mg, 0.37 mmol), causing a color change from yellow to blue-green. The mixture was stirred for 3 h, leading to a precipitation of a blue-green solid. Pentane (10 mL) was added to the suspension while stirring to further precipitate the blue-green solid. This solid was collected by filtration, washed with pentane (2 × 5 mL), and dried to give FeBr$_2$(PN$_2$py) as a green powder. Yield: 89% (210 mg). $^1$H NMR (500 MHz, CD$_2$Cl$_2$): δ 178, 75.7, 67.3, 17.8, 14.6, 13.9, 13.4, 7.71, 7.49, 5.62, 0.18, −1.66, −3.72; *a resonance at 5.33, assigned to CH$_2$Cl$_2$, was observed even after extended drying under vacuum. Anal. Calcd (found) for C$_{30}$H$_{23}$Br$_2$FeN$_2$P·0.5(CH$_2$Cl$_2$): C, 52.29 (52.08); H, 3.45 (3.36); N, 4.00 (4.20).

**CoCl$_2$(Ph$_2$P$_2$C$_6$H$_4$NMe$_2$py).** A THF solution (5 mL) of CoCl$_2$ (8 mg, 0.05 mmol) was combined with a THF solution (2 mL) of Ph$_2$P$_2$C$_6$H$_4$NMe$_2$py (20 mg, 0.05 mmol). After stirring for 6 h, the resulting red-brown suspension was filtered using a medium frit. The red-brown solid was washed with THF (3 mL × 3) to give the target compound as a red powder. Yield: 21 mg (84%). Single crystals suitable for X-ray diffraction were obtained by slow diffusion of pentane into a concentrated CH$_2$Cl$_2$ solution containing the target compound. $^1$H NMR (500 MHz, CD$_2$Cl$_2$): δ 169.45, 68.79, 58.25, 22.36, 18.29, 12.02, 8.99, 4.80, 1.14, −7.75, −12.00, −13.08. The same complex was also prepared by the following "template method." A solution of CoCl$_2$ (51 mg, 0.39 mmol) and (2-diphenylphosphino)aniline (103 mg, 0.37 mmol) in THF (7 mL) to give a blue-green solution. Dropwise addition of a THF (2 mL) solution of 2-acetylpyridine (46 mg, 0.38 mmol) resulted in copious blue precipitate. The reaction vial was then sealed and heated at 65 ºC for 16 h, resulting in a clear solution and a red solid. This solid was collected by filtration and washed with THF (5 mL) and pentane (5 mL). Yield: 149 mg (79 %). Anal. Calcd for C$_{25}$H$_{21}$Cl$_2$CoN$_2$P (found): C, 58.85 (58.65); H, 4.15 (4.08); N, 5.49 (5.65).
**CoCl$_2$**($\text{Ph}_2\text{P}C_6H_4\text{NPh})$. A THF solution (30 mL) of CoCl$_2$ (141 mg, 1.08 mmol) was combined with a THF solution (5 mL) of $\text{Ph}_2\text{P}C_6H_4\text{NPh}$ (480 mg, 1.08 mmol). After stirring for 6 h, the resulting purple-brown suspension was filtered using a medium frit. The purple-brown solid was washed with THF (10 mL $\times$ 3), and recrystallized from CH$_2$Cl$_2$/pentane to give the target compound as dark purple crystals. Yield: 602 mg (97%). Single crystals suitable for X-ray diffraction were obtained by slow diffusion of pentane into a concentrated CH$_2$Cl$_2$ solution containing the target compound. $^1$H NMR (500 MHz, CD$_2$Cl$_2$): $\delta$ 171.17, 66.36, 58.93, 23.39, 17.34, 11.98, 10.48, 10.04, 6.75, $-$7.17, $-$13.10. The same complex was also prepared by the following "template method." A solution of CoCl$_2$ (25 mg, 0.19 mmol), $\text{Ph}_2\text{P}C_6H_4\text{NH}_2$ (55 mg, 0.20 mmol) and 2-benzoylpyridine (36 mg, 0.20 mmol) in THF (10 mL) was sealed in a 20 mL scintillation vial. The reaction vial was heated at 65 ºC where after 15 mins gave a green solution. Further heating for 16 h resulting in a clear solution and a purple-brown solid precipitate. This solid was collected by filtration and washed with THF (5 mL) and pentane (5 mL). Yield: 82 mg (75%). Anal. Calcd for C$_{30}$H$_{23}$Cl$_2$CoN$_2$P (found): C, 62.96 (63.15); H, 4.05 (3.89); N, 4.89 (4.99).

**CoCl$_2$**($\text{iPr}_2\text{P}C_3\text{Nhy})$. A THF solution (10 mL) of CoCl$_2$ (60 mg, 0.46 mmol) was combined with a THF solution (2 mL) of $\text{iPr}_2\text{P}C_3\text{Nhy}$ (180 mg, 0.44 mmol). After stirring for 6 h, the resulting red suspension was filtered using a medium frit. The red solid was washed with THF (5 mL $\times$ 3), and dissolved in CH$_2$Cl$_2$. Filtration of the CH$_2$Cl$_2$ solution through a short plug of Celite gave a red solution and a small amount of bright green solid. The red solution was then concentrated to ca. 10 mL, layered with pentane (5 mL) and kept at $-$35 ºC for 48 h to give the target compound as dark red crystals. Yield: 90 mg (63%). Single crystals suitable for X-ray diffraction were obtained by slow diffusion of pentane into a concentrated CH$_2$Cl$_2$ solution containing the target compound. $^1$H NMR (500 MHz, CD$_2$Cl$_2$): $\delta$ 200.95, 145.47, 109.16, 66.01, 62.61, 21.82, 13.82, 11.88, 10.12, 3.88, $-$0.37, $-$4.57, $-$15.03. Anal. Calcd for C$_{27}$H$_{25}$Cl$_2$CoN$_2$P (found): C, 60.24 (63.15); H, 4.68 (3.89); N, 4.89 (4.99).

**CoCl$_2$**($\text{Ph}_2\text{P}C_3\text{NHpy})$. A THF solution (15 mL) of CoCl$_2$ (142 mg, 1.1 mmol) was combined with a THF solution (5 mL) of $\text{Ph}_2\text{P}C_3\text{NHpy}$ (262 mg, 1 mmol). After stirring for 6 h, the resulting red suspension was filtered using a medium frit. The red solid was
washed with THF (10 mL × 3), and dissolved in CH₂Cl₂. Filtration of the CH₂Cl₂ solution through a short plug of Celite gave a red solution and a small amount of bright green solid. The red solution was then dried under reduced pressure to yield a pink powder that is pure by ¹H NMR spectroscopy. The powder can be further recrystallized from CH₂Cl₂/pentane to give the target compound as dark red crystals. Yield: 256 mg (65%). ¹H NMR (500 MHz, CD₂Cl₂): δ 194.04, 124.47, 100.85, 98.78, 62.50, 47.83, 1.84, 0.54, −2.78, −7.63.

CoCl₂(Ph₂P(C₆H₄)N(4-NMe₂C₅H₅N₃)). A THF (5 mL) solution containing 2-benzoyl-4-diaminopyridine (28 mg, 0.124 mmol) and Ph₂P(C₆H₄)NH₂ (28 mg, 0.124 mmol) was added CoCl₂ (16 mg, 0.123 mmol). This suspension was heated in a 65 °C oil bath while stirring for 16 h, during which time purple-brown solid precipitates formed. After cooling to room temperature, the solid was collected by filtration through a frit. Yield: 53 mg (70%). ¹H NMR (500 MHz, CD₂Cl₂): δ 186.55, 59.40, 57.50, 22.86, 13.74, 12.98, 11.93, 9.56, 8.53, 7.19, 5.59, −6.61, −11.68.

ZnX₂(Ph₂P(C₆H₄)NPh) (X = Cl, I). A solution of ZnCl₂ (26.4 mg, 0.19 mmol) in THF (5 mL) was treated dropwise with a solution of Ph₂P(C₆H₄)N₃Ph (82 mg, 0.19 mmol) in THF (3 mL), resulting in the precipitation of a yellow powder. The solid was collected, washed with THF (2 mL) and pentane (2 mL), and dried under vacuum to give ZnCl₂(Ph₂P(C₆H₄)N₃Ph) as a yellow powder. Yield: 85 % (90 mg, 0.16 mmol). Single crystals suitable for X-ray diffraction were obtained by vapor diffusion of pentane into a CH₂Cl₂ solution. ¹H NMR (500 MHz, CD₂Cl₂): δ 9.63 (ddd, 5.7, 1.7, 0.7, 1H), 7.99 (ddd, 7.8, 7.7, 1.7 Hz, 1H), 7.78 (ddd, 7.7, 5.1, 1.2 Hz, 1H), 7.65 (m, 4H), 7.51 (m, 4H), 7.44 (m, 6H), 7.27 (m, 2H), 7.18 (m, 1H), 6.89 (m, 2H), 6.71 (m, 1H). ³¹P{¹H} NMR (202.4 MHz, CD₂Cl₂): −29.8 (s, 1P) ZnI₂(Ph₂P(C₆H₄)N₃Ph) was prepared in an analogous manner using ZnI₂. ¹H NMR (500 MHz, CD₂Cl₂): δ 9.88 (ddd, J = 5.3, 1.7, 0.8 Hz, 1H), 8.01 (td, J = 7.8, 1.7 Hz, 1H), 7.82 (ddd, J = 7.7, 5.2, 1.3 Hz, 1H), 7.72 (ddd, J = 10.7, 8.3, 1.4 Hz, 4H), 7.52 (td, J = 7.3, 1.4 Hz, 4H), 7.49 – 7.39 (m, 6H), 7.32 – 7.24 (m, 2H), 7.23 – 7.13 (m, 1H), 6.96 – 6.84 (m, 2H), 6.79 – 6.64 (m, 1H). ³¹P{¹H} NMR (202 MHz, CD₂Cl₂): δ – 33.8.
4.9 References


Chapter 5.

Synthesis, reactivity and electronic structure of reduced Co-(PNpy) complexes: mechanistic insights into Co-catalyzed hydrosilylation reactions†

5.1 Introduction

The hydrofunctionalization of alkenes is a widely practiced technology that is completely reliant on catalysis by PGMs and their complexes.¹ Broadly speaking, PGM-based catalysts offer two advantages: (1) extraordinarily high activities, often at the ppm level, and (2) tolerance toward oxygen and water. Given the high costs of PGMs, there is great interest in the discovery of catalysts based on less expensive metals. In recent years, considerable progress has been made with Fe-based systems.² A number of cobalt catalysts for hydrogenation³ and hydroboration⁴ have also been reported to exhibit activities that are far superior than the early cobalt-phosphine⁵ and cobalt-carbonyl⁶ systems (Chart 5.1). However, reports on cobalt hydrosilylation catalysts are comparatively rare, owing to olefin isomerization and competing dehydrogenative silylation.¹a,⁴b,⁸ The few examples include the sigma complex [Cp*Co(P(OMe)₃)CH₂CH₂-μ-H]+ presented by Brookhart et al.,⁹ a Co(II) silyl complex reported by Deng co-workers,¹⁰ and β-diketiminate-supported cobalt(II)-arene complexes.¹¹ With the exception of the [Cp*Co(P(OMe)₃)CH₂CH₂-μ-H]+ system, hydrosilylation catalyzed by these complexes are lacking in mechanistic details, supposedly due to instability of intermediates.

Synthesis of CoCl₂(PNpy) complexes was presented in Chapter 4. We expected that in addition to catalytic activity for hydrofunctionalization reactions, catalytic intermediates generated from Co-(PNpy) would be reasonably stable owing to the σ-donating phosphine. The following chapter presents the characterization of new catalytically active low-valent cobalt complexes. In particular, highly active species that are proposed to be directly involved in the hydrosilylation catalytic cycle are observed using low-temperature NMR spectroscopy.

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Chart 5.1 Cobalt complexes that catalyzes H-X + alkene reactions.
5.2 Synthesis of reduced Co-(PNpy) complexes featuring dimeric structures

We sought out to obtain reduced Co-(PNpy) species using the easily synthesized CoCl$_2$(PNpy) as starting materials. Reduction of Co(II) complexes to give reactive halide-free species is a method adopted by many researchers. A few examples are presented in Figure 5.1. Synthesis of reduced cobalt species containing the previously reported Ph$_2$P$_2$C$_2$N$_2$H$_2$py was first attempted. Since CoCl$_2$(Ph$_2$P$_2$C$_2$N$_2$H$_2$py) was not isolable (see Section 4.3), routes that avoided Co(II) oxidation state was explored. Utilizing the redox properties of the imino-pyridine group, addition of Na to a THF solution of the ligand gave an intensely red species, assigned Na[Ph$_2$P$_2$C$_2$N$_2$H$_2$py]. Addition of CoCl$_2$ to this red solution immediately afforded a dark brown solution that is a Co-chlorido species. This product was sparingly soluble in C$_6$D$_6$ but soluble in THF-$d_8$, and is ostensibly diamagnetic based on its $^1$H NMR spectra in these solvents. Methylation of the Co-chloride was achieved by addition of 1 equiv of MeLi. The resulting Co-methyl complex was afforded in high yield as a C$_6$D$_6$-soluble dark brown powder. The $^{31}$P NMR spectra of both complexes in THF-$d_8$ exhibited a broad resonance centered at $\delta$ 40.0 and $\delta$ 45.8 for Co-chloride and Co-methyl, respectively. The broadness is attributed to the coupling of $^{31}$P nuclei to the quadrupolar $^{59}$Co center. The $^1$H NMR shifts of the chloride and methyl complexes were temperature-
independent over the range 20 to 50 °C (poor solubility prevented studies at lower temperatures), suggesting the absence of low-lying paramagnetic states. Several low-spin four-coordinate reduced cobalt complexes have been described as possessing thermally accessible high-spin states, a physical property that can be identified by examining the NMR spectra at different temperatures. For example, $^1$H NMR resonance for the para-pyridine proton of (alkylDIP)CoCl complexes shift by ca. $\delta$ 20 between the temperature range of –60 to +65 °C.\textsuperscript{14}

\[ \text{Scheme 5.1 Synthesis of [CoCl(Ph}_2\text{P}_2\text{C}_2\text{N}^\text{H}^\text{py})]_2 \text{ and [CoMe(Ph}_2\text{P}_2\text{C}_2\text{N}^\text{H}^\text{py})]_2.} \]

Diamagnetic cobalt complexes are typically pentacordinate or planar. Two aspects of the $^1$H NMR spectrum of both Co-chlorido and Co-methyl are unusual. First, the -CH$_2$- signals for the ligand backbone consist of three multiplets, integrating 1:1:2. This observation suggests that the four methylene protons are diasterotopic (with two overlapping peaks). Such low symmetry is inconsistent with a planar CoXL$_3$ species. Second, the aldimine CH=N resonances are observed at $\delta$ 5.14 and 4.31, respectively, for the chloride and methyl, significantly shifted upfield compared to that of free Ph$_2$P$_2$C$_2$N$_2$py ($\delta$ 8.44).\textsuperscript{15} This chemical shift is also significantly upfield compared to other cobalt complexes containing N-bound imine ligands, typically exhibiting resonances for CH=N in the $\delta$ 8.5 – 9.5 range.\textsuperscript{16} The chemical shifts of the CH=N resonances are close to those that have been observed for $\pi$-bound imine ligands.\textsuperscript{17} On the basis of these observations and analyses, these complexes were reformulated as the dimers [CoR(Ph$_2$P$_2$C$_2$N$_2$py)]$_2$ (R = Cl, Me) (Scheme 5.1).
To further determine the structure of the Co-methyl complex in solution, $^1$H 1D-NOESY spectra were collected for $[\text{CoMe(Ph}_2\text{P}_2\text{C}_2\text{N}_2\text{H}_2\text{py})]_2$ (Figure 5.2). Correlations were revealed between protons that are predicted to have large intramolecular distances, but would be reasonable within a pair CoMe($^\text{Ph}_2\text{P}_2\text{C}_2\text{N}_2\text{H}_2\text{py}$) units that are arranged in a centrosymmetric fashion. Spin inversion of the methyl ($H_a$) selectively affected peaks for the aldimine proton ($H_b$) as well as a signal assigned to the 6-pyridine proton ($H_d$, Figure 5.2, middle). Inversion of the aldimine ($H_b$) signal also affected the methyl ($H_a$) and a peak assigned to the 3-pyridine proton $H_c$ (Figure 5.2, bottom). Overall these NMR spectra support dimeric structures for both $[\text{CoCl(Ph}_2\text{P}_2\text{C}_2\text{N}_2\text{H}_2\text{py})]_2$ and $[\text{CoMe(Ph}_2\text{P}_2\text{C}_2\text{N}_2\text{H}_2\text{py})]_2$ in solution.
Crystallographic analyses of $[\text{CoR(Ph}_2\text{P}_2\text{C}_2\text{N}_2\text{H}_2\text{py})]_2$ ($R=\text{Cl, Me}$) confirmed that they are centrosymmetric dimers in the solid state. Each Co center adopts a trigonal bipyramidal coordination geometry defined by Cl-P-N-N, and an $\eta^2$-imine ligand from the second cobalt center. The imine C=N distances are elongated by ca. 0.1 Å compared to that observed for the PNpy ligands on metal dihalide complexes in Section 4.3.\(^{19}\) This elongation is consistent with an $\eta^2$–imine ligand where significant electron density is transferred from the metal center.\(^{2b,16a}\) No metal-metal bonds were observed; the Co–Co distances in both complexes were ca. 2.9 Å, well above the range for covalent interaction (typically ~ 2.5 Å).\(^{20}\) The structures of these complexes are best described as pentacoordinate CoXL₄ systems, and the crystallographic results are fully consistent with the $^1\text{H}$ NMR spectra. The robustness of the dimeric interaction was further demonstrated by their non-reactivity toward PPh₃, as monitored by $^1\text{H}$ and $^{31}\text{P}$ NMR spectroscopy over the course of 12 h.

Figure 5.3. Solid state representations (50% thermal ellipsoids) of $[\text{CoCl(Ph}_2\text{P}_2\text{C}_2\text{N}_2\text{H}_2\text{py})]_2$ (left) and $[\text{CoMe(Ph}_2\text{P}_2\text{C}_2\text{N}_2\text{H}_2\text{py})]_2$ (right). Hydrogen atoms and solvent removed for clarity.
In contrast to Ph$_2$P$_2$C$_2$N$_2$H$_2$py, the phosphine-kerimine-pyridine ligands do not appear to generate diamagnetic dimeric complexes. Instead, $^1$H NMR spectra for the products of the reaction of CoCl$_2$ with Na[Ph$_2$P$_2$C$_6$H$_4$N$_2$Ph$_2$py] and Na[Ph$_2$P$_2$C$_3$N$_2$Ph$_2$py] indicate paramagnetism, which is typical for quasi-tetrahedral cobalt-halide complexes.\textsuperscript{14,21} Similarly, highly shifted $^1$H NMR resonances were observed for crude solutions of the proposed monochloride complexes obtained from the reduction of CoCl$_2$(Ph$_2$P$_2$C$_6$H$_4$N$_2$Ph$_2$py) or CoCl$_2$(Ph$_2$P$_2$C$_3$N$_2$Ph$_2$py) with 1 equiv of NaBEt$_3$H or KC$_8$.

Reduction of CoCl$_2$(PNpy) using NaBEt$_3$H or MeLi in the presence of PPh$_3$ afforded diamagnetic complexes (Scheme 5.2). We propose that the first equiv of reductant displaces one chloride ligand (by loss of NaCl or LiCl) to form “CoCl(R)(PNpy)” (R = H, Me). This intermediate quickly loses an R-radical to give “CoCl(PNpy)”, followed by reaction with another equiv of NaBEt$_3$H or MeLi in the presence of PPh$_3$ to afford the final product, CoR(PNpy)(PPh$_3$). No reactions were observed when CoCl$_2$(PNpy) was treated with PPh$_3$ alone. These same complexes were obtained when the PPh$_3$ was added after the reduction, but with diminished yields.

Scheme 5.2 Synthesis of CoH(PNpy)(PPh$_3$) and CoMe(PNpy)(PPh$_3$).
Illustrative of the preparative results, treatment of a THF suspension of CoCl$_2$(Ph$_2$P$_3$N$_3$Phpy) with 2 equiv of NaBEt$_3$H in the presence of 1 equiv of PPh$_3$ gave good yields of a brown hydrido complex. The $^{31}$P NMR spectrum consisted of broad resonances at δ 71.1 and 61.0 at room temperature. The $^1$H NMR spectrum showed a doublet-of-doublets at δ −18.3 ($J_{P-H} = 74.5$, 28.6 Hz), consistent with the formula CoH(Ph$_2$PC$_3$N$_3$Phpy)(PPh$_3$). The -(CH$_2$)$_3$- resonances of the Ph$_2$PC$_3$N$_3$Phpy ligand manifested as six multiplets when $^1$H NMR spectra were collected between −20 to 70 °C, suggesting a rigid conformation of the Co-P-(CH$_2$)$_3$-N six-membered ring. Qualitative experiments showed that the related CoH(iPr$_2$PC$_3$N$_3$Phpy)(PPh$_3$) and CoH(Ph$_2$PC$_6$H$_4$N$_3$Phpy)(PPh$_3$) could be prepared analogously. The Co-$H$ resonance in the $^1$H NMR spectra for CoH(iPr$_2$PC$_3$N$_3$Phpy)(PPh$_3$) and CoH(Ph$_2$PC$_6$H$_4$N$_3$Phpy)(PPh$_3$) were observed at δ −18.9 (dd, $J_{P-H} = 74.0$, 34.4 Hz) and δ −20.8 (dd, $J_{P-H} = 65.4$, 34.7 Hz), respectively.

![Figure 5.4](image.png)

**Figure 5.4** Variable temperature NMR spectra of CoMe(Ph$_2$PC$_6$H$_4$N$_3$Phpy)(PPh$_3$) in toluene-$d_8$. Left: $^1$H NMR spectra showing the CH$_3$ resonance. Right: $^{31}$P NMR spectra.

Cobalt methyl complexes were prepared by reduction of CoCl$_2$(PNpy) complexes with 2 equiv of MeLi in the presence of PPh$_3$ in Et$_2$O solution. The complex CoMe(Ph$_2$PC$_6$H$_4$N$_3$Phpy)(PPh$_3$) was isolated in moderate yields after recrystallization from cooling a THF/pentane solution. At 20 °C, the $^{31}$P NMR spectrum showed two broad
resonances (δ 97.3, 58.8), and the ¹H NMR spectrum exhibited a doublet at δ 1.22 (Jₚ-Ｈ = 6.6 Hz), assigned to Co-CH₃. Selective ³¹P NMR decoupling showed the ¹H NMR doublet assigned to Co-CH₃ arises from coupling to the δ 58.8 resonance in the ³¹P NMR spectrum. Upon cooling a sample of CoMe(Ph₂P(C₆H₄)N₃Ph(py)(PPh₃) in toluene-d₈, the Co-CH₃ doublet gradually broadened while the chemical shift remained unchanged (Figure 5.4). At −30 °C, the Co-CH₃ resonance manifested as a broad doublet-of-doublets. ¹H{³¹P} NMR spectroscopy at −30 °C revealed an additional coupling to the low field ³¹P resonance (Jₚ-Ｈ = 5.0 Hz) compared to that at 20 °C. The ³¹P NMR spectrum showed two broad doublets at −30 °C (Jₚ-Ｐ = 48 Hz). Similar to the Co-(Ph₂P(C₆H₄)N₃Ph) dimers, the broadness of ³¹P NMR resonances is possibly due to coupling with the quadrupolar ⁵⁹Co nuclei. The ³¹P NMR spectra did not exhibit changes in the chemical shift at temperatures between −30 and +20 °C, but at temperatures above −10 °C, the ³¹P-³¹P coupling becomes unresolved.

Figure 5.5 Variable temperature ¹H NMR spectra of CoMe(Ph₂P(C₆H₄)N₃Ph(py)(PPh₃).

The Co-CH₃ resonance of complex CoMe(Ph₂P(C₆H₄)N₃Ph(py)(PPh₃) exhibited similar DNMR spectral characteristics (Figure 5.5). Additionally, the -(CH₂)₃- resonances of the
Ph₂PC₃NPhpy manifested as five broad peaks in the ^1H NMR spectrum at 20 °C, roughly integrating as 1:1:1:1:2. At −20 °C, six distinct multiplets were resolved between δ 4.05 and 1.54. At 40 °C, these signals collapsed into three broad resonances with approximately equal intensity. These results are consistent with fast exchange of the PPh₃ ligand. The rapid dissociation of PPh₃ at room temperature causes loss of spin correlation between CH₃ and PPh. This exchange process equivalences the two faces of the six-membered ring defined by Co-P-(CH₂)₃-N (Scheme 5.3).¹³ The lability of PPh₃ in solution is relevant to the catalytic activity of these complexes, as will be discussed in the subsequent section.

Scheme 5.3 Exchange of PPh₃ in CoMe(Ph₂PC₃NPhpy)(PPh₃).

5.4 Crystallographic and computational studies

Figure 5.6 Solid state representation (50% thermal ellipsoids) of CoH(Ph₂PC₃NPhpy)(PPh₃). Selected hydrogen atoms removed for clarity.

The structures of CoH(Ph₂PC₃NPhpy)(PPh₃), CoMe(Ph₂PC₃NPhpy)(PPh₃), and CoMe(Ph₂PC₆H₄NPhpy)(PPh₃) were examined by X-ray crystallography. These five-coordinate complexes adopt geometries intermediate between square-pyramidal and
trigonal-bipyramidal. Coordination of $\text{Ph}_2\text{P}^3\text{N}^\text{Ph}\text{py}$ in CoH($\text{Ph}_2\text{P}^3\text{N}^\text{Ph}\text{py}$)(PPh$_3$) and CoMe($\text{Ph}_2\text{P}^3\text{N}^\text{Ph}\text{py}$)(PPh$_3$) is best described as meridional, with N(1) – Co(1) – P(1) angles very close to 120° (137.8(1)° for the hydrido complex; 125.0(8)° for the methyl complex). On the other hand in CoMe($\text{Ph}_2\text{P}^6\text{H}_4\text{N}^\text{Ph}\text{py}$)(PPh$_3$), the $\text{Ph}_2\text{P}^6\text{H}_4\text{N}^\text{Ph}\text{py}$ ligand coordinates in a facial manner, reflecting the constraint of its smaller bite angle. To better describe the geometry of the complexes, we adopted the $\tau$ notation for differentiating trigonal bipyramidal and square pyramidal structures. CoMe($\text{Ph}_2\text{P}^6\text{H}_4\text{N}^\text{Ph}\text{py}$)(PPh$_3$) adopts a square pyramidal geometry, with the $\tau$ parameter being 0.09. This structure differs from that of the parent CoCl$_2$($\text{Ph}_2\text{P}^6\text{H}_4\text{N}^\text{Ph}\text{py}$) complex, which exhibits a coordination geometry closer to trigonal bipyramidal ($\tau = 0.47$ for CoCl$_2$($\text{Ph}_2\text{P}^6\text{H}_4\text{N}^\text{Ph}\text{py}$)). The hydride ligand of CoH($\text{Ph}_2\text{P}^3\text{N}^\text{Ph}\text{py}$)(PPh$_3$) was located in the electron difference map and refined isotropically. The Co(1) – H(1) distance is 1.46(6) Å, similar to that in the related 5-coordinate CoH(PNP)(PMe$_3$) (PNP = 2,6-bis(di-isopropylphosphinomethyl)pyridine) at 1.45(2) Å.

Bond metrics of the $\alpha$-diimine moiety of PNpy were examined in detail, using the structural parameters of CoCl$_2$($\text{Ph}_2\text{P}^6\text{H}_4\text{N}^\text{Ph}\text{py}$) and CoCl$_2$($\text{Ph}_2\text{P}^3\text{N}^\text{Ph}\text{py}$) as reference. Our analysis indicated that the $\alpha$-diimine ligands are strongly affected upon reduction. The ketimine C=N bond is elongated by ca. 0.055 Å in both CoH($\text{Ph}_2\text{P}^3\text{N}^\text{Ph}\text{py}$)(PPh$_3$) and
CoMe($^{\text{Ph}_2\text{P}^3\text{C}_3\text{N}_\text{Ph}}$)$\text{(PNpy)}$($\text{PPh}_3$) compared to the parent dihalide CoCl$_2$($^{\text{Ph}_2\text{P}^3\text{C}_3\text{N}_\text{Ph}}$)$\text{py}$). Similar ligand bond length distortions have also been reported for cobalt complexes containing reduced diimine radicals, such as (DIP)CoMe and Co($\text{CH}_2\text{SiMe}_2$)$\text{(bis(arylimidazol-2-ylidene)pyridine)}$.\textsuperscript{3c,14,24} Similar to the structures of CoR($^{\text{Ph}_2\text{P}^3\text{C}_3\text{N}_\text{Ph}}$)$\text{(PNpy)}$($\text{PPh}_3$), the ketimine of CoMe($^{\text{Ph}_2\text{P}^6\text{H}_4\text{N}_\text{Ph}}$)$\text{py}$ features an elongated C=N bond of 1.351(2) Å, relative to that in CoCl$_2$($^{\text{Ph}_2\text{P}^6\text{H}_4\text{N}_\text{Ph}}$)$\text{py}$ (1.287(3) Å). These differences are summarized in Figure 5.8.

![Diagram](image_url)

**Figure 5.8** Change of bond lengths from CoCl$_2$(PNpy) to CoR(PNpy)(PPh$_3$).

Caution must be exercised when drawing conclusions solely based on bond metrics. Other researchers have shown that extensive metal-to-ligand $\pi$-backbonding can result in $\alpha$-diimines bond lengths that resemble those of reduced $\alpha$-diimine radicals.\textsuperscript{25} Therefore, additional calculations must be performed to determine the electronic structures of reduced Co-(PNpy) complexes. For complexes with the general formula CoRL$_n$ ($X$ = halide, alkyl) arising from formal 1-electron reduction of the Co($\text{II}$) precursors, three different spin states have been described in literature: (1) $S = 0$ containing formally Co($\text{I}$), (2) $S = 0$ containing
formally Co(\textit{iii}) anti-ferromagnetically coupled to L\textsuperscript{−}, (3) \(S = 1\). Notable literature examples have been summarized in Table 5.1.

**Table 5.1** Classes of CoR\textsubscript{L\textsubscript{n}} Complexes.

<table>
<thead>
<tr>
<th>Illustrative Complex</th>
<th>Spin State, Co oxidation state</th>
</tr>
</thead>
<tbody>
<tr>
<td>((\text{iPrPNP})\text{CoCH}_3)\textsuperscript{26}</td>
<td>(S = 0), Co(\textit{i})</td>
</tr>
<tr>
<td>((\text{iPrPNP})\text{CoCl})\textsuperscript{26} (PPh\textsubscript{3})\textsubscript{3}CoCl\textsuperscript{21}</td>
<td>(S = 1), Co(\textit{i})</td>
</tr>
<tr>
<td>((\text{iPrPNP})\text{CoCH}_2\text{SiMe}_3)\textsuperscript{27}</td>
<td>(S = 0) ground state, low lying (S = 1) state, Co(\textit{i})</td>
</tr>
<tr>
<td>CoMe((\text{Ph}^\text{P}^\text{Ar}^\text{N}^\text{Ph}^\text{py})(\text{PPh}_3)) (this work)</td>
<td>(S = 0), Co(\textit{ii})</td>
</tr>
<tr>
<td>(DIP)CoMe\textsuperscript{3a,24,28}</td>
<td>(S = 0) ground state, low lying (S = 1), Co(\textit{ii})</td>
</tr>
<tr>
<td>(alkylDIP)CoCl\textsuperscript{28}</td>
<td></td>
</tr>
<tr>
<td>(arylDIP)CoCl\textsuperscript{24}</td>
<td></td>
</tr>
<tr>
<td>Co(terpy)CH\textsubscript{2}SiMe\textsubscript{3}\textsuperscript{29}</td>
<td></td>
</tr>
<tr>
<td>[CoR((\text{Ph}^\text{P}^\text{C}^2\text{N}^\text{H}^\text{py})]_2) (this work)</td>
<td>(S = 0), Co(\textit{i}) (essentially CoR\textsubscript{L\textsubscript{4}})</td>
</tr>
</tbody>
</table>

We collaborated with Dr. Maurice van Gastel and Professor Frank Neese to investigate the electronic structures of these complexes by density functional theory (DFT) calculations. These calculations were carried out using the B3LYP functional and the broken symmetry formalism.\textsuperscript{30} Since the reduced complexes, i.e. CoR(PNpy), give NMR spectra with normal chemical shifts, which are only mildly temperature dependent (< 1 ppm shift between −30 and +70 °C), the complexes were assigned singlet (\(S = 0\)) ground states. Thus, the main question to address is whether the apparent diamagnetism arises from Co(\textit{i}) with neutral PNpy ligands or from Co(\textit{ii}) complexes antiferromagnetically coupled to a PNpy radical anion.

Calculations initiated with [CoMe\((\text{Ph}^\text{H}^\text{P}^\text{C}^2\text{N}^\text{H}^\text{py})]_2\), considering the singlet (\(S = 0\)) BS(0,0) and BS(2,2), as well as quintet (\(S = 2\)) states for the molecule. Both singlet calculations converged to the closed-shell BS(0,0) wave function, suggesting absence of any unpaired electrons. The calculated bond distances for BS(0,0) agreed reasonably with the experimental values, with the largest difference being Co(1) – P(1) (difference of 0.071Å). The optimized geometry for the quintet state, which would imply all ferromagnetic coupling between two Co(\textit{ii}) metal centers and two monoanionic \(\text{Ph}^\text{H}^\text{P}^\text{C}^2\text{N}^\text{H}^\text{py}\)
ligands, strongly disagreed with the experimental structure. Extensive distortions of the Co$_2$N$_2$ core in the optimized geometry was observed compared to experimental data, and the $\pi$-bonding interaction of the imine was absent. Moreover, the quintet was 32 kcal/mol higher in energy than the singlet state. These results combined with spectroscopic data point to strictly Co(I) metal centers coordinated by neutral Ph$_2$P$_2$C$_2$N$_2$H$_2$py ligands. Similar calculations were carried out for the chloride dimer and also suggested a diamagnetic Co(I) dimeric metal complex.

For CoMe(Ph$_2$P$_2$C$_6$H$_4$N$_2$Ph$_2$py)(PPh$_3$), the singlet BS(0,0), BS(1,1) and the triplet states were considered. The singlet configuration with BS(1,1), i.e. Co(II) antiferromagenetically coupled to a ligand radical anion, was found to be 9.6 kcal/mol lower in energy than the closed-shell singlet BS(0,0). The two open-shell corresponding orbitals $\alpha$ and $\beta$ of the BS(1,1) calculation along with the localized orbitals with dominant 3d character are shown in Figure 5.9. The $\alpha$ orbital mainly consists of the cobalt 3d$_{z^2}$ orbital (Mulliken population 72%) with only 28% ligand character. The $\beta$ orbital mainly resides

![Figure 5.9 3d orbital structure CoMe(Ph$_2$P$_2$C$_6$H$_4$N$_2$Ph$_2$py)(PPh$_3$). We thank Dr. Maurice van Gastel for providing this figure.](image-url)
on the iminopyridine subunit of the \(^{\text{Ph}_2\text{pC}_{6}\text{H}_4}\text{N}^\text{Ph}\text{py}\) ligand with 11% metal character. Spatial overlap between the two orbitals was calculated to be 0.318. The calculated structure agrees reasonably with crystallographic results, with the exception of Co(1) – P(2) distance giving a 0.256 Å discrepancy between calculated and experimental results. The Co-PPh\(_3\) bond might be expected to be weak due to an unpaired electron occupying the 3d\(_{z^2}\) orbital, which is Co-P antibonding. The differences in energy between experimental and calculated structure amounts 4 kcal/mol, the discrepancy in Co-P distance is tentatively attributed to packing forces in the solid-state, which were not included in the calculation. The longer Co-PPh\(_3\) bond distance found in the solution phase calculation agrees with the experimental observation that the PPh\(_3\) ligand is labile in solution. The triplet state was essentially isoenergetic with the BS(1,1) solution, but is inconsistent with the diamagnetism observed for CoMe\((^{\text{Ph}_2\text{pC}_{6}\text{H}_4}\text{N}^\text{Ph}\text{py})\)(PPh\(_3\)). Thus, CoMe\((^{\text{Ph}_2\text{pC}_{6}\text{H}_4}\text{N}^\text{Ph}\text{py})(\text{PPh}_3)\) is best described as having a singlet, Co(II) \(d^7\) ground-state antiferromagnetically coupled to a monoanionic \(^{\text{Ph}_2\text{pC}_{6}\text{H}_4}\text{N}^\text{Ph}\text{py}\).

**Table 5.2** Selected experimental and calculated bond distances of CoMe\((^{\text{Ph}_2\text{pC}_{6}\text{H}_4}\text{N}^\text{Ph}\text{py})(\text{PPh}_3)\).

<table>
<thead>
<tr>
<th></th>
<th>experimental</th>
<th>BS(0,0)</th>
<th>BS(1,1)</th>
<th>high-spin</th>
</tr>
</thead>
<tbody>
<tr>
<td>relative energies (kcal/mol)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co(1) – N(1)</td>
<td>1.919(1)</td>
<td>1.910</td>
<td>1.973</td>
<td>1.9739</td>
</tr>
<tr>
<td>Co(1) – N(2)</td>
<td>1.935(1)</td>
<td>1.977</td>
<td>2.016</td>
<td>2.0009</td>
</tr>
<tr>
<td>Co(1) – C(1)</td>
<td>2.029(2)</td>
<td>1.999</td>
<td>1.991</td>
<td>1.9874</td>
</tr>
<tr>
<td>Co(1) – P(1)</td>
<td>2.1299(5)</td>
<td>2.1880</td>
<td>2.2042</td>
<td>2.1976</td>
</tr>
<tr>
<td>Co(1) – P(2)</td>
<td>2.2209(6)</td>
<td>2.2636</td>
<td>2.4775</td>
<td>2.7228</td>
</tr>
<tr>
<td>N(2) – C(7)</td>
<td>1.351(2)</td>
<td>1.353</td>
<td>1.359</td>
<td>1.3609</td>
</tr>
<tr>
<td>C(6) – C(7)</td>
<td>1.420(2)</td>
<td>1.420</td>
<td>1.429</td>
<td>1.4311</td>
</tr>
</tbody>
</table>
5.5 Stoichiometric reactions of Co(I) complexes

The mononuclear Co-alkyls are reactive toward H-H, B-H, and Si-H-containing reagents. In contrast, the dimeric [CoMe(Ph2PC6H4Npy)]2 was unreactive with these same substrates.

**Co-Me + H-H and B-H.** Treatment of a C6D6 solution of CoMe(Ph2PC6H4Npy)(PPh3) with H2 (1 atm) gave CoH(Ph2PC6H4Npy)(PPh3) with concomitant formation of CH4, detected by NMR spectroscopy. Under typical conditions, the reaction proceeded to > 95% conversion after 16 h. Similarly, combining 1 equiv of HBpin (pin = 4,4,5,5-tetramethyl-1,3,5-dioxaboralane) and CoMe(Ph2PC6H4Npy)(PPh3) in C6D6 solution resulted in clean conversion to the hydride and MeBpin in 1:1 ratio, as verified by integration of the B-C3H3 (s, δ 0.41) and the Co-H signals in the 1H NMR spectrum.

**Co-Me + Si-H.** Reaction of the cobalt alkyls with silanes was the focus of several experiments since stable cobalt silyl complexes are relatively scarce. Combining CoMe(Ph2PC6H4Npy)(PPh3) with H2SiPh2 immediately afforded Co(SiHPh2)(Ph2PC6H4Npy)(PPh3) and CH4 (Figure 5.10). The 31P{1H} NMR spectrum showed resonances at δ 73.4 and 49.6, supporting the assignment of a diphosphine complex. The 1H NMR spectrum of the product complex showed a distinctive doublet-of-doublets at δ 5.60, assigned to –SiHPh2. The few diamagnetic Co(III) and Co(V) silyl complexes that have been characterized exhibit SiH resonances at similar chemical shifts.31 Selective decoupling of the respective 31P NMR resonances confirmed the three-bond P-SiH coupling arising from both 31P nuclei. The coupling constants (3Jp-H = 6.1, 10.3 Hz) were consistent with related metal silyl complexes, for example, 3Jp-H is 9.2 Hz for (MesB(o-Ph2PC6H4)2)(μ-H)Ni-SiHPh2.32 The 29Si{1H} DEPT NMR spectrum exhibited a doublet at δ ~4.8 with 2Jp-si = 72 Hz,33 attributed to coupling with PNPY. Coupling to the PPh3 group was not observed, suggesting rapid exchange of the PPh3 ligand.
Figure 5.10 Reaction of CoMe\(^{\text{Ph}_2\text{PC}_{6}\text{H}_4\text{N}_{\text{py}}}(\text{PPh}_3)\) with excess Ph\(_2\)SiH\(_2\). Red numbers are coupling constants between the indicated nuclei.

Reaction of CoMe\(^{\text{Ph}_2\text{PC}_{6}\text{H}_4\text{N}_{\text{py}}}(\text{PPh}_3)\) with hydrosilanes is general with sterically unhindered alkyl- and phenyl-silanes. To gain further insight into the Co-Si bond, the related compound Co(SiMe\(_2\)Ph)\(^{\text{Ph}_2\text{PC}_{6}\text{H}_4\text{N}_{\text{py}}}(\text{PPh}_3)\) was examined. According to the proposed structure of the Co-silyl complex, the -SiMe\(_2\)Ph signals are expected to be diastereotopic. Indeed, Co(SiMe\(_2\)Ph)\(^{\text{Ph}_2\text{PC}_{6}\text{H}_4\text{N}_{\text{py}}}(\text{PPh}_3)\) exhibited two broad singlets at \(\delta\) 0.12 and 0.16 in the \(^1\)H NMR spectrum, assigned -SiMe\(_2\)Ph. The \(^{29}\)Si\(^{\text{\{1H\}}\) NMR spectrum exhibited a doublet at \(\delta -15.7\) with \(J_{P,\text{Si}} = 48\) Hz. Similarly, Co(SiHEt\(_2\))\(^{\text{Ph}_2\text{PC}_{6}\text{H}_4\text{N}_{\text{py}}}(\text{PPh}_3)\) exhibited two triplets for the diethylsilyl -CH\(_3\) at \(\delta\) 1.33 and 1.22, and two multiplets for -CH\(_2\)- centered at \(\delta\) 1.01 and 0.88. Interestingly, CoMe\(^{\text{Ph}_2\text{PC}_{6}\text{H}_4\text{N}_{\text{py}}}(\text{PPh}_3)\) was unreactive toward HSi(OEt)_\(_3\).

The reaction of CoMe\(^{\text{Ph}_2\text{PC}_{6}\text{H}_4\text{N}_{\text{py}}}(\text{PPh}_3)\) with PhSiH\(_3\) also gave the silyl complex Co(SiH\(_2\)Ph)\(^{\text{Ph}_2\text{PC}_{6}\text{H}_4\text{N}_{\text{py}}}(\text{PPh}_3)\). The \(^1\)H NMR signals for the diastereotopic SiH groups are easily resolved at \(\delta\) 4.78 and 4.65 and showed coupling to \(^{31}\)P nuclei. When this reaction was monitored at low temperature, an intermediate was detected that provides insight into the mechanism by which the silyl complexes form. This intermediate is a monophosphine complex (free PPh\(_3\) was observed), and features SiH signals of 2:2:1 intensities respectively at \(\delta\) 4.98, 4.94, and –15.2 (doublet). According to the spectral characteristics, this intermediate was assigned as a silyl-silane complex, Co(SiH\(_2\)Ph)\(^{\text{Ph}_2\text{PC}_{6}\text{H}_4\text{N}_{\text{py}}}(\text{PPh}_3)\), that undergoes the exchange process presented in Scheme 5.4. This process equivalences both -SiH\(_2\)Ph groups, explaining the presence of merely two sets of multiplets. The high field resonance is consistent with SiH of a \(\sigma\)-bonded silane. An analogous reaction has been invoked for [(phen)Pd(SiEt\(_3\))(HSiEt\(_3\))]\(^+\),

except that our system is of lower symmetry. The complex
Co(SiH₂Ph)_{(Ph₂PC₆H₄Npy)(PPh₃)} was also obtained by treatment of Co(SiHPh₂)_{(Ph₂PC₆H₄Npy)(PPh₃)} with PhSiH₃.

\[
\text{Co(SiHPh₂)_{(Ph₂PC₆H₄Npy)(PPh₃)}} + \text{PhSiH₃} \rightarrow \text{Co(SiH₂Ph)_{(Ph₂PC₆H₄Npy)(PPh₃)}} + \text{Ph₂SiH₂}
\]

(5.1)

Such a trans-silylation reaction³⁴ has not been previously described in hydrosilation catalysis, probably because it is usually a degenerate process. We suggest that trans-silylation proceeds via the intermediacy of Co(SiHPh₂)_{(Ph₂PC₆H₄Npy)(η²-PhSiH₃)}.

\[
\text{Scheme 5.4 Reaction of CoMe(Ph₂PC₆H₄Npy)(PPh₃) with excess PhSiH₃.}
\]

The solid state structure of Co(SiH₂Ph)_{(Ph₂PC₆H₄Npy)(PPh₃)} was investigated by X-ray crystallography (Figure 5.11). The imine-pyridine moiety of Co(SiH₂Ph)_{(Ph₂PC₆H₄Npy)(PPh₃)} exhibited bond distances similar to CoMe_{(Ph₂PC₆H₄Npy)(PPh₃)}. The imine N(2) – C(6) distance of 1.349(3) Å, and C(5) – C(6) distance of 1.418(3) Å are consistent with the bond distances in the anionic radical [Ph₂PC₆H₄Npy]⁻ ligand seen for CoMe_{(Ph₂PC₆H₄Npy)(PPh₃)}. The Co(1) – Si(1) distance of 2.2615(7) Å is also consistent with typical cobalt-silyl bond distances, typically within the range of 2.22 to 2.32 Å.¹⁰,³¹ᵃ,³¹ᵇ,³⁵ In summary, the structure of Co(SiH₂Ph)_{(Ph₂PC₆H₄Npy)(PPh₃)} bared high resemblance to the Co-methyl precursor, and the electronic structure was proposed to be Co(ii)-SiH₂Ph coordinated by an anionic radical [Ph₂PC₆H₄Npy]⁻ ligand.
Co-H + C=C. The reactivity of CoH(Ph2PC6H4NPhpy)(PPh3) with alkenes was examined by 1H NMR spectroscopy. When CoH(Ph2PC6H4NPhpy)(PPh3) was mixed with 4 equiv of 1-octene, 2-octene was observed as the sole product with full conversion in < 1 h. The Co-H resonance remained in the 1H NMR spectrum as a sharp doublet-of-doublets and undiminished intensity, suggesting fast alkene insertion/β-hydride elimination to give the isomerized 2-octene. This reaction is possibly preceded via substitution of PPh3 by the alkene (Scheme 5.5). Products of alkene insertion into the Co-H bond were not observed between –40 and 20 °C.

![Figure 5.11](image)

Figure 5.11 Solid state representation (50% thermal ellipsoids) of Co(SiH2Ph)(Ph2PC6H4NPhpy)(PPh3). Selected hydrogen atoms removed for clarity.

Co-Si + C=C. In contrast to the Co-H + C=C reaction, the insertion of ethylene into Co-Si bonds is favorable. Such reactions are relevant to the mechanism of hydrosilylation reactions catalyzed by CoR(Ph2PC6H4NPhpy)(PPh3) and related
complexes.\textsuperscript{11,36} When a toluene-$d_8$ solution of Co(SiHPh\(_2\))(Ph\(_2\)pC\(_6\)H\(_4\)N\(_{\text{Ph}}\)py)(PPh\(_3\)) was saturated with ethylene at $-78 \, ^\circ\text{C}$, a color change was observed from the brown color of the starting complex to dark purple. The product, assigned Co(CH\(_2\)CH\(_2\)SiHPh\(_2\))(Ph\(_2\)pC\(_6\)H\(_4\)N\(_{\text{Ph}}\)py)(PPh\(_3\)), exhibited \(^{31}\text{P}\) NMR signals at $\delta$ 91.1 and 57.5. A \(^1\text{H}\) NMR doublet at $\delta$ 9.0, equal in intensity with the SiH resonance at $\delta$ 5.12, is assigned to the 6-pyridyl proton of the new species. Four new resonances between $\delta$ 2.3 and 0.7 are assigned to Co-CH\(_2\)CH\(_2\)SiHPh\(_2\). Decoupling measurements showed correlations between both \(^{31}\text{P}\) resonances and the \(^1\text{H}\) NMR signals $\delta$ 2.16 and 0.76, assigned to the diastereotopic $\alpha$-methylene protons Co-CH\(_2\)CH\(_2\)SiHPh\(_2\). \(^{29}\text{Si}\)-\(^1\text{H}\) HMBC revealed correlation of the \(^{29}\text{Si}\) signal at $\delta$ -19.9 and \(^1\text{H}\) signals at $\delta$ 1.49 and 1.24, assigned to the diastereotopic $\beta$-methylene protons Co-CH\(_2\)CH\(_2\)SiHPh\(_2\). This HMBC spectrum also showed a strong 184 Hz coupling between the same \(^{29}\text{Si}\) site and the \(^1\text{H}\) resonance at $\delta$ 5.12 assigned to SiH. These measurements are consistent with the proposed $\beta$-silyl ethyl complex Co(CH\(_2\)CH\(_2\)SiHPh\(_2\))(Ph\(_2\)pC\(_6\)H\(_4\)N\(_{\text{Ph}}\)py)(PPh\(_3\)) (Scheme 5.6).

For practical reasons, ethylene insertion reactions were easier to manipulate using Et\(_2\)SiH\(_2\), which can be added and removed readily by vacuum transfer. A toluene-$d_8$ solution of Co(SiHEt\(_2\))(Ph\(_2\)pC\(_6\)H\(_4\)N\(_{\text{Ph}}\)py)(PPh\(_3\)) was found to react at 5 °C with ethylene to give Co(CH\(_2\)CH\(_2\)SiHEt\(_2\))(Ph\(_2\)pC\(_6\)H\(_4\)N\(_{\text{Ph}}\)py)(PPh\(_3\)). Closing the catalytic cycle, addition of another equiv of H\(_2\)SiEt\(_2\) to this solution via vacuum transfer gave HSiEt\(_3\), as observed by \(^1\text{H}\) NMR.

\begin{center}
\textbf{Scheme 5.6} Reaction of Co(SiHPh\(_2\))(Ph\(_2\)pC\(_6\)H\(_4\)N\(_{\text{Ph}}\)py)(PPh\(_3\)) with excess ethylene.
\end{center}
Notably, Co(SiH₂Ph)⁷(Ph₂pC₆H₄N³Phpy)(PPh₃) was significantly more stable to ethylene compared to the other cobalt-silyls examined. No reaction was observed at 10 °C. When the sample was warmed to 20 °C for 5 mins, new resonances in the ³¹P NMR spectrum at δ 99.8, 63.2 were assigned the ethylene insertion product due to the similarity of chemical shifts to other Co-(CH₂CH₂SiR₃) complexes. A small singlet at δ 70.5 was also observed, along with a high-field broad resonance (δ 0 to −5) assigned free PPh₃. Though we are unable to assign a structure to the δ 70.5 species in the ³¹P NMR spectrum due to lack of high quality ¹H NMR spectra, the ethylene-substitution products Co(SiH₂Ph)⁷(Ph₂pC₆H₄N³Phpy)(H₂C=CH₂) or (CH₂CH₂SiH₂Ph)(Ph₂pC₆H₄N³Phpy)(H₂C=CH₂) are possible.

Scheme 5.7 Reaction of Co(SiHPh₂)⁷(Ph₂pC₆H₄N³Phpy)(PPh₃) with styrene.

The reaction of Co(SiHPh₂)⁷(Ph₂pC₆H₄N³Phpy)(PPh₃) with styrene contrasted with results of the ethylene experiments. Treatment with excess styrene at −16.9 °C resulted in partial formation (~ 50%) of the alkene complex Co(SiHPh₂)⁷(Ph₂pC₆H₄N³Phpy)(η²-C₆H₅CH=CH₂). Experiments with 25 and 1.2 equiv styrene gave consistent K_eq of ~0.033 for the displacement of PPh₃ (Scheme 5.7). ³¹P NMR measurements on this mixture confirmed a new monophosphine complex (δ 52.1) and free PPh₃. Insertion into the Co-Si bond was not observed. The ¹H NMR resonance values for vinylic protons of styrene (δ 3.95, 2.58, and 1.87) are close to those reported for π-bound styrene complexes.³⁷ Trisphosphine Co(Ι)-alkene complexes exhibit olefinic ¹H resonances between δ 4.72 and 2.17.³⁷c A ³¹P-coupled doublet at δ 5.79 assigned to Co-SiHPh₂ was confirmed by ¹H{³¹P} NMR spectroscopy (³J_P,H = 22.3 Hz). Although this complex was unstable at higher temperatures, addition of Ph₂SiH₂ to this mixture at 0 °C immediately gave C₆H₅C₂H₄Ph₂SiH as the sole

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organic product. The difference in reactivity of Co(SiHPh$_2$)(Ph$_2$P$^\text{C}_6$H$_4$N$_{\text{Ph}}$py)(PPh$_3$) between ethylene and styrene is attributed to higher insertion barriers of bulkier alkenes.

5.6 Catalysis

\[
\text{Catalyst:} \quad \begin{array}{c}
\text{CoCl}_2(\text{PNpy})/2\text{NaBEt}_3\text{H} \\
23 \degree C, \text{neat} \\
< 15 \text{ mins}
\end{array}
\]

Given the high efficiency the reactions of CoMe(Ph$_2$P$^\text{C}_6$H$_4$N$_{\text{Ph}}$py)(PPh$_3$) with H$_2$ and HBpin, the reactivity of Co-(PNpy) complexes was briefly examined for catalytic hydrogenation and hydroboration with alkenes. With 1 mol% of CoCl$_2$(Ph$_2$P$^\text{C}_6$H$_4$N$_{\text{Ph}}$py)/2NaBEt$_3$H, a 1:1 mixture of 1-octene and HBpin converted quantitatively to 1-pinacolborylobtane in 15 min. However, the same catalyst was only mildly active for hydrogenation of styrene (Eq. 5.2 and 5.3).

Hydrosilylation. Using 1-octene/Ph$_2$SiH$_2$ as the test reaction, hydrosilylation catalysis was assessed with cobalt complexes derived from iPr$_2$P$^\text{C}_3$N$_{\text{py}}$, Ph$_2$P$^\text{C}_3$N$_{\text{py}}$, Ph$_2$P$^\text{C}_6$H$_4$N$_{\text{Ph}}$py, and Ph$_2$P$^\text{C}_2$N$_{\text{py}}$. Catalysts were either generated in situ from CoCl$_2$(PNpy)/2NaBEt$_3$H or isolated CoR(PNpy)(PPh$_3$) complexes. Results are shown in Tables 5.3 and 5.4. Important observations are summarized here:

- The optimum rate and selectivity was observed with the catalyst generated in-situ from CoCl$_2$(iPr$_2$P$^\text{C}_3$N$_{\text{py}}$)/2NaBEt$_3$H. As observed by Chirik et al. with Fe-(DIP) catalysts, activity correlates with the electron-richness of the complex. The high regio-selectivity is
possibly associated with the bulkiness of the isopropylphosphine groups.

- The complex $\text{Co(SiHPh}_2\text{)}^{(\text{Ph}_2\text{P}^{\text{C}_6\text{H}_4}\text{N}_\text{Ph}_\text{py})}(\text{PPh}_3)$ exhibited activity comparable to $\text{CoH}^{(\text{Ph}_2\text{P}^{\text{C}_6\text{H}_4}\text{N}_\text{Ph}_\text{py})}(\text{PPh}_3)$, consistent with the intermediacy of cobalt silyl complexes in the catalytic cycle.

- At high loadings of PPh$_3$, the selectivity was unaffected, but the rate of hydrosilylation decreased (Table 5.4). These findings are consistent with CoR(PNpy) functioning as the active catalysts, and PPh$_3$ competes with alkene binding to the metal center.

- The dimeric complexes $[\text{CoMe}^{(\text{Ph}_2\text{P}^{\text{C}_2\text{N}^\text{H}_\text{py}})}]_2$ and $[\text{CoCl}^{(\text{Ph}_2\text{P}^{\text{C}_2\text{N}^\text{H}_\text{py}})}]_2$ (activated with 2 equiv NaBEt$_3$H) are slow catalysts.

- With the exception of CoCl$_2^{(\text{Pr}_2\text{P}^{\text{C}_3\text{N}^\text{H}_\text{py}})}/2\text{NaBEt}_3\text{H}$, all mono-cobalt complexes produce a mixture of Markovnikov and anti-Markovnikov products. This finding highlights the strong influence of the substituents on the phosphine.

Tertiary silanes were also tested for hydrosilylation. Catalysis using HSiMe$_2$Ph and CoCl$_2^{(\text{Ph}_2\text{P}^{\text{C}_6\text{H}_4}\text{N}_\text{Ph}_\text{py})}/2\text{NaBEt}_3\text{H}$ gave high conversion to dehydrogenative silylation products, vinylsilane (12% yield) and allylsilane (23% yield). Isomerization of 1-octene to 2-octene was also observed (30 % yield). Saturated silanes were absent in the catalytic mixture. Using Et$_3$SiH as the silane gave mostly 2-octene and only trace dehydrogenative products (<10 % yield). Interestingly, even though CoCl$_2^{(\text{Pr}_2\text{P}^{\text{C}_3\text{N}^\text{H}_\text{py}})}/2\text{NaBEt}_3\text{H}$ gave the highest rates with H$_2$SiPh$_2$, no activity was observed with tertiary silanes, HSiMe$_2$Ph, HSiEt$_3$, and (EtO)$_3$SiH.
Table 5.3 Catalytic hydrosilylation of 1-octene with Ph$_2$SiH$_2$.

![Chemical Reaction Diagram]

<table>
<thead>
<tr>
<th>catalyst ([Co])</th>
<th>loading</th>
<th>time (h)</th>
<th>a (%)$^c$</th>
<th>b (%)$^c$</th>
<th>c (%)$^c$</th>
<th>total (%)$^d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoCl$_2$($^{\text{Ph}_2\text{P}^3\text{N}^{\text{H}}^\text{py}})$ + 2 NaBEt$_3$H$^b$</td>
<td>0.5 mol%</td>
<td>0.25</td>
<td>97</td>
<td>0</td>
<td>0</td>
<td>&gt;99$^e$</td>
</tr>
<tr>
<td>CoCl$_2$($^{\text{Ph}_2\text{P}^3\text{C}^6\text{H}_4\text{N}^{\text{Ph}}^\text{py}})$ + 2 NaBEt$_3$H$^b$</td>
<td>0.5 mol%</td>
<td>1</td>
<td>46</td>
<td>43</td>
<td>5</td>
<td>99</td>
</tr>
<tr>
<td>CoH($^{\text{Ph}_2\text{P}^3\text{C}^6\text{H}_4\text{N}^{\text{Ph}}^\text{py}}$)(PPh$_3$)</td>
<td>0.5 mol%</td>
<td>1</td>
<td>28</td>
<td>48</td>
<td>5</td>
<td>86</td>
</tr>
<tr>
<td>CoMe($^{\text{Ph}_2\text{P}^3\text{C}^6\text{H}_4\text{N}^{\text{Ph}}^\text{py}}$)(PPh$_3$)</td>
<td>0.5 mol%</td>
<td>2.5</td>
<td>30</td>
<td>37</td>
<td>6</td>
<td>79</td>
</tr>
<tr>
<td>Co(SiHPh$_2$)($^{\text{Ph}_2\text{P}^3\text{C}^6\text{H}_4\text{N}^{\text{Ph}}^\text{py}}$)</td>
<td>0.5 mol%</td>
<td>1.5</td>
<td>15</td>
<td>53</td>
<td>8</td>
<td>84</td>
</tr>
<tr>
<td>CoCl$_2$($^{\text{Ph}_2\text{P}^3\text{C}^6\text{H}_4\text{N}^{\text{Ph}}^\text{py}}$) + 2 NaBEt$_3$H$^b$</td>
<td>1 mol%</td>
<td>2.5</td>
<td>42</td>
<td>38</td>
<td>4</td>
<td>88</td>
</tr>
<tr>
<td>CoH($^{\text{Ph}_2\text{P}^3\text{C}^3\text{N}^{\text{Ph}}^\text{py}}$)(PPh$_3$)</td>
<td>1 mol%</td>
<td>14</td>
<td>43</td>
<td>23</td>
<td>3</td>
<td>78</td>
</tr>
<tr>
<td>CoCl$_2$($^{\text{ArF}^3\text{N}^{\text{H}}^\text{py}}$) + 2 NaBEt$_3$H$^b$</td>
<td>1 mol%</td>
<td>1</td>
<td>22</td>
<td>0</td>
<td>0</td>
<td>&gt;99$^f$</td>
</tr>
<tr>
<td>CoCl$_2$($^{\text{Ph}_2\text{P}^3\text{C}^6\text{H}_4\text{N}^{\text{Ph}}^\text{py}}$)DMAP + 2 NaBEt$_3$H</td>
<td>1 mol%</td>
<td>0.25</td>
<td>0</td>
<td>71</td>
<td>28</td>
<td>&gt;99</td>
</tr>
<tr>
<td>[CoCl($^{\text{Ph}_2\text{P}^2\text{C}^2\text{N}^{\text{H}}^\text{py}}$)]$_2$ + 2 NaBEt$_3$H$^b$</td>
<td>0.5 mol%</td>
<td>48</td>
<td>45</td>
<td>6</td>
<td>0</td>
<td>51</td>
</tr>
<tr>
<td>[CoCl($^{\text{Ph}_2\text{P}^2\text{C}^2\text{N}^{\text{H}}^\text{py}}$)]$_2$</td>
<td>0.5 mol%</td>
<td>48</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>[CoMe($^{\text{Ph}_2\text{P}^2\text{C}^2\text{N}^{\text{H}}^\text{py}}$)]$_2$</td>
<td>0.5 mol%</td>
<td>48</td>
<td>11</td>
<td>&gt;1</td>
<td>0</td>
<td>11</td>
</tr>
</tbody>
</table>

$^a$ Conditions: 0.004 mmol [Co], 0.8 mmol 1-octene, 0.88 mmol Ph$_2$SiH$_2$, 23 °C. $^b$ 10 µL NaBEt$_3$H solution (1M in toluene) was added to activate the catalyst. $^c$ Yields were determined by integration of product Si-H resonances to mesitylene in the $^1$H NMR spectra of crude reaction mixtures (see Supporting Information). $^d$ Total conversions were determined by integration of 1-octene resonances to mesitylene in the $^1$H NMR spectra of crude reaction mixtures. $^e$ 2-octene was detected in < 2% yield in the $^1$H NMR spectrum. $^f$ 2-octene was detected in > 77% yield.
Overview and conclusions

We have presented here a general synthetic route to five-coordinate reduced Co-(PNpy) complexes. CoCl₂(PNpy) were easily reduced using NaBEt₃H or MeLi, and stable species were isolated when PPh₃ is present in the reaction. The four-coordinate derivatives of reduced Co-(PNpy) are unstable, though they are proposed to be catalytically active. The Ph₂P₂C₂N₃H₆py ligand represented a case where “CoCl₂(Ph₂P₂C₂N₃H₆py)” was not isolable. Therefore, the reduced compound was prepared using the ligand radical anion, a method that further extends the generality of the reducibility of α-diimines.³⁸

The phosphine-imine-pyridine platform is a hybrid of a strong donor site (PR₃) and a redox-active iminopyridine.³⁹ DFT calculations support this description such that these ligands are neutral when attached to CoCl₂ center, but are radical anions when bound to a reduced Co-(PPh₃) site. The influence of the fifth ligand of this redox equilibrium is indicated by the finding that PNpy is redox innocent in the dimeric [CoR(PNpy)]₂.

Table 5.4 Catalytic hydrosilylation in the presence of added PPh₃.

<table>
<thead>
<tr>
<th>[Co]:PPh₃</th>
<th>loading</th>
<th>time (m)</th>
<th>a (%)⁺</th>
<th>b (%)⁺</th>
<th>c (%)⁺</th>
<th>total (%)⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>0.25 mol%</td>
<td>15</td>
<td>47</td>
<td>0</td>
<td>0</td>
<td>49</td>
</tr>
<tr>
<td>1:1⁺</td>
<td>0.25 mol%</td>
<td>15</td>
<td>36</td>
<td>0</td>
<td>0</td>
<td>38</td>
</tr>
<tr>
<td>1:5⁺</td>
<td>0.25 mol%</td>
<td>15</td>
<td>20</td>
<td>0</td>
<td>0</td>
<td>22</td>
</tr>
</tbody>
</table>

⁻ Conditions: 0.004 mmol [Co], 10 μL NaBEt₃H solution (1M in toluene), 1.6 mmol 1-octene, 1.76 mmol Ph₂SiH₂, 23 °C. ⁺ Yields were determined by integration of product Si-H resonances to mesitylene in the ^1H NMR spectra of crude reaction mixtures. ⁺⁺ Total conversions were determined by integration of 1-octene resonances to mesitylene in the ^1H NMR spectra of crude reaction mixtures. In all catalysis runs, ~2% of 2-octene was observed. ⁺⁺⁺PPh₃ was stirred with 1-octene and Ph₂SiH₂ prior to addition to the activated catalyst.

5.7 Overview and conclusions

We have presented here a general synthetic route to five-coordinate reduced Co-(PNpy) complexes. CoCl₂(PNpy) were easily reduced using NaBEt₃H or MeLi, and stable species were isolated when PPh₃ is present in the reaction. The four-coordinate derivatives of reduced Co-(PNpy) are unstable, though they are proposed to be catalytically active. The Ph₂P₂C₂N₃H₆py ligand represented a case where “CoCl₂(Ph₂P₂C₂N₃H₆py)” was not isolable. Therefore, the reduced compound was prepared using the ligand radical anion, a method that further extends the generality of the reducibility of α-diimines.³⁸

The phosphine-imine-pyridine platform is a hybrid of a strong donor site (PR₃) and a redox-active iminopyridine.³⁹ DFT calculations support this description such that these ligands are neutral when attached to CoCl₂ center, but are radical anions when bound to a reduced Co-(PPh₃) site. The influence of the fifth ligand of this redox equilibrium is indicated by the finding that PNpy is redox innocent in the dimeric [CoR(PNpy)]₂.
complexes, and may have important implications in the mechanism where the catalytic intermediates have varying co-ligands.

A critical factor in this work is the stability conferred to the reduced Co complexes by PPh₃. The choice of PPh₃ was fortunate since it allowed isolation of several catalytic intermediates, yet it was labile for catalysis. The reversible displacement by styrene is notable. In the absence of a stabilizing co-ligand, reduction of CoCl₂(PNpy) complexes afforded unstable derivatives. The PPh₃-free catalytic species are probably comparable to (alkylDIP)CoCl, which exhibit paramagnetic spectroscopic features at room temperature.¹⁴ That the PPh₃ is labile is established by variable temperature NMR spectroscopy, rates of catalysis and its displacement by styrene. Dissociation of PPh₃ produces CoR(PNpy) derivatives related to Chirik's hydrido and alkyl Co-(DIP) complexes.⁴⁰

Since catalytically active reduced Co-silyl complexes are elusive,³⁵,⁴¹ the catalytic intermediates Co(SiH₂₅R₆)(Ph₂PC₆H₄NPh)(PPh₃) were examined in detail by NMR spectroscopy. The Co-Si bond forms via replacement of PPh₃ by the silane and subsequent formation of a silyl-silane complex. Catalytically active cobalt-silyl complexes were characterized as the phosphine and styrene adducts, Co(SiR₃)(PNpy)(L). For ethylene, insertion was observed directly. Closing the catalytic cycle, the resulting β-silylalkyl cobalt(i) complexes readily react with hydrosilane to generate ethylsilane (Scheme 5.8). Previously, insertion of styrene into M-Si bond was observed for [(phenanthroline)Pd(SiEt₃)₂H]⁺ to give the π-stabilized complex, (phen)Pd(η³-CH(Ph)CH₂SiEt₃)⁺.¹⁷b

The varying activity and selectivity of the different catalysts underscore the influence of the phosphine substituents on PNpy. Alkyl-phosphines favor anti-Markovnikov hydrosilylation at a high rate, while electron-withdrawing fluoroaryl-phosphines give mostly alkene isomerization. However, our system performs poorly when tertiary silanes are used. One possible route to improve this shortcoming is to utilize less sterically demanding alkyl-phosphines, for example Et₂PC₃N⁺py or Me₂PC₃N⁺py.
5.8 Experimental section

Materials and Methods. Unless otherwise indicated, reactions were conducted using standard Schlenk techniques under an N$_2$ atmosphere at room temperature with stirring. Solvents were high-performance liquid chromatography grade, dried and deoxygenated on a Glass Contour System or MBraun solvent purification system, and stored over 4 Å molecular sieves. Ph$_2$PC$_2$N$_2$H$_2$py was prepared according to literature procedure. The CoCl$_2$(PNpy) complexes were prepared according to procedures given in Chapter 4. The following compounds were used as received from Sigma-Aldrich: CoCl$_2$, NaBEt$_3$H (1 M in toluene) MeLi (1.6 Et$_2$O solution). The following compounds were received from Sigma-Aldrich, deoxygenated and stored over 4 Å molecular sieves prior to use: PhSiH$_3$, Et$_2$SiH$_2$, styrene, 1-octene, mesitylene. The following compounds were received from Gelest, Inc., deoxygenated and stored over 4 Å molecular sieves prior to use: Ph$_2$SiH$_2$, Me$_2$PhSiH. Research Purity ethylene gas was purchased from Matheson TRIGAS. $^1$H and $^{31}$P{$^1$H} NMR spectra were acquired on Varian Unity Inova 500NB and Unity 500 NB instruments at 20 °C unless otherwise noted. $^1$H NMR were referenced to residual solvent relative to tetramethylsilane, $^{31}$P{$^1$H} NMR spectra were referenced to an external 85% H$_3$PO$_4$ standard. $^{29}$Si NMR spectra were acquired on a 600 MHz Varian
Unity Inova NMR instrument. Crystallographic data were collected using either a Siemens SMART diffractometer equipped with a Mo Kα source (λ = 0.71073 Å) and an Apex II detector, or a Bruker D8 Venture diffractometer equipped with a Mo Kα microfocus source and a Photon 100 detector. Elemental analyses were performed by the School of Chemical Sciences Microanalysis Laboratory utilizing a model CE 440 CHN analyzer. Where THF was identified by X-ray crystallography or ¹H NMR, it was included in the calculation of the expected elemental analysis.

Calculations were performed with the ORCA package. Starting structures have been taken from the crystallographic data. Geometry optimization has been carried out in two steps. First the positions of the protons have been optimized, followed by a full geometry optimization performed with the B3LYP functional, Def2-SVP basis set and relativistic corrections by ZORA. For CoMe(Ph₂P₂C₆H₄N₃Phpy)(PPh₃) this encompassed separate optimizations of the high-spin triplet (S = 1) and broken-symmetry singlet (S = 0), BS(1,1) states; for [CoCl(Ph₂p₂C₂N₃Hpy)]₂ geometry optimizations have been performed for a quartet (S = 3/2) and a broken-symmetry doublet (S = 1/2), BS(2,1); for [CoMe(Ph₂p₂C₂N₃Hpy)]₂ the geometry optimizations have been carried out for the quintet (S = 2) state, as well as the singlet BS(2,2) state, the latter resulting in a closed shell wave function with two Co(II) ions and neutral ligands. The cartesian coordinates of all modeled structures are provided as Supporting Information. The singly occupied orbitals plotted in the figures are associated with the unpaired electrons and are so-called corresponding orbitals. The doubly occupied orbitals are localized quasi-restricted orbitals.

[CoCl(Ph₂p₂C₂N₃Hpy)]₂. CoCl₂ (81.5 mg, 0.62 mmol) was dissolved in THF (200 mL) and stirred in room temperature for 1 h. In a separate flask, sodium spheres (17.4 mg, 0.76 mmol) and Ph₂P₂C₂N₃Hpy (200 mg, 0.63 mmol) were combined in THF (20 mL) and stirred to give a dark red mixture that is Na[Ph₂p₂C₂N₃Hpy]. After 1 h, the Na[Ph₂p₂C₂N₃Hpy] solution was filtered through celite into the stirred CoCl₂ solution to give a dark purplish-brown mixture. After 16 h, this mixture was filtered and solvents were removed under reduced pressure. The resulting purplish-brown solids were redissolved in a minimal amount of THF and added pentane. The mixture was kept at –35 ºC for 18 h, filtered, washed with diethylether to obtain the desired product as purplish-brown microcrystals. Yield: 189 mg (72%). Single crystals suitable for X-ray diffraction were obtained by
diffusion of pentane into a THF solution containing the target compound. $^1$H NMR (500 MHz, CD$_2$Cl$_2$): $\delta$ 8.90 – 8.81 (m, 1H), 7.89 (dd, $J = 9.6, 7.3$ Hz, 2H), 7.63 – 7.45 (m, 4H), 7.40 – 7.23 (m, 6H), 6.96 – 6.90 (m, 1H), 5.14 (s, 1H), 2.26 (t, $J = 12.1$ Hz, 1H), 2.01 – 1.87 (m, 2H), 1.68 – 1.56 (m, 1H). $^{31}$P{$_^1$H} NMR (202.4 MHz, THF-d$_8$): $\delta$ 40.0 (s, 1P).

Anal. Calcd. for C$_{20}$H$_{19}$ClCoN$_2$P (found): C, 58.2 (57.36); H, 4.64 (4.25); N, 6.79 (6.22).

$[\text{CoMe}(\text{Ph}_2\text{PC}_2\text{N}^\text{H}^\text{Npy})]_2$. A suspension of Co(Ph$_2$P$_2$C$_2$N$^\text{H}$N$^\text{H}$)Cl (100 mg, 0.24 mmol) in Et$_2$O (5 mL) was cooled to –35 ºC. A MeLi solution (0.18 mL, 1.6 M in Et$_2$O, 0.28 mmol) was added to the cooled suspension and stirred in room temperature for 18 hours. The solution was then filtered and dried under reduced pressure. The resulting dark solid was recrystallized from a THF solution layered with pentane under –35 ºC to give the target compound as dark purple crystals. Single crystals suitable for X-ray diffraction were also obtained this way. $^1$H NMR (500 MHz, C$_6$D$_6$): $\delta$ 8.27 (d, $J = 5.6$ Hz, 1H), 7.47 – 7.52 (m, 2H), 7.34 – 7.27 (m, 2H), 7.01 – 6.94 (m, 6H), 6.71 (t, $J = 7.05$, 1H), 6.64 (t, $J = 7.05$, 1H), 6.48 (d, $J = 8.1$ Hz, 1H), 4.31 (s, 1H), 2.48 – 2.33 (m, 1H), 1.97 (m, 1H), 1.85 – 1.70 (m, 2H), –0.28 (d, $J = 7.1$ Hz, 3H). $^{31}$P{$_^1$H} NMR (202.4 MHz, THF-d$_8$): $\delta$ 45.8 (s, 1P).

$\text{CoMe}(\text{Ph}_2\text{P}_6\text{C}_6\text{H}_4\text{N}^\text{Ph}^\text{py})(\text{PPh}_3)$. A suspension containing PPh$_3$ (21 mg, 0.08 mmol) and CoCl$_2$(P$_{\text{Ar}}$N$^\text{Ph}^\text{py}$) (46 mg, 0.08 mmol) in Et$_2$O (50 mL) was cooled to in an isopropanol/CO$_2$ bath. A MeLi solution (100 $\mu$L, 1.6 M in Et$_2$O, 0.16 mmol) was added to the suspension. The mixture was slowly warmed to room temperature over a period of 1 h to give a dark purple solution. After stirring for 16 h, the mixture was concentrated to ca. 3 mL and filtered using a medium frit. The dark purple solid that was collected was extracted using THF (30 mL) and filtered through a short plug of Celite. This THF solution was concentrated to 3 mL, followed by addition of 10 mL of pentane, and immediately filtered through a short plug of Celite. The filtrate was stored under inert atmosphere at 20 ºC for 36 h. After decanting the solution, the target compound was collected as purple crystals. Yield: 32 mg (51%). Single crystals suitable for X-ray diffraction were obtained by slow diffusion of pentane into a concentrated THF solution containing the target compound. $^1$H NMR (500 MHz, C$_6$D$_6$): $\delta$ 9.25 (d, $J = 6.4$ Hz, 1H), 8.01 – 7.98 (m, 2H), 7.57 (t, $J = 7.6$ Hz, 1H), 7.41 (t, $J = 6.4$ Hz, 1H), 7.32 – 7.23 (m, 4H), 7.11 – 6.78 (m, 30H), 6.68 (t, $J = 7.8$ Hz, 1H), 1.22 (d, $J = 6.6$ Hz, 3H). $^{31}$P{$_^1$H} NMR (202.4 MHz, C$_6$D$_6$): $\delta$
CoH(Ph2PC6H4NPh(py))(PPh3). A suspension containing PPh3 (19 mg, 0.07 mmol) and CoCl2(PArNPhpy) (41 mg, 0.07 mmol) in THF (15 mL) was cooled to in an isopropanol/CO2 bath. A NaHBEt3 solution (150μL, 1M in toluene, 0.015 mmol) was added to the suspension to give a dark brown solution. After warming to 23 ºC and stirring for 16 h, the mixture was filtered through a short plug of Celite, and the filtrated was dried under reduced pressure. The resulting brown solid was recrystallized by dissolving in Et2O (ca. 2 mL) and layering with pentane (15 mL) and stored at -35 ºC for 48 h to obtain the target compound as dark brown crystals. Yield: 35 mg (64 %).

1H NMR (500 MHz, C6D6): δ 9.36 (d, J = 4.4 Hz, 1H), 8.05 – 7.92 (m, 2H), 7.53 (t, J = 7.4 Hz, 1H), 7.28 – 7.20 (m, 4H), 7.06 – 6.98 (m, 15H), 6.91 – 6.89 (m, 11H), 6.80 (dt, J = 15.7, 7.3 Hz, 1H), 6.69 – 6.57 (m, 3H), -20.83 (dd, J = 65.4, 34.7 Hz, 1H). 31P{1H} NMR (202 MHz, C6D6): δ 83.60 (br, 1P), 64.88 (br, 1P).

CoMe(Ph2PC3NPh(py))(PPh3). A suspension containing PPh3 (17 mg, 0.06 mmol) and CoCl2(Ph2PC3NPh(py)) (35 mg, 0.06 mmol) in Et2O (20 mL) was cooled to in an isopropanol/CO2 bath. A MeLi solution (85μL, 1.6M in Et2O, 0.014 mmol) was added to the suspension, and slowly warmed to 23 ºC to give a dark red-orange solution. After stirring for 16 h, the mixture was filtered through a short plug of Celite. The red-orange residue was dissolved in a 1:5 mixture of Et2O and pentane, and stored at -35 ºC for 48 h to afford the target compound as dark orange crystals. Yield: 18 mg (37%). Single crystals suitable for X-ray diffraction were obtained by solvent diffusion of pentane into a concentrated THF solution. 1H NMR (500 MHz, C6D6): δ 9.74 (d, J = 6.6 Hz, 1H), 7.41 (t, J = 5.8 Hz, 1H), 7.34 (t, J = 7.8 Hz, 6H), 7.27 (t, J = 7.8 Hz, 1H), 7.12 – 6.54 (m, 25H) 3.98 (br, 1H), 3.49 (br, 1H), 2.45 (br, 1H), 2.12 (br, 1H), 1.65 (br, 2H), 1.11 (d, J = 8.8 Hz, 5H). 31P{1H} NMR (202 MHz, C6D6): δ 67.91 (br, 1P), 59.49 (br, 1P). Anal. Calcd. for C46H43CoN2P2: C, 74.19 (71.31); H, 5.82 (5.68); N, 3.76 (3.46). Analysis on 5 separate crystalline samples of the compound showed low percentage on C content, possibly due to extreme O2 sensitivity.

CoH(Ph2PC2NPh(py))(PPh3). A suspension containing PPh3 (30 mg, 0.11 mmol) and CoCl2(Ph2PC2NPh(py)) (60 mg, 0.11 mmol) in THF (15 mL) was cooled to – 35 ºC. A
NaHBEt$_3$ solution (230μL, 1M in toluene, 0.23 mmol) was added to the suspension to give a dark brown solution. After warming to 23°C and stirring for 16 h, the mixture was filtered through a short plug of celite, and the filtrated was dried under reduced pressure. The resulting brown solid was recrystallized by dissolving in Et$_2$O (ca. 2 mL) and layering with pentane (15 mL) and stored at –35 °C for 48 h to obtain the target compound as dark brown crystals. Yield: 45 mg (56 %). $^1$H NMR (500 MHz, C$_6$D$_6$): δ 9.94 (d, $J$ = 6.2 Hz, 1H), 7.51 (t, $J$ = 8.1 Hz, 2H), 7.23 – 7.09 (m, 14H), 6.97 (q, $J$ = 7.9 Hz, 9H), 6.89 – 6.82 (m, 7H), 6.69 – 6.61 (m, 1H), 4.33 – 4.21 (m, 1H), 3.31 – 3.24 (m, 1H), 2.35 – 2.19 (m, 1H), 2.12 – 2.06 (m, 1H), 1.93 – 1.76 (m, 1H), 1.75 – 1.61 (m, 1H), −18.30 (dd, $J$ = 73.7, 28.9 Hz, 1H).

$^{31}$P,$^1$H NMR (202 MHz, C$_6$D$_6$): δ 71.43 (br, 1P), 61.20 (br, 1P).

Anal. Calcd. for C$_{45}$H$_{41}$CoN$_2$P$_2$·0.5THF (found): C, 73.36 (73.1); H, 5.92 (5.61); N, 3.65 (4.02).

Co(SiH$_2$Ph)(Ph$_2$P$_2$C$_6$H$_4$N$_{Ph}$py)(PPh$_3$). A THF solution (5 mL) of CoMe(Ph$_2$P$_2$C$_6$H$_4$N$_{Ph}$py)(PPh$_3$) (38 mg, 0.049 mmol) was added 5 drops of PhSiH$_3$ (~ 100 mg). The solution color immediately changed from purple to brown. After stirring this solution for 30 mins, pentane (10 mL) was added to this solution and quickly filtered through a short plug of Celite. The filtrate was stored at –35 °C for 24 h to afford the target compound as dark brown crystals. Single crystals suitable for X-ray diffraction were obtained by this crystallization method. Yield: 30 mg (70%). $^1$H NMR (500 MHz, toluene-$d_8$): δ 9.62 (d, $J$ = 6.3 Hz, 1H), 7.42 (d, $J$ = 7.3 Hz, 2H), 7.36 – 7.28 (m, 4H), 7.25 (dd, $J$ = 10.8, 7.7 Hz, 2H), 7.12 – 6.75 (m, 29H), 6.74 – 6.65 (m, 4H), 6.60 (t, $J$ = 7.7 Hz, 1H), 4.74 (dd, $J$ = 15.6, 5.4 Hz, 1H), 4.61 (d, $J$ = 18.7 Hz, 1H). $^{31}$P{$^1$H} NMR (202 MHz, C$_6$D$_6$): δ 71.43 (br, 1P), 61.20 (br, 1P).

In-situ synthesis and characterization of Co(SiR$_3$)(Ph$_2$P$_2$C$_6$H$_4$N$_{Ph}$py)(PPh$_3$). A toluene-$d_8$ solution containing CoMe(Ph$_2$P$_2$C$_6$H$_4$N$_{Ph}$py)(PPh$_3$) (10 mg, 0.013 mmol) was loaded in an NMR tube and added 1 equiv of Ph$_2$SiH$_2$ (2.5 μL, 0.013 mmol) via a microsyringe. NMR spectra were recorded after 5 mins. $^1$H NMR (500 MHz, toluene-$d_8$): δ 10.01 (d, $J$ = 6.8 Hz, 1H), 7.60 – 7.44 (m, 3H), 7.22 (td, $J$ = 7.6, 1.5 Hz, 1H), 6.76 – 6.66 (m, 3H), 6.46 – 6.41 (m, 1H), 6.36 (dd, $J$ = 8.4, 4.0 Hz, 1H), 5.49 (dd, $J_{P\cdot H}$ = 10.5, 6.4 Hz, 1H). $^{31}$P{$^1$H} NMR (202 MHz, toluene-$d_8$):
δ 73.43 (br, 1P), 49.58 (br, 1P). $^{29}$Si NMR (119 MHz, THF- $d_8$): δ −4.80 (d, $J = 72.4$ Hz, 1Si).

$^{13}$C NMR (119 MHz, THF- $d_8$): δ −4.80 (d, $J = 72.4$ Hz, 1Si).

$^{29}$Si NMR (119 MHz, THF- $d_8$): δ −4.80 (d, $J = 72.4$ Hz, 1Si).

In situ synthesis and characterization of $\text{Co}(\text{SiHEt}_2)(\text{Ph}_2\text{P}^\text{C}_6\text{H}_4\text{N}^\text{Ph}_2\text{py})(\text{PPh}_3)$. This compound was prepared in a manner similar to $\text{Co}(\text{SiHPh}_2)(\text{Ph}_2\text{P}^\text{C}_6\text{H}_4\text{N}^\text{Ph}_2\text{py})(\text{PPh}_3)$ using $\text{CoMe}(\text{Ph}_2\text{P}^\text{C}_6\text{H}_4\text{N}^\text{Ph}_2\text{py})(\text{PPh}_3)$ (4.7g, 0.006 mmol) and a 0.25 M toluene-$d_8$ solution of $\text{Et}_2\text{SiH}_2$ (24 μL, 0.006 mmol). $^1$H NMR (500 MHz, toluene-$d_8$): δ 9.89 (d, $J = 6.3$ Hz, 1H), 7.68 – 7.61 (m, 1H), 7.44 – 7.37 (m, 2H), 7.31 (dd, $J = 9.7$, 7.6 Hz, 2H), 7.24 – 6.79 (m, 30H), 6.53 (t, $J = 7.5$ Hz, 1H), 6.29 (dd, $J = 8.2$, 4.0 Hz, 1H), 4.27 (dt, $J = 12.5$, 3.7 Hz, 1H), 1.28 (t, $J = 7.7$ Hz, 3H), 1.16 (t, $J = 7.8$ Hz, 3H), 1.01 – 0.90 (m, 2H), 0.86 – 0.74 (m, 2H). $^{31}$P$^1$H NMR (202 MHz, $\text{C}_6\text{D}_6$): δ 73.03 (s, 1P), 54.95 (s, 1P).

In situ synthesis and characterization of $\text{Co}((\text{CH}_2\text{CH}_2\text{SiHPh}_2)(\text{Ph}_2\text{P}^\text{C}_6\text{H}_4\text{N}^\text{Ph}_2\text{py})(\text{PPh}_3)$. A toluene-$d_8$ solution of $\text{Co}((\text{CH}_2\text{CH}_2\text{SiHPh}_2)(\text{Ph}_2\text{P}^\text{C}_6\text{H}_4\text{N}^\text{Ph}_2\text{py})(\text{PPh}_3)$ was frozen in a J-Young tube. The headspace was evacuated, refilled with ca. 1 atm ethylene and slowly warmed to −78 °C. After the solution was thawed, it was inserted into an NMR spectrometer that was pre-cooled to −20 °C. The reaction was monitored at this temperature until reaction was complete (ca. 1 h). The solution was then re-cooled to −40 °C to prevent further reaction while data was collected. $^1$H NMR (600 MHz, toluene-$d_8$, −40 °C): δ 9.00 (d, $J = 6.5$ Hz, 1H), 7.57 – 6.53 (m, 47H) 5.12 (br, 1H), 2.25 – 2.11 (m, 1H), 1.54 – 1.45(m, 1H), 1.28 – 1.18 (m, 1H), 0.82 – 0.68 (m, 1H). $^{31}$P$^1$H NMR (243 MHz, toluene-$d_8$, −40 °C): δ 91.07 (d, $J = 44.2$ Hz, 1P), 57.54 (d, $J = 44.2$ Hz, 1P). $^{29}$Si NMR (119 MHz, toluene-$d_8$, −40 °C): δ −19.9 (s, 1Si).

In situ synthesis and characterization of $\text{Co}((\text{SiHPh}_2)(\text{Ph}_2\text{P}^\text{C}_6\text{H}_4\text{N}^\text{Ph}_2\text{py})(\eta^2\text{-}\text{CH}_2\text{CH}_2\text{C}_6\text{H}_5)$). A toluene-$d_8$ solution of $\text{Co}((\text{SiHPh}_2)(\text{Ph}_2\text{P}^\text{C}_6\text{H}_4\text{N}^\text{Ph}_2\text{py})(\eta^2\text{-}\text{CH}_2\text{CH}_2\text{C}_6\text{H}_5)$ was frozen in an J-Young NMR tube. In a separate J-Young NMR tube was added a toluene-$d_8$ solution of styrene (125 μL, 0.979 M), then vacuum transferred into the frozen solution of $\text{Co}((\text{SiHPh}_2)(\text{Ph}_2\text{P}^\text{C}_6\text{H}_4\text{N}^\text{Ph}_2\text{py})(\text{PPh}_3)$, and slowly warmed to −78 °C. After the solution was thawed, it was inserted into an NMR spectrometer that was pre-cooled to −16.9 °C. The reaction was monitored at this temperature until equilibrium was reached (ca. 30 mins), giving ~50% yield of $\text{Co}((\text{SiHPh}_2)(\text{Ph}_2\text{P}^\text{C}_6\text{H}_4\text{N}^\text{Ph}_2\text{py})(\eta^2\text{-}\text{CH}_2\text{CH}_2\text{C}_6\text{H}_5)$. The solution was then
re-cooled to −40 °C to prevent further reaction while data was collected. $^1$H NMR (600 MHz, toluene-$d_8$, −40 °C): δ 8.54 (d, $J = 6.4$ Hz, 1H), 7.75 − 6.31 (m, 37H), 5.87 (d, $J = 22.3$, 1H), 3.95 − 3.92 (m, 1H), 2.59 − 2.57 (m, 1H), 1.89 − 1.88 (m, 1H). $^{31}$P{$^1$H} NMR (243 MHz, toluene-$d_8$, −40 °C): δ 52.13 (s, 1P).

**General procedure for catalysis using CoCl$_2$(PNpy).** A substrate mixture containing 1-octene (11.2 g, 100 mmol), Ph$_2$SiH$_2$ (20.3 g, 110 mmol) and mesitylene (2 g, 16.67 mmol) was pre-made and used in small portions in the catalytic studies using the procedures described below. *Catalytic reactions using 1 mol% loading:* At room temperature, a scintillation vial was loaded with the cobalt complex (0.004 mmol, ca. 2 mg), and the pre-made substrate mixture (134 mg, 100 equiv). To this stirred homogeneous mixture was added a 1M NaBEt$_3$H in toluene (10 μL, 0.01 mmol). The red suspension immediately turned dark brown (for catalysis experiments preformed with CoR(PNpy)(PPh$_3$) catalysts (R = H, Me, SiHPh$_2$), the NaBEt$_3$H activation step was omitted). Aliquots for analysis were diluted with CDCl$_3$, and yields were determined by $^1$H NMR spectroscopy by integrating the Si-$H$ signal vs mesitylene (see SI for illustrative spectra). For catalyst loadings < 0.5 mol%, the activation of CoCl$_2$(PNpy) was slow, as indicated by the slow color evolution. In these cases, a scintillation vial was loaded with the cobalt complex (0.004 mmol), and the pre-made substrate mixture (134 mg, 100 equiv). To this stirring mixture was then added a 1M solution of NaBEt$_3$H in toluene (10 μL, 0.01 mmol). The red suspension immediately turned into a dark brown solution upon the addition of the NaBEt$_3$H. After all the cobalt complex has been dissolved (ca. 1 min), this solution was immediately diluted with additional substrate mixture to the desired concentration (134 mg, 100 equiv). Analysis was performed as above.

**Hydrogenation of styrene using 4 atm H$_2$.** A C$_6$D$_6$ (1.2 mL) solution containing styrene (50 μL, 0.44 mmol) and mesitylene (60 μL, 0.44 mmol) was loaded in a Fisher-Porter tube, followed by addition of CoCl$_2$(Ph$_2$PC$_6$H$_4$N$_2$py) (5 mg, 0.0087 mmol) and a 1M solution of NaBEt$_3$H toluene (18 μL, 0.18 mmol). The sample was frozen immediately after preparation and the head space was evacuated. The Fisher-Porter tube was then refilled with 60 psi H$_2$ (4 atm). After 15 h, the reaction mixture was analyzed by $^1$H NMR,
and the yield was determined by integration of the \(-\text{CH}_3\) triplet of ethylbenzene vs. mesitylene.

**Procedure for catalytic hydroboration of 1-octene.** A scintillation vial was charged with HBpin (120 mg, 0.96 mmol), 1-octene (97 mg, 0.87 mmol) and mesitylene (40 \(\mu\)L, 0.29 mmol), followed by the addition of \(\text{CoCl}_2(\text{Ph}_2\text{P}^\text{C}_6\text{H}_4\text{N}^\text{Ph}_\text{py})\) (5 mg, 0.0087 mmol). To this stirred heterogeneous mixture was added a 1M NaBE\(_3\)H solution in toluene (18 \(\mu\)L, 0.018 mmol). The red suspension immediately turned dark brown. After 15 mins, an aliquot of this reaction mixture was diluted with CDCl\(_3\) and analyzed by \(^1\text{H}\) NMR spectroscopy, the yield was determined by integration of \(-\text{CH}_3\) triplet of 1-pinacolborylooctaine vs. mesitylene.

### 5.9 Supporting information

![Figure 5.12](image)

Figure 5.12. \(^1\text{H}\) NMR spectrum of \([\text{CoCl}(\text{Ph}_2\text{P}^\text{C}_3\text{N}^\text{H}_\text{py})]\)_2 in C\(_6\)D\(_8\).
Figure 5.13 $^1$H NMR spectrum of [CoMe(P$_{C_2}N$py)$_2$]$_2$ in C$_6$D$_6$.

Figure 5.14 Variable temperature $^1$H NMR spectra of CoMe($^{Ph_2}P$C$_6$H$_4$N$^{Ph}$py)(PPh$_3$) in toluene-$d_8$ showing Co-CH$_3$ resonance. Left: $^1$H NMR spectra. Middle: selective $^{31}$P decoupled $^1$H NMR spectra, decoupler set at $\delta$ 65. Right: selective $^{31}$P decoupled $^1$H NMR spectra, decoupler set at $\delta$.
Figure 5.15 $^1$H NMR spectra of Co(SiHPh$_2$)($^{29}$P$_2$CoH$_4$N$_{Ph}$py)(PPh$_3$) in C$_6$D$_6$ showing the SiH resonance. Purple trace: $^1$H NMR spectrum. Blue trace: selective $^{31}$P decoupled $^1$H NMR spectra, decoupler set at $\delta$ 49.6. Green trace: selective $^{31}$P decoupled $^1$H NMR spectra, decoupler set at $\delta$ 73.4. Red trace: $^1$H{$^{31}$P} NMR spectrum.

Figure 5.16 $^1$H NMR spectra of reaction of CoH($^{29}$P$_2$CoH$_4$N$_{Ph}$py)(PPh$_3$) with 1-octene in C$_6$D$_6$. Bottom: recorded after 10 mins. Top: recorded after 1 h.
Figure 5.17 $^1$H NMR spectrum of reaction mixture of Co(SiHPh$_2$)(Ph$_2$PC$_6$H$_4$N$_{Ph}$py)(PPh$_3$) with ethylene in toluene-$d_8$ at $-20$ °C after 1 h. Peak at $\delta-1.24$ overlaps with signals of byproducts.

Figure 5.18 Enlarged $^1$H NMR spectra of reaction mixture of Co(SiHPh$_2$)(Ph$_2$PC$_6$H$_4$N$_{Ph}$py)(PPh$_3$) with ethylene in toluene-$d_8$ at $-20$°C after 1h. Bottom: $^1$H NMR spectrum. Middle: $^1$H{$^31$P} NMR spectrum, decoupler set at $\delta$ 91.1. Top: $^1$H{$^31$P} NMR spectrum, decoupler set at $\delta$ 57.7.
Figure 5.19 $^{29}$Si-1H HMBC NMR spectrum of reaction mixture of Co(SiHPh$_2$)(Ph$_2$PC$_6$H$_4$NN$_{py}$)(PPh$_3$) with ethylene in toluene-d$_8$ at $-40 \, ^\circ$C.

Figure 5.20 $^{31}$P-1H NMR spectrum of reaction of Co(SiHPh$_2$)(Ph$_2$PC$_6$H$_4$NN$_{py}$)(PPh$_3$) with styrene in toluene-d$_8$ at $-16.9 \, ^\circ$C after 40 mins.
Figure 5.21 Enlarged $^1$H NMR spectra of reaction of Co(SiHPh$_2$)$_2$(Ph$_2$P)$_2$C$_6$H$_4$N$_2$py)(PPh$_3$) with styrene in toluene-$d_8$ at $-20$ °C after 50 mins. Bottom: $^1$H NMR spectrum. Top: selective $^{31}$P decoupled $^1$H NMR spectra, decoupler set at $\delta$ 52.1.

Figure 5.22 $^1$H 1D-TOCSY NMR of reaction of Co(SiHPh$_2$)$_2$(Ph$_2$P)$_2$C$_6$H$_4$N$_2$py)(PPh$_3$) with styrene in toluene-$d_8$ at $-20$ °C after 50 mins by selective excitation at $\delta$ 3.94.
Figure 5.23 $^1$H NMR spectrum of catalytic mixture in CDCl$_3$. Condition: 0.004 mmol CoCl$_2$(iPr$_2$P=C$_3$N$_2$H$_2$py), 0.01 mmol NaBEt$_3$H (10 μL, 1 M solution in toluene), 0.8 mmol 1-octene, 0.88 mmol Ph$_2$SiH$_2$, 23 °C, 15 mins.

Figure 5.24 $^1$H NMR spectrum of catalytic mixture in CDCl$_3$. Condition: 0.0087 mmol CoCl$_2$(Ph$_2$P=C$_6$H$_4$N$_2$H$_2$py), 0.018 mmol NaBEt$_3$H (18 μL, 1 M solution in toluene), 0.87 mmol 1-octene, 0.96 mmol HBpin, 23 °C, 15 mins.
Reduction of CoCl$_2$(iPr$_2$P$_{C3N}$H$_{py}$) using NaBEt$_3$H in the presence of PPh$_3$. A THF (ca. 10 mL) suspension containing CoCl$_2$(iPr$_2$P$_{C3N}$H$_{py}$) (24 mg, 0.061 mmol) and PPh$_3$ (16 mg, 0.061 mmol) was cooled to –35 °C. To this solution was added a 1 M toluene solution of NaBEt$_3$H (120 µL, 0.120 mmol), immediately resulting in a dark brown solution. This solution was warmed to room temperature and further stirred for 16 h, followed by filtration through a short plug of Celite. The filtrate was evaporated under reduced pressure, dissolved in a small amount of C$_6$D$_6$, and the NMR spectra were collected. Formation of a hydride species was confirmed by a high field resonance at $\delta$ –19.9 in the $^1$H NMR spectrum.

![Figure 5.25 $^{31}$P NMR spectrum of crude reaction mixture of CoCl$_2$(iPr$_2$P$_{C3N}$H$_{py}$)/PPh$_3$/2NaBEt$_3$H, recorded in C$_6$D$_6$.](image)

Reaction of CoMe(Ph$_2$P$_{C6H4N}$Ph$_{py}$)(PPh$_3$) with H$_2$. A small amount of CoMe(Ph$_2$P$_{C6H4N}$Ph$_{py}$)(PPh$_3$) was loaded in an J-Young NMR tube and dissolved in C$_6$D$_6$. This purple solution was frozen, the head space of the NMR tube was evacuated, and refilled with 1 atm H$_2$. $^1$H and $^{31}$P{$^1$H} NMR spectra were recorded at 0.5 and 16 h. Conversion was determined by relative integration of the hydride resonance of CoH(Ph$_2$P$_{C6H4N}$Ph$_{py}$)(PPh$_3$) at $\delta$ –20.5, to the 6-pyridyl proton resonance of
CoMe(\text{Ph}_2\text{P}\text{C}_6\text{H}_4\text{N}^{\text{Ph}}\text{py})(\text{PPh}_3) \) at \( \delta 9.25 \) in the \( ^1\text{H} \) NMR spectra. Conversion was 10\% at 0.5 h, and > 95 \% at 16 h.

**Figure 5.26** \( ^1\text{H} \) NMR spectrum of reaction CoMe(\text{Ph}_2\text{P}\text{C}_6\text{H}_4\text{N}^{\text{Ph}}\text{py})(\text{PPh}_3) \) with \( \text{H}_2 \) in \( \text{C}_6\text{D}_6 \), recorded after 16 h.

**Figure 5.27** \( ^{31}\text{P}\{^1\text{H}\} \) NMR spectrum of reaction CoMe(\text{Ph}_2\text{P}\text{C}_6\text{H}_4\text{N}^{\text{Ph}}\text{py})(\text{PPh}_3) \) with \( \text{H}_2 \) in \( \text{C}_6\text{D}_6 \), recorded after 16 h.
**Reaction of CoMe\textsubscript{Ph2}P\textsubscript{C6H4}N\textsubscript{Ph}py)(PPh\textsubscript{3}) with HBpin.** A small amount of CoMe\textsubscript{Ph2}P\textsubscript{C6H4}N\textsubscript{Ph}py)(PPh\textsubscript{3}) was loaded in an J-Young NMR tube and dissolved in C\textsubscript{6}D\textsubscript{6}. To this purple solution was added 1 drop HBpin at room temperature, resulting in an immediate color change to brown. The \textsuperscript{1}H NMR spectrum was recorded immediately.

*Figure 5.28*  \textsuperscript{1}H NMR spectrum of crude reaction mixture of CoMe\textsubscript{Ph2}P\textsubscript{C6H4}N\textsubscript{Ph}py)(PPh\textsubscript{3}) with excess pinacolborane in C\textsubscript{6}D\textsubscript{6}.
Low temperature reaction of CoMe(Ph₂pC₆H₄NPhpy)(PPh₃) with excess PhSiH₃. In a J-Young NMR tube was loaded CoMe(Ph₂pC₆H₄NPhpy)(PPh₃) (4.4 mg, 0.0056 mmol) and dissolved in toluene-ᵈ₈. This solution was frozen, and a 2.8 M toluene-ᵈ₈ solution of PhSiH₃ (40 µL, 0.112 mmol) was vacuum transferred into the NMR tube. The sample was quickly thawed in an acetone/CO₂ bath and inserted into an NMR instrument that was pre-cooled to –32 °C. The reaction was monitored by ¹H NMR spectroscopy.

![1H NMR spectra of reaction of Co(SiH₂Ph)(Ph₂pC₆H₄NPhpy)(PPh₃) with excess PhSiH₃ in toluene-ᵈ₈. Bottom: after 150 s at –32 °C. Middle: after 540 s at –32 °C. Top: warmed to 20 °C.](image)

**Figure 5.29** ¹H NMR spectra of reaction of Co(SiH₂Ph)(Ph₂pC₆H₄NPhpy)(PPh₃) with excess PhSiH₃ in toluene-ᵈ₈. Bottom: after 150 s at –32 °C. Middle: after 540 s at –32 °C. Top: warmed to 20 °C.
Figure 5.30 $^{31}$P NMR spectra of reaction of Co(SiH$_2$Ph)(Ph$_2$P$_2$C$_6$H$_4$N$_{Ph}$py)(PPh$_3$) with excess PhSiH$_3$ in toluene-$d_8$ after 600 s at $-32$ °C.

**Reaction of Co(SiH$_2$H$_2$)(Ph$_2$P$_2$C$_6$H$_4$N$_{Ph}$py)(PPh$_3$) with ethylene.** The step-by-step reaction $^1$H NMR is shown in Figure 5.31. A J-Young NMR tube was loaded with CoMe(Ph$_2$P$_2$C$_6$H$_4$N$_{Ph}$py)(PPh$_3$) (4.2 mg, 0.0054 mmol) and dissolved in toluene-$d_8$. To this purple solution was added a 0.25 M toluene-$d_8$ solution of Et$_2$SiH$_2$ (21 µL, 0.0052 mmol). The $^1$H and $^{31}$P NMR spectra were recorded to confirm full conversion to Co(SiH$_2$H$_2$)(Ph$_2$P$_2$C$_6$H$_4$N$_{Ph}$py)(PPh$_3$) (samples needed to be prepared fresh due to instability of the silyl complex). The solution was then frozen, the head space of the NMR tube evacuated, refilled with 1 atm ethylene, and slowly thawed in an acetone/CO$_2$ bath. The sample tube was then inserted into an NMR instrument that was pre-cooled to 5 °C, and the reaction was monitored by $^1$H NMR spectroscopy. After full conversion to the ethylene insertion product (ca. 15 mins), the sample was ejected from the NMR instrument and frozen again. After evacuating the head space of the NMR tube, additional Et$_2$SiH$_2$ solution (25 µL, 0.0063 mmol) was vacuum transferred into the sample. After slow thawing in an acetone/CO$_2$ bath, the sample was reinjected into the NMR instrument. The $^1$H NMR spectrum was recorded to confirm formation of Et$_3$SiH.
Figure 5.31 $^1$H NMR spectra of step-by-step reaction in toluene-$d_8$. Purple trace: Co(SiHEt$_2$)(Ph$_2$P-C$_6$H$_4$N$_{Phpy}$)(PPh$_3$) with excess ethylene at $-40 \, ^\circ C$ (no reaction). Blue trace: Co(SiHEt$_2$)(Ph$_2$P-C$_6$H$_4$N$_{Phpy}$)(PPh$_3$) with excess ethylene at 5 $^\circ C$ after 12 mins. Teal trace: at $-20 \, ^\circ C$ after second addition of Et$_2$SiH$_2$. Green trace: warmed to $-2 \, ^\circ C$. Red trace: warmed to 10 $^\circ C$ for 5 mins.

$K_{eq}$ determination. The sample of Co(SiHPh$_2$)(Ph$_2$P-C$_6$H$_4$N$_{Phpy}$)(η$^2$-CH$_2$CHC$_6$H$_5$) was prepared as described in the experimental section. After vacuum transfer of styrene, the NMR tube was warmed to $-78 \, ^\circ C$ in an acetone/CO$_2$ bath, then inserted into an NMR instrument that was pre-cooled to $-16.9 \, ^\circ C$. The reaction was monitored by $^1$H NMR spectroscopy until the concentrations of the reactants stopped changing (ca. 25 mins). Relative concentrations were determined by integration of the 6-pyridyl protons of Co(SiHPh$_2$)(Ph$_2$P-C$_6$H$_4$N$_{Phpy}$)(η$^2$-CH$_2$CHC$_6$H$_5$), Co(SiHPh$_2$)(Ph$_2$P-C$_6$H$_4$N$_{Phpy}$)(PPh$_3$), and the terminal olefinic protons of styrene. $K_{eq}$ was determined using the following equation:

$$K_{eq} = \frac{[Co(SiHPh$_2$)(styrene)][PPh$_3$]}{[Co(SiHPh$_2$)(PPh$_3$)][styrene]}$$

(5.4)
with the assumption that

\[ \text{[Co(SiHPh\textsubscript{2})(styrene)]} = [PPh\textsubscript{3}] \]

The same procedure was performed for 25 and 1.2 equiv styrene.

**Figure 5.32** Reaction of Co(SiHPh\textsubscript{2})(\textsubscript{Ph\textsubscript{2}}\textsubscript{P}C\textsubscript{6}H\textsubscript{4}N\textsubscript{Ph}py)(PPh\textsubscript{3}) with styrene at –16.9 C, recorded in toluene-\textsubscript{d\textsubscript{8}} after 30 mins.
5.10 References


Chapter 6.

Electrochemistry and catalytic activity of reduced iron complexes containing PNpy†

6.1 Introduction

Iron complexes containing α-diiimine ligands have shown the most promise among first-row transition metals to promote PGM-like activity. Most notably in the area of catalytic H-X (X = SiR₃, BR₃, H) addition to alkenes, several complexes have reported high activity for hydrosilylation of alkenes using tertiary silanes, which is an important reaction in industrial crosslinking processes. The applicability of iron catalysts in industry was elegantly demonstrated by the Fe(DIP)(N₂)₂ catalyzed crosslinking reaction of two industrial silicon fluids at a loading of 500 ppm. Currently, iron-catalyzed hydrofunctionalization of alkenes typically invoke reduced metal species as the active catalysts. In fact, many catalytic systems employ the method of in-situ generation of active catalysts by addition of a reductant to an iron(II)-dihalide precatalyst.

Facilitated by low reduction potentials, α-diimines can either be directly reduced by added reductants (see Section 5.2), or reduced via electron transfer of an electron-rich transition metal center. Owing to the high reactivity, isolation of reduced iron hydrofunctionalization catalysts containing these ligands are difficult, which is an obstacle to the accurate analysis of the electronic structures of these species. As a compromise, the corresponding iron-carbonyl species were used in many studies to probe electronic properties of metal-(α-diimine) functionality. Representative examples of iron-dicarbonyl complexes containing α-diimine tridentate ligands are shown in Chart 6.1.

† Portions of this chapter are reproduced from the following publication with permission from the authors: Gilbert-Wilson, R.; Chu, W.-Y.; Rauchfuss, T. B. Inorg. Chem. 2015, 54, 5596.
While dicarbonyl complexes are convenient and stable derivatives of reduced iron species, it has been shown that the electronic structures of redox-active ligands can vary significantly with different auxiliary ligands.  

In this chapter, the collection of PNpy complexes are expanded to include reduced iron species. Stable Fe(PNpy)(CO)$_2$ are presented, and the electrochemistry examined using cyclic voltammetry. These measurements revealed redox properties of the PNpy ligands that are unique among the currently known redox-active tridentate ligands. Moreover, semi-stable catalytically active species for hydrosilylation were observed using NMR spectroscopy.

6.2 CO derivatives of Fe-(PNpy)

![Scheme 6.1 Synthesis of Fe(PNpy)(CO)$_2$.]

To facilitate the electronic analysis of our complexes, iron-dicarbonyls containing PNpy were synthesized. Stirring a THF solution of Fe(bda)(CO)$_3$ with Ph$_2$P(C$_6$H$_4$NMe$_2$)py in room temperature gave Fe(Ph$_2$P(C$_6$H$_4$NMe$_2$)py)(CO)$_2$ as the major product after 24 h. $^{31}$P NMR spectral analysis in THF revealed three species at $\delta$ 72.0 (68 %), 63.3 (15 %), and 57.3 (17 %). The IR spectrum of the crude reaction mixture also indicated multiple carbonyl species and was unresolved. Gratifyingly, Fe(Ph$_2$P(C$_6$H$_4$NMe$_2$)py)(CO)$_2$ was obtained as a dark brown crystal after repeated recrystallization, albeit in low yield (38%). The crude reaction mixture of Fe(Ph$_2$P(C$_6$H$_4$NPh$_2$)py)(CO)$_2$, obtained in manner similar to Fe(Ph$_2$P(C$_6$H$_4$NMe$_2$)py)(CO)$_2$, also exhibited 2 minor species in addition to the major product at $\delta$ 78.1. The minor species are proposed to arise from monodentate PNpy complex, specifically Fe($\kappa^1$-PNpy)$_n$(CO)$_{5-n}$. Formation of by-products greatly inhibited the yields for Fe(PNpy)(CO)$_2$. Alternatively, FeBr$_2$(Ph$_2$P(C$_6$H$_4$NPh$_2$)py) can be reduced by 2 equiv NaBEt$_3$H in the presence of CO to give Fe(Ph$_2$P(C$_6$H$_4$NPh$_2$)py)(CO)$_2$. This route afforded high yields and by-products were not observed.
The solid state structures of \( \text{Fe}^{(\text{Ph}_2\text{P} \text{C}_6\text{H}_4\text{NMe})_(\text{CO})_2} \) and \( \text{Fe}^{(\text{Ph}_2\text{P} \text{C}_6\text{H}_4\text{NPh})_(\text{CO})_2} \) were analyzed by X-ray diffraction (Figure 6.1). Both complexes exhibited highly distorted structures from square pyramidal (\( \tau = 0.41 \) for \( \text{Fe}^{(\text{Ph}_2\text{P} \text{C}_6\text{H}_4\text{NMe})_(\text{CO})_2} \) and \( \tau = 0.40 \) for \( \text{Fe}^{(\text{Ph}_2\text{P} \text{C}_6\text{H}_4\text{NPh})_(\text{CO})_2} \)). The imine C=N bond lengths are significantly longer than expected for typical \( \kappa^1 \)-imines. Comparing C=N bond lengths of \( \text{Fe}^{(\text{Ph}_2\text{P} \text{C}_6\text{H}_4\text{NPh})_(\text{CO})_2} \) with \( \text{FeCl}_2^{(\text{Ph}_2\text{P} \text{C}_6\text{H}_4\text{NPh})} \) revealed significant elongation of the double bond in the structure of the dicarbonyl complex (1.341(2) Å compared to 1.296(4) Å for \( \text{FeCl}_2^{(\text{Ph}_2\text{P} \text{C}_6\text{H}_4\text{NPh})} \)). This suggests significant transfer of electron density from the metal to the \( \alpha \)-diimine moiety. Calculations carried out on related \( \text{FeL}_3(\text{CO})_2 \) complexes containing tridentate redox-active ligands (\( \text{L}_3 \)) generally point to chelation of neutral \( \text{L}_3 \) to an iron(0) metal center, even when large distortions of the \( \alpha \)-diimine ligands were observed in the solid state. The significant increase of C=N bond distance in \( \text{Fe}^{(\text{Ph}_2\text{P} \text{C}_6\text{H}_4\text{NPh})_(\text{CO})_2} \) compared to strictly neutral \( \text{Ph}_2\text{P} \text{C}_6\text{H}_4\text{NPh} \) is best attributed to \( \pi \)-backbonding from Fe(0).

Both dicarbonyl complexes exhibited two strong signals in the IR spectra, and the frequencies are summarized in Table 6.1. The IR spectral details of related iron dicarbonyls containing pyridine-derived \( \alpha \)-diimine ligands are also included for comparison. The IR frequencies suggested comparable electron donating properties with other \( \alpha \)-diimine phosphine ligands (\( \text{P}^{\text{O}}\text{NN}, \text{P-bipy} \)), which are stronger donors than diiminopyridine (DIP).
Electrochemical measurements were carried out on free \( \text{Ph}_2\text{P}^\text{C}_6\text{H}_4^\text{N}^\text{Ph}^\text{py} \), \( \text{Fe}(\text{Ph}_2\text{P}^\text{C}_6\text{H}_4^\text{N}^\text{Ph}^\text{py})(\text{CO})_2 \) and \( \text{Fe}(\text{Ph}_2\text{P}^\text{C}_6\text{H}_4^\text{N}^\text{Me}^\text{py})(\text{CO})_2 \) in THF using a glassy-carbon working electrode (Figure 6.2). The redox potentials of \( \text{Fe}(\text{Ph}_2\text{P}^\text{C}_6\text{H}_4^\text{N}^\text{Ph}^\text{py})(\text{CO})_2 \) are positively shifted by ca. 0.12V when compared to the \( \text{Fe}(\text{Ph}_2\text{P}^\text{C}_6\text{H}_4^\text{N}^\text{Me}^\text{py})(\text{CO})_2 \) analogue. This difference is likely due to higher degree of electron delocalization on the Ph substituent compared to Me.

Three redox events were observed respectively for both compounds between \(-0.3 \) and \(-2.8 \) V. The reversible event at ca. \(-0.7 \) V is consistent with the \([\text{Fe}(\text{P}^\text{O}^\text{NN})(\text{CO})_2]^{0/+}\) and \([\text{Fe}(\text{P-bipy})(\text{CO})_2]^{0/+}\) couples, though significantly lower in potential than \([\text{Fe}(\text{DIP})(\text{CO})_2]^{0/+}\). Chemical oxidation of \( \text{Fe}(\text{Ph}_2\text{P}^\text{C}_6\text{H}_4^\text{N}^\text{Ph}^\text{py})(\text{CO})_2 \) using \( \text{FcBF}_4 \) resulted in shifts of \( \nu_{\text{CO}} \) from 1949 and 1890 cm\(^{-1}\) to 2005 and 1951 cm\(^{-1}\). This corresponded to \( \Delta \nu_{\text{CO}} \approx 53 \) cm\(^{-1}\), consistent with oxidation of \( \text{Fe}(0) \rightarrow \text{Fe}(1) \). The \([\text{Fe}(\text{DIP})(\text{CO})_2]^{0/+}\) couple is associated with \( \Delta \nu_{\text{CO}} \approx 60 \) cm\(^{-1}\), whereas \([\text{Fe}(\text{P}^\text{O}^\text{NN})(\text{CO})_2]^{0/+}\) and \([\text{Fe}(\text{P-bipy})(\text{CO})_2]^{0/+}\) are associated with \( \Delta \nu_{\text{CO}} \approx 50 \) cm\(^{-1}\).

The reversible 1e\(^-\) reduction at ca. \(-2.3 \) V is similar to that of the \([\text{Fe}(\text{DIP})(\text{CO})_2]^{0/-}\), but contrasts the irreversibility of the couples \([\text{Fe}(\text{P}^\text{O}^\text{NN})(\text{CO})_2]^{0/-}\) and \([\text{Fe}(\text{P-bipy})_2]^{0/-}\). Curiously, the \([\text{Fe}(\text{Ph}_2\text{P}^\text{C}_6\text{H}_4^\text{N}^\text{Ph}^\text{py})(\text{CO})_2]^{0/-}\) couple is much more mild than other phosphine complexes, though comparable to \([\text{Fe}(4\text{-CF}_3\text{-DIP})(\text{CO})_2]^{0/-}\). Additionally, the reduction event at ca. \(-2.6 \) V of \( \text{Fe}(\text{Ph}_2\text{P}^\text{C}_6\text{H}_5^\text{N}^\text{Ph}^\text{py})(\text{CO})_2 \) and \( \text{Fe}(\text{Ph}_2\text{P}^\text{C}_6\text{H}_5^\text{N}^\text{Me}^\text{py})(\text{CO})_2 \) is unique when compared to complexes in Table 6.1. These cathodic waves are quasi-reversible, giving

### Table 6.1 Redox potentials and IR frequencies of iron dicarbonyls containing pyridine-derived \( \alpha \)-diimine ligands

<table>
<thead>
<tr>
<th></th>
<th>Reduction (V)(^{a})</th>
<th>Oxidation (V)(^{a})</th>
<th>( \nu_{\text{CO}} ) (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Ph}_2\text{P}^\text{C}_6\text{H}_4^\text{N}^\text{Ph}^\text{py} )</td>
<td>-2.45</td>
<td></td>
<td>1961, 1906 (pentane)</td>
</tr>
<tr>
<td>( \text{P}^\text{O}^\text{NN} )</td>
<td>-2.74</td>
<td></td>
<td>1943, 1884 (CH(_2)Cl(_2))</td>
</tr>
<tr>
<td>( \text{DIP} )</td>
<td>-2.62</td>
<td></td>
<td>1956, 1902 (pentane)</td>
</tr>
<tr>
<td>( \text{Fe}(\text{Ph}_2\text{P}^\text{C}_6\text{H}_4^\text{N}^\text{Ph}^\text{py})(\text{CO})_2 )</td>
<td>-2.25</td>
<td>-0.64</td>
<td>1925, 1863 (CH(_2)Cl(_2))</td>
</tr>
<tr>
<td>( \text{Fe}(\text{Ph}_2\text{P}^\text{C}_6\text{H}_4^\text{N}^\text{Me}^\text{py})(\text{CO})_2 )</td>
<td>-2.37</td>
<td>-0.77</td>
<td>1974, 1914 (pentane)</td>
</tr>
<tr>
<td>( \text{Fe}(\text{P-bipy})(\text{CO})_2 )</td>
<td>-2.54</td>
<td>-0.65</td>
<td>1983, 1925 (pentane)</td>
</tr>
<tr>
<td>( \text{Fe}(\text{DIP})(\text{CO})_2 )</td>
<td>-2.46</td>
<td>-0.49</td>
<td></td>
</tr>
</tbody>
</table>

\(^{a}\) Recorded in THF at a scan rate of 0.1 Vs\(^{-1}\).
$i_{pa}/i_{pc} = 0.59$ and $0.35$ for $[\text{Fe}^{(\text{Ph}2\text{pC6H5}N\text{Phpy})(\text{CO})_2}]^{1/2-}$ and $[\text{Fe}^{(\text{Ph}2\text{pC6H5}N\text{Phpy})(\text{CO})_2}]^{1/2-}$, respectively at a scan rate of $0.1 \text{ V s}^{-1}$.

These electrochemical measurements revealed high similarities of $[\text{Fe}^{\text{PNpy})(\text{CO})_2}]^{3/4+}$ and $[\text{Fe}^{(\text{PNpy})(\text{CO})_2}]^{0/-}$ with the redox events of $\text{Fe(DIP)(CO)}_2$ in terms of reversibility and potential, therefore the structures of $[\text{Fe}^{\text{PNpy})(\text{CO})_2}]^{x}$ generated electrochemically are proposed to be analogous to $\text{Fe(DIP)(CO)}_2$, shown in Scheme 6.2. When $1\text{e}^{-}$ is introduced into the system, it first reduces the metal to $\text{Fe}^{(-1)}$ state, which quickly transfers $2\text{e}^{-}$ to the $\alpha$-diimine ligand, giving $[\text{Fe}(0)(\text{PNpy})^{2-}(\text{CO})_2]^{-}$. The second reduction, which is unique to our PNpy containing system, is proposed to reduce the metal, giving $[\text{Fe}(0)(\text{PNpy})^{2-}(\text{CO})_2]^{2-}$. The above results point to redox non-innocent PNpy ligands containing an $\alpha$-diimine moiety with low reduction potentials.
6.3 Reduction of FeBr$_2$(Ph$_2$P$_2$C$_6$H$_4$N$_2$Ph$_2$py) in the presence of Ph$_2$SiH$_2$ or PPh$_3$

Attempts to isolate carbonyl-free reduced Fe-(PNpy) complexes were made. When 2 equiv NaBEt$_3$H was added to a THF suspension of FeBr$_2$(Ph$_2$P$_2$C$_6$H$_4$N$_2$Ph$_2$py), a dark brown solution evolved. The recorded $^1$H and $^{31}$P NMR spectra showed no observable signals, suggesting paramagnetism of the product. The IR spectrum did not reveal any metal-bound N$_2$ signals. We suspected the reduced Fe-(PNpy) species was unstable in the absence of strongly binding ligands. When this reduction reaction was conducted in the presence of excess Ph$_2$SiH$_2$, the green species Fe(Ph$_2$P$_2$C$_6$H$_4$N$_2$Ph$_2$py)(Ph$_2$SiH$_2$)$_2$ was formed, supposedly via the following reaction:

$$\text{FeBr}_2(\text{Ph}_2\text{P}_2\text{C}_6\text{H}_4\text{N}_2\text{Ph}_2\text{py}) + 2\text{NaBEt}_3\text{H} + 2\text{Ph}_2\text{SiH}_2 \rightarrow \text{Fe}(\text{Ph}_2\text{P}_2\text{C}_6\text{H}_4\text{N}_2\text{Ph}_2\text{py})(\text{Ph}_2\text{SiH}_2)_2 + \text{H}_2 + 2\text{NaBr} + 2\text{BEt}_3$$

(6.1)

This silane complex was characterized by a high-field resonance in the $^1$H NMR spectrum. Though instability of Fe(Ph$_2$P$_2$C$_6$H$_4$N$_2$Ph$_2$py)(Ph$_2$SiH$_2$)$_2$ in solution precluded further analysis of the structure, comparison of the $^1$H NMR resonances with the related Fe(DIP)(PhSiH$_3$)$_2$ suggested a bis(σ-silane) complex (Figure 6.3).
In view of the mechanistic insights provided by CoR(P\textsuperscript{Ph}N\textsuperscript{Ph}py)(PPh\textsubscript{3}) (see Chapter 5), the effect of PPh\textsubscript{3} was briefly evaluated with the FeBr\textsubscript{2}(P\textsuperscript{Ph}N\textsuperscript{Ph}py)/2NaBEt\textsubscript{3}H reaction. Reduction of FeBr\textsubscript{2}(P\textsuperscript{Ph}N\textsuperscript{Ph}py) by 2 equiv of NaBEt\textsubscript{3}H in the presence of PPh\textsubscript{3} afforded a 1:1 complex, nominally Fe(P\textsuperscript{Ph}N\textsuperscript{Ph}py)(PPh\textsubscript{3}), characterized by \textsuperscript{31}P NMR spectrum (δ 78, 72; \textit{J}_{P-P} = 25 Hz). This complex was highly unstable to loss of PPh\textsubscript{3} and formed untraceable iron species. Samples were always contaminated with free PPh\textsubscript{3} and decomposition products. Nevertheless, these solutions react with CO to give, sequentially, Fe(P\textsuperscript{Ph}N\textsuperscript{Ph}py)(PPh\textsubscript{3})(CO) (δ 82.2, 71.6; \textit{J}_{P-P} = 27 Hz), and, more slowly, Fe(Ph\textsubscript{2}pC\textsubscript{6}H\textsubscript{4}N\textsuperscript{Ph}py)(CO)\textsubscript{2}. Having thus verified the existence of tractable reduced Fe-PNpy complexes, the reaction of Fe(P\textsuperscript{Ph}N\textsuperscript{Ph}py)(PPh\textsubscript{3}) toward silanes was examined. Upon addition of excess Ph\textsubscript{2}SiH\textsubscript{2}, the solution immediately turns from brown to green. NMR spectroscopy analysis indicated partial conversion of Fe(P\textsuperscript{Ph}N\textsuperscript{Ph}py)(PPh\textsubscript{3}) to a new compound, assigned Fe(P\textsuperscript{Ph}N\textsuperscript{Ph}py)(PPh\textsubscript{3})(H\textsubscript{2}SiPh\textsubscript{2}), with two new broad resonances observed at δ 80 and 73 in the \textsuperscript{31}P NMR spectrum. A high field resonance at δ -12.6 in the \textsuperscript{1}H NMR spectrum was assigned to a single SiH (ddd, \textit{J}_{P-H} = 33, 17 Hz, \textit{J}_{H-H} = 4.5).
larger couplings were attributed to contributions from $^{31}\text{P}$ nuclei, which was confirmed by $^1\text{H} \{^{31}\text{P}\}$ NMR spectroscopy. The smallest coupling is proposed to arise from coupling to the other SiH proton. This compound was stable in solution up to days when kept in an inert atmosphere. Moreover, Fe($^{31}\text{P}$PhN$^\text{Ph}$py)(PPh$_3$)(H$_2$SiPh$_2$) was significantly more stable than the PPh$_3$ free complex, Fe($^{31}\text{P}$N$^\text{Ph}$py)(H$_2$SiPh$_2$)$_2$.

6.4 Catalytic studies of PNpy containing Fe complexes

Table 6.2 Hydrosilylation using FeBr$_2$(Ph$_2$PC$_6$H$_4$N$_{\text{Ph}}$py) ([Fe]).

<table>
<thead>
<tr>
<th>alkene</th>
<th>H-X</th>
<th>mol% [Fe]</th>
<th>temp °C</th>
<th>time</th>
<th>$\alpha^b$</th>
<th>$\beta^b$</th>
<th>$\gamma^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-octene</td>
<td>Ph$_2$SiH$_2$</td>
<td>0.1</td>
<td>23</td>
<td>0.5 h</td>
<td>$&gt;99%$</td>
<td>0 %</td>
<td>0 %</td>
</tr>
<tr>
<td>1-octene</td>
<td>HB(pinacolate)</td>
<td>0.1</td>
<td>23</td>
<td>2 h</td>
<td>95 %</td>
<td>0 %</td>
<td>0 %</td>
</tr>
<tr>
<td>VPDMS</td>
<td>Ph$_2$SiH$_2$</td>
<td>0.1</td>
<td>23</td>
<td>0.5 h</td>
<td>$&gt;99%$</td>
<td>0 %</td>
<td>0 %</td>
</tr>
<tr>
<td>VPDMS</td>
<td>HMTS</td>
<td>0.5</td>
<td>55</td>
<td>2.5 h</td>
<td>0 %</td>
<td>31 %</td>
<td>-</td>
</tr>
</tbody>
</table>

$^a$Conditions: [Fe] 0.001 mmol, 1 M NaBEt$_3$H in toluene: 0.0025 mmol, THF-$d_8$: 0.4 mL, mesitylene as internal standard $^b$Yields were determined by integrating the $HSi$ resonance with respect to mesitylene in the $^1\text{H}$ NMR spectra.
$^c$Yields were determined by integrating the olefinic resonances with respect to mesitylene in the $^1\text{H}$ NMR spectra.

The complex FeBr$_2$(Ph$_2$PC$_6$H$_4$N$_{\text{Ph}}$py) is a precursor to an active catalyst for hydrosilylation and hydroboration of alkenes. Treatment of the dibromide complex with 2 equiv of NaBEt$_3$H in the presence of alkene and silane gave a dark brown solution. With 0.1 mol% catalyst loading in a 1-octene and Ph$_2$SiH$_2$ mixture, > 99% conversion to the anti-Markovnikov product, 1-diphenylsilyloctane, was observed after 30 mins. Catalytic hydroboration exhibited slightly slower rates using FeBr$_2$(Ph$_2$PC$_6$H$_4$N$_{\text{Ph}}$py)/2NaBEt$_3$H, giving 95% conversion to the anti-Markovnikov product after 2 h. Optimization of reaction conditions showed the best activity was obtained by diluting the reaction mixture to half the concentration using THF. Slower rates observed in neat reaction conditions is attributed to the modest solubility of the metal complex. Hydrosilylation of VPDMS is considered a useful model for the industrial curing of siloxane polymers.$^{2-3,12}$ When Ph$_2$SiH$_2$ was used as the hydrosilylating agent with 0.1 mol% catalyst loading, 98% conversion to the anti-Markovnikov product was observed after 30 mins. However, using
HMTS as the hydrosilylating agent did not afford any hydrosilylation products in room temperature. When the reaction was conducted under 55°C, the dehydrogenative silylation product (Me₃SiO)₂MeSiCHCHSiMe₂OSiMe₃ was observed in 31% yield after 2.5 h, with concomitant formation of equal quantity of EtSiMe₂OSiMe₃.

Though pure samples of Fe(Ph₂P(C₆H₄)NPhpy)(Ph₂SiH₂)₂ and Fe(Ph₂P(C₆H₄)NPhpy)(PPh₃)(Ph₂SiH₂) could not be obtained, the catalytic activity was qualitatively evaluated in the reaction 1-octene/Ph₂SiH₂. Both were found to be active as catalysts to selectively give the anti-Markovnikov hydrosilylation product. This suggested silane-bound complexes to be plausible catalytic intermediates.

6.5 Conclusions

A series of Fe-(PNpy) complexes were synthesized. The dicarbonyl complexes proved useful as models for analyzing the redox properties of PNpy. Currently known P-N-N platforms give rise to iron-dicarbonyl complexes with higher reduction potentials than N-N-N platforms. However, the first reduction of Fe(Ph₂P(C₆H₄)NPhpy)(CO)₂ is comparable to the electron deficient Fe(4-CF₃-DIP)(CO)₂ compound. Thus, our method of incorporating phosphines in the ligand does not sacrifice the low reduction potentials that are meant to promote redox non-innocence. Generally speaking, Ph₂P(C₆H₄)NPhpy has the smallest gaps between the different redox events compared to the complexes in Table 6.1, suggesting it to be especially facile in redox reactions. It is also unique that the second reduction to give fully reduced [Fe(0)(PNpy)²(CO)₂]²⁻ is so mild that it was observed within the redox window of THF.

The low valent silyl complexes of Fe-(PNpy) were either unstable or difficult to isolate. However, they were proven catalytically active and exhibited high selectivity to give exclusively anti-Markovnikov products, a feature similar to the FeBr₂(Ph₂P(C₆H₄)NPhpy)/2NaBEt₃H catalytic system. In addition, catalytic mixtures that were exposed to CO post-catalysis showed formation of Fe(Ph₂P(C₆H₄)NPhpy)(CO)₂ (see Section 6.7), suggesting the phosphine-imine-pyridine moiety to be intact in the catalytic cycle. Though it has been shown by other workers that reduction of metal complexes containing redox-active ligands occasionally results in a hydride or alkyl group transfer to the ligands,¹³ it is not the case for the reaction of FeBr₂(Ph₂P(C₆H₄)NPhpy)/NaBEt₃H.
Reaction of hydrosilanes with reduced iron complexes give \( \sigma \)-silane complexes or the oxidative addition product. The reactivity is highly reliant on the electronic properties of the ligand, with electron-withdrawing N-N-N platforms giving \( \sigma \)-silane complexes,\(^6\) and electron-donating P-N-P systems giving iron-hydrido-silyl oxidative addition products.\(^{14}\) The PNpy platform represents a case of intermediate electron-donating properties, and interaction of Ph\(_2\)SiH\(_2\) with the diphos complex Fe(P\(_{\text{Ph}}\)N\(_{\text{Ph}}\)py)(PPh\(_3\)) is ambiguous (Figure 6.4). Future efforts will be focused on detailed characterization of Fe(P\(_{\text{Ph}}\)N\(_{\text{Ph}}\)py)(HSiR\(_3\))\(_2\) and Fe(P\(_{\text{Ph}}\)N\(_{\text{Ph}}\)py)(PPh\(_3\))(HSiR\(_3\)), with emphasis on analysis of structure and electronic relationships with hydrosilylation activity.

### 6.6 Experimental

**Materials and Methods.** Unless otherwise indicated, reactions were conducted using standard Schlenk techniques under an N\(_2\) atmosphere at room temperature with stirring. Solvents were high-performance liquid chromatography grade, dried and deoxygenated on a Glass Contour System or MBraun solvent purification system, and stored over 4 Å molecular sieves. FeBr\(_2\)(Ph\(_2\)P\(_{\text{C6}}\)H\(_4\)N\(_{\text{Ph}}\)py) was prepared according to
procedures given in Chapter 4. Fe(bda)(CO)₃ was prepared according to literature procedure.¹⁵ NaBE₃H (1 M in toluene) was purchased from Sigma-Aldrich and used without further purification. PPh₃ was purchased from Strem and used without further purification. The following compounds were received from Sigma-Aldrich, deoxygenated and stored over 4 Å molecular sieves prior to use: styrene, 1-octene, mesitylene. The following compounds were received from Gelest, Inc., deoxygenated and stored over 4 Å molecular sieves prior to use: Ph₂SiH₂, VPDMS, HMTS. Research Purity CO was purchased from SJ Smith. ¹H and ³¹P{¹H} NMR spectra were acquired on Varian Unity Inova 500NB and Unity 500 NB instruments at 20 °C unless otherwise noted. ¹H NMR were referenced to residual solvent relative to tetramethylsilane, ³¹P{¹H} NMR spectra were referenced to an external 85% H₃PO₄ standard. Crystallographic data were collected using either a Siemens SMART diffractometer equipped with a Mo Kα source (λ = 0.71073 Å) and an Apex II detector, or a Bruker D8 Venture diffractometer equipped with a Mo Kα microfocus source and a Photon 100 detector. Fourier transform infrared spectra were recorded on a Perkin-Elmer 100 spectrometer.

Fe(Ph₂P(C₆H₄)NMe py)(CO)₂. A THF solution (ca. 10 mL) containing Fe(bda)(CO)₃ (22.6 mg, 0.089 mmol) was added P(Ph₂P(C₆H₄)NMe py) (30 mg, 0.078 mmol). The orange solution gradually turns dark brown as it was stirred in room temperature for 24 h. The solution was then dried under reduced pressure to obtain a dark brown oil. Purification was achieved by recrystallization from a concentrated pentane solution stored at −35 °C for 2 days. The recrystallization was repeated for a second time to obtain the target compound as dark brown crystals. Yield: 15 mg (38%). Single crystals suitable for X-ray diffraction were obtained by layering pentane over a concentrated Et₂O solution. ¹H NMR (500 MHz, CD₂Cl₂): δ 9.32 (dd, J = 6.4, 1.3 Hz, 1H), 7.59 (ddt, J = 8.2, 4.6, 0.7 Hz, 1H), 7.50–7.33 (m, 13H) 7.26 – 7.16 (m, 1H), 6.99 (ddd, J = 8.7, 6.5, 1.4 Hz, 1H), 6.57 (td, J = 6.5, 1.5 Hz, 1H), 2.37 (d, J = 2.2 Hz, 3H). ³¹P{¹H} NMR (CD₂Cl₂, 202.4 MHz): δ 74.9 (1P, s). IR(CH₂Cl₂): 1943, 1884 cm⁻¹.

Fe(Ph₂P(C₆H₄)NMe py)(CO)₂. A Et₂O suspension (ca. 30 mL) containing FeBr₂(PNPh py) (43 mg, 0.065 mmol) was purged with CO. A 1 M toluene solution of NaHBE₃ (130 µL, 0.13 mmol) was diluted with Et₂O (ca. 5 mL) and transferred via
cannula into the FeBr$_2$(PN$_{Ph}$py) suspension under positive CO pressure. The solution gradually darkens to give a green mixture. After stirring under CO for 16 h, the solution was filtered through a short plug of Celite and dried under reduced pressure. The resulting green powders were recrystallized by layering pentane over a concentrated Et$_2$O solution to obtain the target compound as dark green crystals. Yield: 28 mg (77%). Single crystals suitable for X-ray diffraction were also obtained this way. $^1$H NMR (500 MHz, CD$_2$Cl$_2$): $\delta$ 9.39 (dd, $J = 6.4$, 1.4 Hz, 1H), 7.54 (ddd, $J = 11.3$, 8.2, 1.5 Hz, 4H), 7.49 – 7.25 (m, 12H), 7.09 – 7.03 (m, 2H), 7.00 – 6.95 (m, 1H), 6.90 (ddd, $J = 8.5$, 6.5, 1.4 Hz, 1H), 6.65 – 6.52 (m, 2H). $^{31}$P NMR (202 MHz, CD$_2$Cl$_2$): $\delta$ 78.1 (s, 1P).

Reduction of FeBr$_2$(PN$_{Ph}$py) by 2 equiv NaBEt$_3$H in the presence of Ph$_2$SiH$_2$. A Et$_2$O (10 mL) suspension containing FeBr$_2$(PN$_{Ph}$py) (16 mg, 0.024 mmol) and 12 mg Ph$_2$SiH$_2$ (12 mg, 0.065 mmol) was cooled to –35 °C, followed by addition of a 1 M toluene solution of NaBEt$_3$H (50 mL, 0.050 mmol). A green solution immediately evolved. After stirring for 5 mins, the solution was filtered through a short plug of Celite, and the filtrate dried under reduced pressure to afford a sticky green residue. This residue was dissolved in a small amount of Et$_2$O and added pentane (20 mL) to obtain a dark green precipitate. The green precipitate was collected by filtration through a frit, dissolved in C$_6$D$_6$, and the NMR spectra were recorded.

Reduction of FeBr$_2$(PN$_{Ph}$py) by 2 equiv NaBEt$_3$H in the presence of PPh$_3$. A Et$_2$O (10 mL) suspension containing FeBr$_2$(PN$_{Ph}$py) (77 mg, 0.12 mmol) and PPh$_3$ (31 mg, 0.12 mmol) was cooled to –35 °C. To this stirring solution was added a 1M NaBEt$_3$H solution in toluene (235 mL, 0.24 mmol), and the green suspension immediately turned dark brown. This solution was kept at –35 °C for 24 h, then filtered through a short plug of Celite. After removal of Et$_2$O under reduced pressure, the brown solid was dissolved in C$_6$D$_6$ and NMR spectra of the crude material were recorded. $^1$H NMR (499 MHz, C$_6$D$_6$): $\delta$ 9.17 (d, $J = 6.5$ Hz, 1H), 7.94 – 7.79 (m, 2H), 7.49 (dd, $J = 8.4$, 6.9 Hz, 1H), 7.15 – 6.85 (m, 51H) 6.59 (m, 3H), 6.49 (dd, $J = 8.4$, 6.9 Hz, 1H). $^{31}$P{$^1$H} NMR (202 MHz, C$_6$D$_6$): $\delta$ 76.71 (d, $J = 27.4$ Hz, 1P), 72.22 (d, $J = 27.4$ Hz, 1P). The integration between 7.15 – 6.85 is larger than expected due to contamination from residual
toluene and benzene. A peak in $^1H$ NMR spectrum ($\delta 7.39$) and $^{31}P\{^1H\}$ NMR spectrum ($\delta -4.2$) were identified for free PPh$_3$.

**Reaction of CO with Fe($^{\text{Ph}_2\text{P}^\text{C}_6\text{H}_4\text{N}^\text{Ph}^\text{py}}\)(PPh$_3$).** A small amount of crude Fe($^{\text{Ph}_2\text{P}^\text{C}_6\text{H}_4\text{N}^\text{Ph}^\text{py}}\)(PPh$_3$) was dissolved in C$_6$D$_6$ in an NMR tube. The head space of the NMR tube was evacuated and refilled with CO (1 atm). After 10 mins, a $^{31}P\{^1H\}$ NMR spectrum was recorded. $^{31}P\{^1H\}$ NMR (202 MHz, C$_6$D$_6$): $\delta$ 82.18 (d, $J = 27.3$ Hz, Fe($^{\text{Ph}_2\text{P}^\text{C}_6\text{H}_4\text{N}^\text{Ph}^\text{py}}\)(PPh$_3$)(CO)), 79.64 (s, Fe($^{\text{Ph}_2\text{P}^\text{C}_6\text{H}_4\text{N}^\text{Ph}^\text{py}}\)(CO)$_2$), 71.63 (d, $J = 27.3$ Hz, Fe($^{\text{Ph}_2\text{P}^\text{C}_6\text{H}_4\text{N}^\text{Ph}^\text{py}}\)(PPh$_3$)(CO)), $-4.20$ (s, free PPh$_3$).

**Reaction of Ph$_2$SiH$_2$ with Fe($^{\text{Ph}_2\text{P}^\text{C}_6\text{H}_4\text{N}^\text{Ph}^\text{py}}\)(PPh$_3$).** A small amount of crude Fe($^{\text{Ph}_2\text{P}^\text{C}_6\text{H}_4\text{N}^\text{Ph}^\text{py}}\)(PPh$_3$) was dissolved in C$_6$D$_6$ in an NMR tube. Excess Ph$_2$SiH$_2$ was added to the solution, and a color change from brown to dark green was observed. The crude $^1H$ and $^{31}P\{^1H\}$ NMR spectra were recorded. The green complex, assigned Fe($^{\text{Ph}_2\text{P}^\text{C}_6\text{H}_4\text{N}^\text{Ph}^\text{py}}\)(PPh$_3$)(Ph$_2$SiH$_2$), was characterized by a high field resonance in the $^1H$ NMR spectrum ($\delta -12.64$, ddd, $J = 32.7$, 17.2, 4.5), and two broad resonances in the $^{31}P\{^1H\}$ NMR spectrum ($\delta 76.8$, 73.5). Repeated precipitation of Fe($^{\text{Ph}_2\text{P}^\text{C}_6\text{H}_4\text{N}^\text{Ph}^\text{py}}\)(PPh$_3$)(Ph$_2$SiH$_2$), though Ph$_2$SiH$_2$ and PPh$_3$ was still present.

**General procedure for hydrosilylation.** In a J-Young NMR tube was loaded 1 mmol of olefin, 1 mmol of silane or borane, 0.001 mmol of FeBr$_2$($^{\text{Ph}_2\text{P}^\text{C}_6\text{H}_4\text{N}^\text{Ph}^\text{py}}\)$, 0.4 mL of THF-$d_8$, and two drops of the mesitylene. The $^1H$ NMR spectrum was recorded on the resulting slurry (colorless solution) to establish the ratio of the mesitylene:reactants. This solution was then treated with a 1 M NaBEt$_3$H in toluene (2.5 $\mu$L, 2.5 mmol), immediately affording a dark brown solution. The NMR tube was vigorously shaken, and the catalytic reaction was monitored using $^1H$ NMR spectroscopy at specific time points.

**Detection of Fe-(Ph$_2$P$^\text{C}_6$H$_4$N$^\text{Ph}$py) species in the catalytic mixture.** In a schlenk tube was loaded FeBr$_2$(Ph$_2$P$^\text{C}_6$H$_4$N$^\text{Ph}$py) (17.8 mg, 0.027 mmol), 1-octene (12.2 mg, 0.11 mmol) and Ph$_2$SiH$_2$ (20 mg, 0.11 mmol). To this stirring mixture was added a 1 M toluene solution of NaBEt$_3$H (50 mL, 0.050 mmol) to give a dark green solution that quickly turnedbrown after ca. 0.5 mins. After stirring for 10 mins, the solution was purged with 1 atm
CO. After 3 mins stirring in CO, a green solution evolved. This mixture was then dissolved in pentane, and IR spectrum recorded.

6.7 Supporting information

Figure 6.5 $^{31}$P$[^{1}H]$ NMR spectrum recorded in C$_6$D$_6$ of a crude reaction mixture of FeBr$_2$(Ph$_2$P$^{6H4}$NPh$_2$py) with 2 equiv NaBEt$_3$H in the presence of Ph$_2$SiH$_2$.

Figure 6.6 $^1$H NMR spectrum of crude Fe(Ph$_2$P$^{6H4}$NPh$_2$py)(PPh$_3$) in C$_6$D$_6$. 
Figure 6.7 $^{31}$P{^1}H NMR spectrum of crude Fe$(\text{Ph}_2\text{P}^\text{C}_6\text{H}_4^\text{N}^\text{Ph}^\text{py})(\text{PPh}_3)$ in C$_6$D$_6$. The broad resonance between □ 0 to −5 is attributed to free PPh$_3$.

Figure 6.8 $^{31}$P{^1}H NMR spectrum recorded in C$_6$D$_6$ of reaction of Fe$(\text{Ph}_2\text{P}^\text{C}_6\text{H}_4^\text{N}^\text{Ph}^\text{py})(\text{PPh}_3)$ with 1 atm CO.
Figure 6.9 $^{31}$P$\{^1\text{H}\}$ NMR spectrum of Fe($\text{Ph}_2\text{P}^\text{C}_6\text{H}_4\text{N}^\text{Ph}\text{py})(\text{PPh}_3)(\text{Ph}_2\text{SiH}_2)$ in $\text{C}_6\text{D}_6$. Inset is the high field $^1\text{H}$ NMR spectrum $\text{C}_6\text{D}_6$.

Figure 6.10 IR spectrum of CO-exposed catalytic mixture recorded in pentane. Signal at 1889 cm$^{-1}$ is proposed to be the monocarbonyl species Fe($\text{Ph}_2\text{P}^\text{C}_6\text{H}_4\text{N}^\text{Ph}\text{py})(\text{CO})(\text{L})$, where L = solvent, 1-octene, or Ph$_2$SiH$_2$. 
6.8 References


(13) (a) Sugiyama, H.; Aharonian, G.; Gambarotta, S.; Yap, G. P. A.; Budzelaar, P. H. M. 
13168.


Chapter 7.

Complexes containing phosphine-amine-pyridine and phosphine-amide-pyridine ligands:
synthesis and reactivity of Fe-, Co-, and Ni-complexes

7.1 Introduction

Ever since the pioneering works of Noyori,\textsuperscript{1} incorporation of “NH” functionality into organometallic frameworks has become an important aspect of organometallic activation of small molecules and catalysis.\textsuperscript{2} Especially of interest to us are complexes containing metal-bound amine or amido functionalities due to their potential in metal-ligand cooperative reactions.\textsuperscript{3} In fact, homogeneous hydrogenation and transfer-hydrogenation catalysis of polar unsaturated bonds has been dominated by complexes of this type.\textsuperscript{4} Incorporation of chiral amines into metal complexes is an important method to promote catalytic asymmetric hydrogenation.\textsuperscript{4c,5} Complexes of the type RuCl(Ts-dpen)(\rho-cymene) (Ts = tosyl, dpen = H\textsubscript{2}NCHPhCHPhN\textsuperscript{−}) and MCp*Cl(Ts-dpen) (M = Ir, Ru) containing chiral ligands are widely used in industry for synthesis of herbicides and medicine.\textsuperscript{4c}

\begin{center}
\includegraphics[width=\textwidth]{chart71}
\end{center}

\textbf{Chart 7.1} Asymmetric transfer hydrogenation catalysts.

Reported catalytic TON and TOFs of homogenous base-metal catalyzed reactions have greatly enhanced in the past decade, with many examples of catalysts functioning through MLC of metal-nitrogen bonds. Iron(II) catalysts containing tetradentate P\textsubscript{2}N\textsubscript{2}-ligands developed by Morris and coworkers exhibit asymmetric transfer-hydrogenation of ketones with TONs up to 6000.\textsuperscript{5-6} These iron(II)-catalysts function by transfer addition of H\textsubscript{2} from isopropanol to an Fe-N. The cationic cobalt complex [Co(CH\textsubscript{2}SiMe\textsubscript{3})(PN\textsuperscript{HP})]\textsuperscript{+} (PN\textsuperscript{HP} = HN[(CH\textsubscript{2})\textsubscript{2}PR\textsubscript{2}]\textsubscript{2}) is active for hydrogenation of C=C, C=O and C=N bonds. The
participation of the NH functional group in PNHP at high temperatures was indicated by showing the relative inactivity of the aprotic derivative, [Co(CH₂SiMe₃)(PMeMe₃)]⁺ (PMeMe₃ = MeN[(CH₂)₂PR₂]₂).⁷ A diphosphineamidoiron(ii) complex FeH(PNP)CO (PNP = N[(CH₂)₂PR₂]₂) is an effective catalyst for hydrogenation of esters and acceptorless dehydrogenation of alcohols.⁸

![Chart 7.2 Metal-amino/amido catalysts that function through MLC mechanisms, with highlights on the cooperative moiety.](image)

The majority of reported MLC metal-amine/amido catalysts of base metals contain phosphine-amino or phosphine-amido functionality. Tridentate and tetradeionate ligand platforms that also incorporate pyridines are very rare, though iron complexes containing dearomatized PhP-bipy ligands have been reported.⁹ The phosphine-imine-pyridine ligands presented in Chapter 4 are expected to be reduced easily to form amide/amine ligands. Reduction of Ph₂P(C₂N)⁺Ph by addition of Na to form Na[Ph₂P(C₂N)⁺Ph] was demonstrated in Chapter 5. In this chapter, the derivatization of Ph₂P(C₆H₄)N⁺Ph by to reduced amide or amine ligands is presented. The resulting Ph₂P(C₆H₄)(amide)⁺Ph and Ph₂P(C₆H₄)NH⁺Ph ligands are expected to be less electron-donating compared to the diporphine ligands in Chart 7.1, and may exhibit different activity. The corresponding Fe-, Co-, and Ni-complexes were synthesized and their reactivity investigated with emphasis on MLC reactions.

### 7.2 Synthesis of reduced Ph₂P(C₆H₄)NH⁺Ph ligands

![Scheme 7.1 Synthesis of Ph₂P(C₆H₄)NH⁺Ph.](image)
The phosphine-imine-pyridine ligands can be easily reduced using hydride reagents. Addition of 1 equiv of NaBEt₃H to a toluene solution of Ph₂P⁺C₆H₄N⁺py afforded the amido salt Na[Ph₂P⁺C₆H₄(amide)⁺py] by hydride transfer to the electrophilic imine carbon. This salt was isolated as a yellow powder. The sodium salt was expected to be a racemic mixture of both (R)- and (S)-enantiomers. When exposed to moisture, Na[Ph₂P⁺C₆H₄(amide)⁺py] gradually loses color to give the white phosphine-amine-pyridine Ph₂P⁻C₆H₄NH⁻py. The amine compound was characterized by a doublet at δ 5.6 in the ¹H NMR collected in C₆D₆, attributed to the methyne proton (Figure 7.1), and a singlet at δ -18.8 in the ³¹P NMR spectrum. Protonation was achieved in high conversion when Na[Ph₂P⁺C₆H₄(amide)⁺py] was dissolved in MeOH, and Ph₂P⁻C₆H₄NH⁻py was isolated by recrystallization from concentrated MeOH solutions. As with the sodium salt, Ph₂P⁻C₆H₄NH⁻py exists as both (R)- and (S)-enantiomers. The amine NH was not located in the ¹H NMR.

**Figure 7.1** ¹H NMR spectrum of Ph₂P⁻C₆H₄NH⁻py in CDCl₃.

### 7.3 Synthesis of iron complexes of Ph₂P⁻C₆H₄NH⁻py and Ph₂P⁺C₆H₄(amide)⁺py

Addition of Ph₂P⁻C₆H₄NH⁻py to a THF solution of FeBr₂ gave FeBr₂(Ph₂P⁻C₆H₄NH⁻py) as a pale yellow solid precipitate. The ¹H NMR spectrum of FeBr₂(Ph₂P⁻C₆H₄NH⁻py) exhibited a pattern similar to FeBr₂(Ph₂P⁻C₆H₄NH⁻py) in the low field region (Figure 7.2). The most down field shifted resonance at δ 94.2 was very broad, in addition to two sharper resonances at δ 52.8 and 46.3, all of which were attributed to pyridine protons.
In a related reaction, the amido salt Na\[
\text{Ph}_2\text{P}^\equiv\text{C}_6\text{H}_4\text{(amide)}\text{Ph}_2\text{py}\] was treated with THF solutions of FeBr\(_2\) to initially give a brown solution. After stirring for 2 h, the solid was collected by filtration through a frit and dried under reduced pressure to give a dark solid residue. The \(^1\text{H} \text{NMR}\) spectrum recorded in THF-\(d_8\) showed broadened resonances between \(\delta\) 20 and 0. Extracting the solid into CH\(_2\)Cl\(_2\) gave a green solution and brown precipitate, suggesting the formation of multiple species. \(^1\text{H} \text{NMR}\) of the green species showed paramagnetically shifted resonances between \(\delta\) 74.2 and –47.8 (the spectroscopy of the brown species was not investigated). Though the identity of these compounds were not further investigated, it is proposed here that the reaction first gives a four-coordinate FeBr\(\text{Ph}_2\text{P}^\equiv\text{C}_6\text{H}_4\text{(amide)}\text{Ph}_2\text{py}\) complex that is highly unstable and could form [FeBr\(\text{Ph}_2\text{P}^\equiv\text{C}_6\text{H}_4(\mu-N)^\text{Ph}_2\text{py}\)]\(_2\) through bridging amido ligands (Figure 7.3).\(^{10}\) A possible reaction pathway is presented in the following equations:

\[
\text{FeBr}_2 + \text{Na}[\text{Ph}_2\text{P}^\equiv\text{C}_6\text{H}_4(\text{amide})^\text{Ph}_2\text{py}] \rightarrow \text{FeBr}(\text{Ph}_2\text{P}^\equiv\text{C}_6\text{H}_4(\text{amide})^\text{Ph}_2\text{py})
\]

\[
2 \text{FeBr}(\text{Ph}_2\text{P}^\equiv\text{C}_6\text{H}_4(\text{amide})^\text{Ph}_2\text{py}) \rightarrow [\text{FeBr}(\text{Ph}_2\text{P}^\equiv\text{C}_6\text{H}_4(\mu-N)^\text{Ph}_2\text{py})]_2
\]
To prevent the formation of undesirable amide-bridged complexes, CO was used as an auxiliary ligand. Hence, under 1 atm of CO, addition of Na[Ph₂P(C₆H₄)(amide)Ph]py] to FeBr₂ in THF gave a greenish-brown solution. The IR spectrum of the crude solution after stirring for 10 h showed 2 peaks with approximately equal intensity at 2028 and 1975 cm⁻¹, suggesting a cis-dicarbonyl species. Purification of the sample was achieved by evaporation of THF, and extraction into CH₂Cl₂ followed by precipitation using pentane. The ¹H NMR spectrum recorded in CD₂Cl₂ showed characteristic resonances at δ 9.01, assigned to the 6-pyridyl proton, and a broad resonance at δ 6.02 assigned to the methyne proton (Figure 7.4, top). These spectral characters point to a diamagnetic complex that can be formulated as FeBr(Ph₂P(C₆H₄)(amide)Ph)py)(CO)₂. Interestingly, the ³¹P NMR showed 2 resonances at δ 68.7 and 66.2 in ~1:6 ratio even after repeated recrystallization (Figure 7.4, bottom).

Figure 7.4 NMR spectra of FeBr(Ph₂P(C₆H₄)(amide)Ph)py)(CO)₂ in CD₂Cl₂. Top: ¹H NMR spectrum. Bottom: ³¹P NMR spectrum.
The persistence of these two unequal signals is tentatively attributed to conformational isomers arising from different arrangements of the cis-carbonyl and bromide ligands (Figure 7.5). It is noted here that though \((R)\)- and \((S)\)-enantiomers are both expected to be present in solution, they are not distinguishable by NMR spectroscopy. Apparently, these two species were not distinguishable by IR spectroscopy, exhibiting only two signals at 2034 and 1980 cm\(^{-1}\) (Figure 7.6).

![Figure 7.5 Possible isomers of FeBr\((\text{Ph}_2\text{P}C_6\text{H}_4\text{amide})\text{Phpy})(\text{CO})_2\).](image)

![Figure 7.6 IR spectrum of FeBr\((\text{Ph}_2\text{P}C_6\text{H}_4\text{amide})\text{Phpy})(\text{CO})_2\).](image)

With the aim of obtaining a coordinatively unsaturated compound, FeBr\((\text{Ph}_2\text{P}C_6\text{H}_4\text{amide})\text{Phpy})(\text{CO})_2\) was further treated with NaBAr\(^{+}\text{F}_4\) to remove the bromido ligand. When conducted in CH\(_2\)Cl\(_2\), this reaction initially gave a purple solution. The IR spectrum exhibited two signals at 2141 and 1991 cm\(^{-1}\), giving a shift of \(\Delta\nu_{\text{CO(avg)}}\) 59 cm\(^{-1}\).
$^{31}$P NMR spectrum indicated a single new species at $\delta$ 73.6, and the $^1$H NMR spectrum also indicated a single species. This purple complex is proposed to be the five-coordinate complex salt [Fe($^\text{Ph}_2$P$_{\text{C6H4}}$(amide)$^\text{Ph}$py)(CO)$_2$]BAr$_4^+$.

Similar to FeBr($^\text{Ph}_2$P$_{\text{C6H4}}$(amide)$^\text{Ph}$py), the coordinatively unsaturated iron(II) amido [Fe($^\text{Ph}_2$P$_{\text{C6H4}}$(amide)$^\text{Ph}$py)(CO)$_2$]BAr$_4^+$ was unstable in CH$_2$Cl$_2$. After merely 4 h of stirring in room temperature, a new species was observed in the IR spectrum at 2067 and 2025 cm$^{-1}$. The $^1$H NMR exhibited several new signals, and the $^{31}$P NMR showed a new resonance at $\delta$ 78.2 that grew in intensity when the reaction was monitored over the course of 16 h. When excess NaBAr$_4^+$ was used (2 to 5 equiv), the decomposition rate significantly decreased, and the IR and NMR spectra remained unchanged after 16 h in CH$_2$Cl$_2$ (Figure 7.7). This decomposition reaction is attributed to dimerization of [Fe($^\text{Ph}_2$P$_{\text{C6H4}}$(amide)$^\text{Ph}$py)(CO)$_2$]$^+$, a process that may be inhibited by the presence of the Lewis-acidic Na$^+$ ions that stabilizes the complex from dimerization by coordinating to the amide.

![1H NMR spectrum of [Fe($^\text{Ph}_2$P$_{\text{C6H4}}$(amide)$^\text{Ph}$py)(CO)$_2$]BAr$_4^+$ in CD$_2$Cl$_2$ the presence of excess NaBAr$_4^+$.](image)

The coordinatively unsaturated iron(II) amido [Fe($^\text{Ph}_2$P$_{\text{C6H4}}$(amide)$^\text{Ph}$py)(CO)$_2$]$^+$ represents a platform for possible metal-ligand cooperative activation of small molecules.$^{8b,8c,11}$ When a purple CD$_2$Cl$_2$ solution of [Fe($^\text{Ph}_2$P$_{\text{C6H4}}$(amide)$^\text{Ph}$py)(CO)$_2$]BAr$_4^+$ was exposed to 1 atm H$_2$, new high-field resonances were immediately observed at $\delta$ −4.77 and −5.2, suggesting the formation of iron-hydrido species. The $^{31}$P NMR spectrum recorded at this point showed new resonances at $\delta$ 64.3, 61.4 in addition to the signal of the decomposition product of [Fe($^\text{Ph}_2$P$_{\text{C6H4}}$(amide)$^\text{Ph}$py)(CO)$_2$]BAr$_4^+$ at $\delta$ 78.2. Selective
$^{31}$P nuclei decoupling experiments confirmed that the doublets observed in the high-field $^1$H NMR spectrum arise from coupling with the new species observed in the $^{31}$P NMR spectrum (Figure 7.8). Allowing this mixture to sit in room temperature for 16 h gives multiple new iron-hydrido species at $\delta$ −3.29, −14.6, −14.8, −15.5 (see Section 7.9). The total conversion to the hydrido complexes were ~50%, and significant amount of starting material was still present. Though the identities of the iron-hydrido complexes were not further investigated, it is proposed here the heterolytic cleavage of H$_2$ by the iron-amido functionality to give aminoiron(II) hydrides by the following equation:

$$[\text{Fe}^{(\text{Ph}_2\text{P}C_6\text{H}_4(\text{amide})\text{Ph}_2}\text{py})\text{CO})_2\text{BAr}_4^+] + \text{H-H} \rightarrow [\text{FeH}^{(\text{Ph}_2\text{P}C_6\text{H}_4\text{NH})\text{Ph}_2}\text{py})(\text{CO})_2\text{BAr}_4^+]$$

(7.3)

Given the complexity of the reaction of $[\text{Fe}^{(\text{Ph}_2\text{P}C_6\text{H}_4(\text{amide})\text{Ph}_2}\text{py})(\text{CO})_2\text{BAr}_4^+]$ with H$_2$, alternative methods were sought to derivatize FeBr$^{(\text{Ph}_2\text{P}C_6\text{H}_4(\text{amide})\text{Ph}_2}\text{py})(\text{CO})_2}$ to hydrido complexes. Reaction of 1 equiv NaBEt$_3$H with FeBr$^{(\text{Ph}_2\text{P}C_6\text{H}_4(\text{amide})\text{Ph}_2}\text{py})(\text{CO})_2}$ gave a new species that exhibited paramagnetically shifted resonances in the $^1$H NMR spectrum. The IR spectrum indicates the preservance of both CO ligands, though the signals were shifted to 1953, 1884 cm$^{-1}$. The significant shift of v$_{CO}$ to lower energy compared to the starting material is indicative of reduction from Fe(II)$\rightarrow$Fe(I), and the new complex was proposed to be Fe$^{(\text{Ph}_2\text{P}C_6\text{H}_4(\text{amide})\text{Ph}_2}\text{py})(\text{CO})_2}$, afforded via the following reactions:

Figure 7.8 $^1$H NMR spectra of reaction of $[\text{Fe}^{(\text{Ph}_2\text{P}C_6\text{H}_4(\text{amide})\text{Ph}_2}\text{py})(\text{CO})_2\text{BAr}_4^+]$ with H$_2$ in CD$_2$Cl$_2$. Red trace: $^1$H NMR spectrum. Green trace: $^1$H{$^{31}$P} NMR spectrum selectively decoupled at $\delta$ 61.4. Blue trace: $^1$H{$^{31}$P} NMR spectrum selectively decoupled at $\delta$ 64.3.
FeBr\(_{(\text{Ph}_2\text{P} \text{C}_6\text{H}_4 \text{amide})\text{Ph}_\text{py}}\)(CO)\(_2\) + NaBEt\(_3\) \rightarrow \text{FeH}_{(\text{Ph}_2\text{P} \text{C}_6\text{H}_4 \text{amide})\text{Ph}_\text{py}}\)(CO)\(_2\) + NaBr + BEt\(_3\) \hspace{1cm} (7.4)

2FeH\(_{(\text{Ph}_2\text{P} \text{C}_6\text{H}_4 \text{amide})\text{Ph}_\text{py}}\)(CO)\(_2\) \rightarrow 2\text{Fe}_{(\text{Ph}_2\text{P} \text{C}_6\text{H}_4 \text{amide})\text{Ph}_\text{py}}\)(CO)\(_2\) + H\(_2\) \hspace{1cm} (7.5)

Given the instability exhibited by the related complexes, the coordinatively unsaturated Fe\(_{(\text{Ph}_2\text{P} \text{C}_6\text{H}_4 \text{amide})\text{Ph}_\text{py}}\)(CO)\(_2\) may possibly be dimeric in nature, ie. [Fe(CO)\(_2\)(\text{Ph}_2\text{P} \text{C}_6\text{H}_4(\text{N} \text{Ph}_\text{py})\)]\(_2\).

![Figure 7.9 NMR spectra of [FeBr(\text{Ph}_2\text{P} \text{C}_6\text{H}_4 \text{amide})\text{Ph}_\text{py})(\text{CO})(\text{PMe}_3)_2]Br in CD\(_2\)Cl\(_2\). Top: \(^1\text{H}\) NMR spectrum. Bottom: \(^{31}\text{P}\) NMR spectrum. Bottom: \(^{31}\text{P}\) NMR spectrum.]

The bromido ligand can also be removed by addition of phosphines. When a CH\(_2\)Cl\(_2\) solution of FeBr\(_{(\text{Ph}_2\text{P} \text{C}_6\text{H}_4 \text{amide})\text{Ph}_\text{py}}\)(CO)\(_2\) was added excess PMe\(_3\), the originally
greenish-brown solution gradually changes to a dark yellow solution. The IR spectrum of the crude mixture showed a signal at 1935 cm\(^{-1}\), suggesting a mono-carbonyl species. After preliminary workup of the reaction mixture, an orange powder was obtained. The \(^{31}\)P NMR spectrum of this orange complex pointed to a tris-phosphine species. A broad singlet at \(\delta \) 63.5 was assigned to \(P\)-amide-py, and the remaining two doublets at \(\delta \) 17.0 were 7.61 were attributed to the PMe\(_3\) ligands. Given the large coupling constant between the PMe\(_3\) resonances (\(J_{P,P} = 164\) Hz) and unresolved small coupling of the respective PMe\(_3\) with \(P\)-amide-py, the PMe\(_3\) ligands were assumed to be mutually trans. The PMe\(_3\) ligands were also identified in the \(^1\)H NMR spectrum as broad resonances at \(\delta \) 0.73 and 0.45 (Figure 7.9). The new complex was formulated as the cationic [Fe(Ph\(_2\)P\(_{C6H4}\)(amide)\(_{Ph}\)py)(CO)(PMe\(_3\))\(_2\)]Br according to spectral evidence, with the structure proposed in Scheme 7.2.

![Figure 7.10](image)

**Figure 7.10** IR spectra of [Fe(Ph\(_2\)P\(_{C6H4}\)(amide)\(_{Ph}\)py)(CO)(PMe\(_3\))\(_2\)]\(^+\) in CH\(_2\)Cl\(_2\) solution. Black trace: [Fe(Ph\(_2\)P\(_{C6H4}\)(amide)\(_{Ph}\)py)(CO)(PMe\(_3\))\(_2\)]Br. Red trace: [Fe(Ph\(_2\)P\(_{C6H4}\)(amide)\(_{Ph}\)py)(CO)(PMe\(_3\))\(_2\)]BAr\(_F^4\).

One explanation for the broadness of the \(^1\)H NMR spectral signals is weak association of the outer-sphere Br\(^-\) ligand with the metal center. Removal of this bromide was achieved via ion exchange with NaBAr\(_F^4\). Though only small shifts were observed for the IR (\(v_{CO} 1936\) cm\(^{-1}\) compared to 1935 cm\(^{-1}\) for [Fe(Ph\(_2\)P\(_{C6H4}\)(amide)\(_{Ph}\)py)(CO)(PMe\(_3\))\(_2\)]Br) (Figure 7.10) and \(^{31}\)P NMR spectral signals, the PMe\(_3\) resonances in the \(^1\)H NMR spectrum
sharpened compared to the bromide salt and manifested as two doublets at δ 0.73, 0.48 (see Section 7.9). A summary of the reactions of iron-(P-amido-py) complexes is given in Scheme 7.2.

Scheme 7.2  Reactions of iron complexes containing reduced $\text{Ph}_2\text{P}\text{C}_6\text{H}_4\text{NH}^\text{Ph}\text{py}$.

### 7.4 Synthesis of cobalt complexes containing $\text{Ph}_2\text{P}\text{C}_6\text{H}_4\text{NH}^\text{Ph}\text{py}$ and $\text{Ph}_2\text{P}\text{C}_6\text{H}_4(\text{amide})^\text{Ph}\text{py}$

The complex CoCl$_2(\text{Ph}_2\text{P}\text{C}_6\text{H}_4\text{NH}^\text{Ph}\text{py})$ was prepared in a straightforward manner by addition of $\text{Ph}_2\text{P}\text{C}_6\text{H}_4\text{NH}^\text{Ph}\text{py}$ to a THF solution of CoCl$_2$. This lavender complex precipitated from the THF mixture after 5 mins of stirring and was isolated by filtration. The CD$_2$Cl$_2$-soluble CoCl$_2(\text{Ph}_2\text{P}\text{C}_6\text{H}_4\text{NH}^\text{Ph}\text{py})$ gave a paramagnetic $^1\text{H}$ NMR spectrum (Figure 7.11) that bears high resemblance to CoCl$_2$(PNpy) complexes (see Section 4.3).
Synthesis of the related amido complex was attempted. Addition of Na[Ph₂P(C₆H₄)(amide)Phpy] to a THF solution of CoCl₂ afforded a dark mixture. Filtration to remove NaCl and evaporation of solvent under reduced pressure gave a purplish-brown solid. The ¹H NMR spectrum recorded in C₆D₆ exhibited paramagnetically shifted resonances between δ 20 and −5. Though further spectroscopic data was not obtained, it was assumed the chlorido complex CoCl(Ph₂P(C₆H₄)(amide)Phpy) was formed from this reaction. Surprisingly, this same complex was crystallized from the reaction mixture of CoCl₂/(Ph₂P(C₆H₄)NPhpy)/2MeLi. A possible route to formation of CoCl(Ph₂P(C₆H₄)(amide)Phpy) is presented in Scheme 7.3. When CoCl₂(Ph₂P(C₆H₄)NPhpy) was treated with 1 equiv MeLi, a putative “CoCl(Ph₂P(C₆H₄)NPhpy)” can be formed via loss of a methyl-radical. This mono-reduced was expected to possess significant radical ligand character, similar to the mono-reduced CoR(Ph₂P(C₆H₄)NPhpy)(PPh₃) complexes (R = H, Me) (see Section 5.4), and may abstract a hydrogen atom to give the final CoCl(Ph₂P(C₆H₄)(amide)Phpy). The ¹H NMR spectra of single crystals of CoCl(Ph₂P(C₆H₄)NPhpy) in C₆D₆ showed matching resonances with the solid obtained from the CoCl₂/Na[Ph₂P(C₆H₄)(amide)Phpy] reaction, supporting formation of the same species from two different routes.

![Figure 7.11 ¹H NMR spectrum CoCl₂(Ph₂P(C₆H₄)NPhpy) in CD₂Cl₂.](image-url)
The solid-state structure of \( \text{CoCl}(\text{Ph}_2\text{PCH}_4\text{H}(\text{amide})\text{Ph}_2\text{py}) \) was determined by X-ray crystallography (Figure 7.12). The unit cell contained both (\( R \))- and (\( S \))-enantiomers. In contrast to the imine derivatives, \( \text{Ph}_2\text{PCH}_4\text{H}(\text{amide})\text{Ph}_2\text{py} \) coordinates in a near-planar fashion, with the average \( \text{P} - \text{Co} - \text{N}_{\text{py}} \) being 170.3° and \( \text{Cl} - \text{Co} - \text{N}_{\text{amide}} \) 178.4. The average distance of \( \text{Co} - \text{N}_{\text{amide}} \) 1.832 Å is significantly shortened compared to the unreduced imine derivative \( \text{Co} - \text{N}_{\text{imine}} \) distance (2.255(2) Å), reflecting the more electrostatic nature of cobalt-amide bond. The \( (\text{N}_{\text{amide}} - \text{C}_{\text{picolyl}})_{\text{avg}} \) of 1.466 Å is characteristic of a nitrogen-carbon single bond.

Scheme 7.3 Formation of \( \text{CoCl}(\text{Ph}_2\text{PCH}_4\text{H}(\text{amide})\text{Ph}_2\text{py}) \) via two different routes.
A similar reduction at the ligand was observed in the reaction of CoCl$_2$(Ph$_2$P$_{C6H_4}(amide)$)$_{Phpy}$ with 2 equiv NaBEt$_3$H under 1 atm of CO. The $^{31}$P NMR spectrum exhibited a singlet at $\delta$ 69.1, suggesting reduction by 1e$^-$ to form a diamagnetic species. The $^1$H NMR spectrum showed a broad multiplet at $\delta$ 5.38, which is characteristic for a methyne proton in these systems (see $^1$H NMR spectra for Ph$_2$P$_{C6H_4}NH_{Phpy}$). No resonances were observed in the high field region. IR spectrscopy revealed a monocarbonyl species, exhibiting a signal at 1909 cm$^{-1}$ for $\nu$CO in Et$_2$O solution (Figure 7.13). These spectral characteristics point to the cobalt-amido-carbonyl complex Co(Ph$_2$P$_{C6H_4}(amide)$)$_{Phpy}$(CO) (Eq. 7.6). This result contrasts to conducting the reaction of CoCl$_2$(Ph$_2$P$_{C6H_4}N_{Phpy}$) with 2 equiv NaBEt$_3$H in the presence of PPh$_3$, which gave the cobalt-hydrido-triphenyl phosphine complex with the Ph$_2$P$_{C6H_4}N_{Phpy}$ ligand intact (see Section 5.3). Ligand participation in reduction reactions of metal complexes containing redox-active ligands have been investigated for several DIP complexes.$^{12}$ Hydride migration from metal center to the redox-active ligand was also described for a bis(arylimidazol-2-ylidene)pyridine cobalt complex.$^{13}$ The implication of different auxiliary ligands affecting the fate of H$^-$ in reduction of redox-active ligand containing complexes is significant for catalytic systems.

Figure 7.12  Solid state representation (50 % thermal ellipsoids) of CoCl(Ph$_2$P$_{C6H_4}(amide)$)$_{Phpy}$. Only the (S)-enantiomer is shown.
generated in-situ using hydride reagents as the reductant.\textsuperscript{14} Thus, caution must be excercised when proposing the structure for active metal species in these catalytic reactions when different substrates are present.

\begin{align*}
\text{Ph}_2\text{P} &\text{C}_6\text{H}_4\text{NHPh} \\
\text{N} &\text{Co} &\text{Cl} \\
\text{Ph}_2 &\text{Cl}
\end{align*}

Thus, caution must be excercised when proposing the structure for active metal species in these catalytic reactions when different substrates are present.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure7.14}
\caption{IR spectrum of Co(\text{Ph}_2\text{P}^\text{C}_6\text{H}_4\text{NHPh})(\text{py})(\text{CO}) in Et_2O solution.}
\end{figure}

\subsection*{7.5 Synthesis of nickel complexes containing Ph\text{P}^\text{C}_6\text{H}_4\text{NHPh}py}

Synthesis of nickel complexes containing the Ph\text{P}^\text{C}_6\text{H}_4\text{NHPh}py ligand was initiated by reaction of the amine with a nickel-halide source. Addition of Ph\text{P}^\text{C}_6\text{H}_4\text{NHPh}py to a purple solution of NiBr\textsubscript{2}(dme) immediately gave a dark yellow solution, from which an orange solid precipitated formed after a few minutes. The \textsuperscript{1}H NMR spectrum of this solid in CD\textsubscript{2}Cl\textsubscript{2} solution showed slightly broadened resonances between \( \delta \) 11.3 and 6.11 at 20 \degree C. Interestingly, a broad NMR signal could be detected for the \textsuperscript{31}P nuclei at \( \delta \) 39.4 in 20 \degree C (Figure 7.14). The new complex was deduced to be NiBr\textsubscript{2}Ph\text{P}^\text{C}_6\text{H}_4\text{NHPh}py.
Removal of one of the bromide ligands of $\text{NiBr}_2(\text{Ph}_2\text{P}_2\text{C}_6\text{H}_4\text{NH}_\text{Ph}_\text{py})$ was achieved by ion exchange with NaBAr$_4^F$. This salt $[\text{NiBr}(\text{Ph}_2\text{P}_2\text{C}_6\text{H}_4\text{NH}_\text{Ph}_\text{py})](\text{BAr}_4^F)$ was characterized by $^1\text{H}$, $^{31}\text{P}$ NMR spectroscopy and X-ray diffraction (Figures 7.15 and 7.16). This four-coordinate complex is square planar, giving a diamagnetic ground state and is indicated by sharp signals in the NMR spectra. The methyne proton was located at $\delta 5.85$ as a doublet in the $^1\text{H}$ NMR. Decoupling of the $^{31}\text{P}$ nuclei revealed a long-range coupling between the methyne proton and the phosphine ($J^P_{\text{P-H}} = 2.5$). Single crystals of $[\text{NiBr}(\text{Ph}_2\text{P}_2\text{C}_6\text{H}_4\text{NH}_\text{Ph}_\text{py})](\text{BAr}_4^F)$ contained both the ($R$)- and ($S$)-enantiomers in the unit cell. For the sake of discussion, bond lengths cited here are of the ($R$)-enantiomer. N(1) – C(19) exhibited a long distance of 1.503(5) Å, indicative of a N-C single bond. The amine proton was located in the electron density map and allowed to refine, giving N(1) – H(1)A of...
Nickel-coordinated amines exhibit a wide range of N-H distances between 0.830 and 0.930 Å. Compared to the cobalt-amide analogue, Ni – Namine distance was drastically elongated by ca. 0.45 Å, consistent with coordination of a neutral amine vs. anionic amide. The planarity exhibited by the Ph²Pc₆H₄NHPhpy ligand contrasts the coordination geometry of the unreduced Ph²Pc₆H₄NPhpy.

Figure 7.15 ¹H NMR spectrum of [NiBr(Ph²Pc₆H₄NHPhpy)]BArF₄ in CD₂Cl₂.

Figure 7.16 Solid state representation (50 % thermal ellipsoids) of [NiBr(Ph²Pc₆H₄NHPhpy)](BArF₄). Selected hydrogen atoms, solvent, and anion removed for clarity. Only the (R)-isomer is shown.
7.6 Catalytic studies

The reactivity of \([\text{Fe(Ph}_2\text{P}_C\text{H}_4\text{(amide)}\text{Ph})\text{py}(\text{CO})_2]\)\(\text{BArF}_4\) with \(\text{H}_2\) encouraged the investigation of catalytic hydrogenation. However, catalytic turnover was not observed for hydrogenation of styrene or benzaldehyde when up to 4 atm \(\text{H}_2\) was used at 60 °C.

Hydrosilylation catalyzed by \(\text{CoCl}_2(\text{Ph}_2\text{P}_C\text{H}_4\text{NH})\text{Ph})/2\text{NaBEt}_3\text{H}\) was tested using 1-octene/\(\text{Ph}_2\text{SiH}_2\). No reactivity was observed when this reaction was conducted at 23 °C using 1 mol% loading. When the reaction temperature was elevated to 55 °C, a complicated mixture containing vinyl-silane, allyl-silane, 2-octene, octane and 1-silyloctane was obtained (yields cannot be determined by \(^1\text{H}\) NMR spectroscopy due to overlapping peaks of the products). Though this catalyst system is closely related to phosphine-imine-pyridine catalyst \(\text{CoCl}_2(\text{Ph}_2\text{P}_C\text{H}_4\text{NH})\text{Ph})/2\text{NaBEt}_3\text{H}\) (see Section 5.6), starkly different selectivity and activity was observed.

Hydrosilylation promoted by \([\text{NiBr(Ph}_2\text{P}_C\text{H}_4\text{NH})\text{Ph})\]\(\text{BArF}_4\) was first tested using the model reaction 1-octene and \(\text{Ph}_2\text{SiH}_2\). Though no reaction was seen when \([\text{NiBr(Ph}_2\text{P}_C\text{H}_4\text{NH})\text{Ph})\]\(\text{BArF}_4\) was used directly as the catalyst at 23 °C, 11 % conversion of the anti-Markovnikov hydrosilylation product (\(\text{a}\)) was observed after heating at 55 °C for 16 h. Notably, 1-octene was completely consumed to give 88 % 2-octene. To increase activity for hydrosilylation, \(\text{NaBEt}_3\text{H}\) was used as an activator. Using \([\text{NiBr(Ph}_2\text{P}_C\text{H}_4\text{NH})\text{Ph})\]\(\text{BArF}_4\)/\(\text{NaBEt}_3\text{H}\) as catalyst at 23 °C, product \(\text{a}\) was observed as the sole product in 93 % yield after 3 h, and eventually reached 99 % yield after 6 h. Encouraged by the high selectivity of this catalytic system, hydrosilylation of VPDMS using HMTS was tested. No reaction was observed at 23 °C, but 22 % yield of the dehydrogenative silylation product (\(\text{b}\)) was afforded when the reaction was conducted under 85 °C. These results are summarized in Table 7.1.
The stoichiometric reaction of NaBEt$_3$H with [NiBr($^\text{Ph}_2$P$_{\text{C}_6\text{H}_4}$NH$_{\text{Ph}}$py)]BAr$_4$ was investigated to gain insight into the mechanism of nickel-catalyzed hydrosilylation.

Several high-field resonances were observed in the $^1$H NMR spectrum immediately after addition of 1 equiv NaBEt$_3$H to a CD$_2$Cl$_2$ solution of [NiBr($^\text{Ph}_2$P$_{\text{C}_6\text{H}_4}$NH$_{\text{Ph}}$py)]BAr$_4$ (Figure 7.17). The importance of a hydride activator for catalysis points to nickel-hydrido species being the active catalyst. Activation by addition of NaBEt$_3$H is proposed to follow eq. 7.7:

$$
\text{[NiBr($^\text{Ph}_2$P$_{\text{C}_6\text{H}_4}$NH$_{\text{Ph}}$py)]BAr}_4 + \text{NaBEt}_3\text{H} \rightarrow \text{[NiH($^\text{Ph}_2$P$_{\text{C}_6\text{H}_4}$NH$_{\text{Ph}}$py)]BAr}_4 + \text{NaBr + “BEt}_3”}
$$

(7.7)

In the cases of hydrosilylation in the absence of an activator, activation of pre-catalyst [NiBr($^\text{Ph}_2$P$_{\text{C}_6\text{H}_4}$NH$_{\text{Ph}}$py)]BAr$_4$ may follow eq. 7.8:

$$
\text{[NiBr($^\text{Ph}_2$P$_{\text{C}_6\text{H}_4}$NH$_{\text{Ph}}$py)]BAr}_4 + \text{HSiR}_3 \rightarrow \text{[NiH($^\text{Ph}_2$P$_{\text{C}_6\text{H}_4}$NH$_{\text{Ph}}$py)]BAr}_4 + R’_3\text{SiBr}
$$

(7.8)

A similar activation pathway has been described by Tilley et al. for nickel hydrosilylation catalysts containing diphosphineamine pincer ligands.$^{16}$ In our system, this reaction

---

**Table 7.1** Hydrosilylation using [NiBr($^\text{Ph}_2$P$_{\text{C}_6\text{H}_4}$NH$_{\text{Ph}}$py)]BAr$_4$.$^a$

<table>
<thead>
<tr>
<th>activator (mol%)</th>
<th>alkene/silane</th>
<th>temperature</th>
<th>time</th>
<th>a$^b$</th>
<th>b$^b$</th>
<th>c$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1-octene/Ph$_2$SiH$_2$</td>
<td>23 °C</td>
<td>2 h</td>
<td>0 %</td>
<td>0 %</td>
<td>0 %</td>
</tr>
<tr>
<td>-</td>
<td>1-octene/Ph$_2$SiH$_2$</td>
<td>55 °C</td>
<td>16 h</td>
<td>11 %</td>
<td>0 %</td>
<td>88%</td>
</tr>
<tr>
<td>NaBEt$_3$H (2)</td>
<td>1-octene/Ph$_2$SiH$_2$</td>
<td>23 °C</td>
<td>3 h</td>
<td>93 %</td>
<td>0 %</td>
<td>0 %</td>
</tr>
<tr>
<td>NaBEt$_3$H (2)</td>
<td>1-octene/Ph$_2$SiH$_2$</td>
<td>23 °C</td>
<td>6 h</td>
<td>&gt; 99 %</td>
<td>0 %</td>
<td>0 %</td>
</tr>
<tr>
<td>NaBEt$_3$H (2)</td>
<td>VPMDS/HMTS</td>
<td>23 °C</td>
<td>3 h</td>
<td>0 %</td>
<td>0 %</td>
<td>0 %</td>
</tr>
<tr>
<td>NaBEt$_3$H (2)</td>
<td>VPMDS/HMTS</td>
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<td>3 h</td>
<td>0 %</td>
<td>22 %</td>
<td>0 %</td>
</tr>
</tbody>
</table>

$^a$Conditions: [Ni] 0.004 mmol, alkene: 0.20 mmol, silane: 0.24 mmol, activator: 0.016 mmol, mesitylene: 0.066 mmol (as internal standard). $^b$Yields were determined by dissolving aliquots of the catalytic mixture in CDCl$_3$ and integrating the HSi resonance with respect to mesitylene in the $^1$H NMR spectra. $^c$Yields were determined by integrating the olefinic resonances with respect to mesitylene in the $^1$H NMR spectra.
requires high temperatures where 1-octene isomerization by nickel-hydrido complexes is facile. This is similar to the 1-octene isomerization reactions observed for cobalt-hydrido complexes described in Chapter 5.

![Image of NMR spectra](image)

**Figure 7.17** $^1$H NMR spectra (high-field region) of reaction of 1 equiv NaBEt$_3$H with [NiBr(Ph$_2$P$_{C_6H_4}$NH$_{Ph}$py)]BAR$_4$ in CD$_2$Cl$_2$.

### 7.7 Conclusions

The new ligands [Ph$_2$P$_{C_6H_4}$(amide)$_{Ph}$py] and its protonated form, Ph$_2$P$_{C_6H_4}$NH$_{Ph}$py, can be readily prepared by reduction of the corresponding imine Ph$_2$P$_{C_6H_4}$N$_{Ph}$py using a hydride reagent. These ligands offer different reactivity compared the unreduced imine counterpart. Anionic [Ph$_2$P$_{C_6H_4}$(amide)$_{Ph}$py]$^-$ contains a highly basic amido moiety that tends to react with multiple metal centers and form multinuclear species.

Though iron(II)-amido functionality has been successfully implemented in a number of catalytic systems, but the development of our system containing phoshine-amide-pyridine ligands are still at a preliminary stage. The absence of catalytic turnover for [Fe(Ph$_2$P$_{C_6H_4}$(amide)$_{Ph}$py)(CO)$_2$]BAR$_4$ catalyzed benzaldehyde hydrogenation could be attributed to one of the following reasons:

a. Insufficient nucleophilicity of iron-hydride or electrophilicity of the amine proton for H$_2$ transfer via an outer-sphere mechanism.

b. The coordinately saturated metal center prevents an inner-sphere mechanism for hydrogenation.

In Scheme 7.4, possible cycles for outer-sphere and inner-sphere mechanisms are proposed. Alternative proton-assisted hydrogenation mechanisms have also been described.$^{3a}$ In
addition, the unsaturated $[\text{Fe}^{\text{Ph}^2\text{p}^{\text{C}6\text{H}4}(\text{amide})^{\text{Ph}^3}\text{py}}](\text{CO})_2]^{\text{BAr}^4}$ also represents a possible platform for catalytic alcohol dehydrogenation.\textsuperscript{7b,8a,8b,17}

The isolation of the cobalt-amido complex $\text{Co}^{\text{II}}(\text{Ph}^2\text{p}^{\text{C}6\text{H}4}(\text{amine})^{\text{Ph}^3}\text{py})(\text{CO})$ demonstrates the vulnerability of imine carbons to undergo nucleophilic attack. It is likely that reduction of $\text{Co}(\text{II}) \rightarrow \text{Co}(\text{I})$ is promoted by coordination of the $\pi$-acidic CO, whereas $\sigma$-donating phosphines support the $\text{Co}(\text{II})$-(PNpy) electronic structure proposed for $\text{CoH}(\text{PNpy})(\text{PPh}_3)$ in Section 5.4. The sluggish activity of $\text{CoCl}_2(\text{Ph}^2\text{p}^{\text{C}6\text{H}4}\text{NHPh}^{\text{Ph}^3}\text{py})/2\text{NaBEt}_3\text{H}$ for hydrosilylation starkly contrasts that of the $\text{CoCl}_2(\text{Ph}^2\text{p}^{\text{C}6\text{H}4}\text{N}^{\text{Ph}^3}\text{py})/2\text{NaBEt}_3$ system shown in Section 5.6. This suggests that reduction of the imine in PNpy by NaBEt₃H is not an active pathway in the catalyst systems of $\text{CoCl}_2(\text{PNpy})/2\text{NaBEt}_3$, i.e. the phosphine-imine-pyridine ligands are intact. Activity of the amido complex $\text{CoCl}^{\text{Ph}^2\text{p}^{\text{C}6\text{H}4}(\text{ame})^{\text{Ph}^3}\text{py}}$ was left unexplored. As was stated for the related iron complexes, Co-$^{\text{Ph}^2\text{p}^{\text{C}6\text{H}4}(\text{ame})^{\text{Ph}^3}\text{py}}$ species are also possible platforms for transfer hydrogenation and alcohol dehydrogenation catalysis. Transformation of

\begin{center}
\textbf{Scheme 7.4} Proposed mechanisms for hydrogenation using iron(II)-amido catalysts.
\end{center}
CoCl\((\text{Ph}_2\text{P}C_6\text{H}_4\text{(amide)Phpy})\) to halide-free derivatives can be achieved by the following proposed route:

\[
\text{CoCl}(\text{Ph}_2\text{P}C_6\text{H}_4\text{(amide)Phpy}) + \text{LiR} \rightarrow \text{CoR}(\text{Ph}_2\text{P}C_6\text{H}_4\text{(amide)Phpy}) + \text{LiCl}
\]

\[R = \text{CH}_2\text{SiMe}_3, \text{Me}\]

(7.9)

Current examples of selective nickel-catalyzed alkene hydrosilylation systems are scarce.\(^{18}\) Reported here is a new system showing promising activity and selectivity at 23 °C employing the cationic \([\text{NiBr}(\text{Ph}_2\text{P}C_6\text{H}_4\text{NHPhpy})]\text{BAR}_4\). In addition, the Ni(II)-catalyst was stable to brief exposure of air. This enhanced stability to oxygen and moisture compared to the low-valent Fe- and Co-catalysts presented in Chapters 5 and 6 is a highly desirable property for industrial applications. The activation step \([\text{NiBr}(\text{Ph}_2\text{P}C_6\text{H}_4\text{NHPhpy})]\text{BAR}_4 \rightarrow [\text{NiH}(\text{Ph}_2\text{P}C_6\text{H}_4\text{NHPhpy})]\text{BAR}_4\) is slow when hydride reagents are not used. A possible improvement to this system is to use Ni-OR or Ni-F precursors that can react with hydrosilanes to form strong Si-OR or Si-F bonds and give Ni-H via the following reaction:

\[
[\text{NiX}(\text{Ph}_2\text{P}C_6\text{H}_4\text{NHPhpy})]\text{BAR}_4 + \text{HSiR}_3 \rightarrow [\text{NiH}(\text{Ph}_2\text{P}C_6\text{H}_4\text{NHPhpy})]\text{BAR}_4 + \text{XSiR}_3
\]

\[X = \text{OR, F}\]

(7.10)

7.8 Experimental

Materials and Methods. Unless otherwise indicated, reactions were conducted using standard Schlenk techniques under an N\(_2\) atmosphere at room temperature with stirring. Solvents were high-performance liquid chromatography grade, dried and deoxygenated on a Glass Contour System or MBraun solvent purification system, and stored over 4 Å molecular sieves. The compounds \(\text{Ph}_2\text{P}C_6\text{H}_4\text{NHPhpy}\)\(^{19}\) was prepared according to the procedure presented in Chapter 4. NiBr\(_2\)(dme) and NaBAR\(_4\)\(^{20}\) were prepared according to literature. The following compounds were used as received from Sigma-Aldrich: FeBr\(_2\), CoCl\(_2\), NaBEt\(_3\)H (1 M in toluene). The following compounds were received from Sigma-Aldrich, deoxygenated and stored over 4 Å molecular sieves prior to use: styrene, 1-octene, mesitylene. PMe\(_3\) was received from Strem and used without further purification. The following chemicals were received from Gelest, Inc., deoxygenated and stored over 4 Å molecular sieves prior to use: Ph\(_2\)SiH\(_2\), VPDMS, HMTS.

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Research Purity CO and H\textsubscript{2} gas was purchased from SJ Smith. \textsuperscript{1}H and \textsuperscript{31}P{\textsuperscript{1}H} NMR spectra were acquired on Varian Unity Inova 500NB and Unity 500 NB instruments at 20 °C unless otherwise noted. \textsuperscript{1}H NMR were referenced to residual solvent relative to tetramethyilsilane, \textsuperscript{31}P{\textsuperscript{1}H} NMR spectra were referenced to an external 85% H\textsubscript{3}PO\textsubscript{4} standard. Crystallographic data were collected using a Siemens SMART diffractometer equipped with a Mo K\textsubscript{α} source (\(\lambda = 0.71073\) Å) and an Apex II detector. FT-IR spectra were recorded on a Perkin-Elmer 100 FT-IR spectrometer.

\textbf{Na[Ph\textsubscript{2}P\textsubscript{C\textsubscript{6}H\textsubscript{4}}(amide)\textsubscript{Ph}py].} A toluene solution (10 mL) of Ph\textsubscript{2}P\textsubscript{C\textsubscript{6}H\textsubscript{4}}N\textsubscript{Ph}py (400 mg, 0.95 mmol) was added a 1 M toluene solution of NaBEt\textsubscript{3}H (1 mL, 1 mmol). As NaBEt\textsubscript{3}H was added, the solution color turned from yellow to green, then back to yellow after addition was complete. After stirring for 30 mins, yellow precipitates formed. The solution was stirred for an additional 16 h, concentrated to ca. 3 mL, then added 10 mL of pentane to further precipitate the yellow powder. The product was collected via filtration through a frit. Yield: 370 mg (83 %). This compound was used in subsequent steps without further purification.

\textbf{Ph\textsubscript{2}P\textsubscript{C\textsubscript{6}H\textsubscript{4}}NH\textsubscript{Ph}py.} A toluene solution (5 mL) of Ph\textsubscript{2}P\textsubscript{C\textsubscript{6}H\textsubscript{4}}N\textsubscript{Ph}py (139 mg, 0.33 mmol) was added a 1 M toluene solution of NaBEt\textsubscript{3}H (330 mL, 0.33 mmol). This solution was stirred for 16 h, during which time yellow precipitates formed. Toluene was removed from this yellow mixture under reduced pressure to give a yellow oil. The oil was dissolved using MeOH (3 mL) to give a pale yellow solution, from which white crystals formed after storing at −10 °C for 24 h. The target compound was obtained by filtration of this mixture as white crystals. Yield: 100 mg (72 %). \textsuperscript{1}H NMR (500 MHz, C\textsubscript{6}D\textsubscript{6}): \(\delta 8.30 (d, J = 4.7\ Hz, 1H), 7.59 – 7.40 (m, 4H), 7.33 – 7.22 (m, 3H), 7.16 – 6.98 (m, 9H), 6.93 (t, J = 7.3 Hz, 1H), 6.86 – 6.82 (m, 2H), 6.72 (dd, J = 7.9, 5.0 Hz, 1H), 6.59 (t, J = 7.3 Hz, 1H), 6.45 – 6.36 (m, 1H), 5.60 (d, J = 4.8 Hz, 1H). \textsuperscript{31}P{\textsuperscript{1}H} NMR (202 MHz, CDCl\textsubscript{3}): \(\delta –18.8\) (s, 1P).

\textbf{FeBr(Ph\textsubscript{2}P\textsubscript{C\textsubscript{6}H\textsubscript{4}}(amide)\textsubscript{Ph}py)(CO)\textsubscript{2}.} In a schlenk flask was loaded Na[Ph\textsubscript{2}P\textsubscript{C\textsubscript{6}H\textsubscript{4}}(amide)\textsubscript{Ph}py] (90mg, 0.19 mmol) and FeBr\textsubscript{2} (42 mg, 0.19 mmol). The flask was then flushed with CO, followed by addition of THF (30 mL) while stirring. The brown solution was stirred continuously for 16 h, then filtered using a short plug of Celite to remove NaBr. The solution was then vacuum dried under reduced pressure, and the brown
residue was extracted into CH$_2$Cl$_2$ followed by addition of pentane to precipitate the target compound as a greenish-brown powder. Yield: 72 mg (59 %). $^1$H NMR (499 MHz, CD$_2$Cl$_2$): $\delta$ 9.01 (d, $J = 5.6$ Hz, 1H), 7.90 (br, 1H), 7.72 – 7.22 (m, 17H), 7.19 – 7.09 (m, 1H), 7.07 – 7.00 (m, 1H), 6.56 (dd, $J = 8.7, 6.0$ Hz, 1H), 6.51 – 6.36 (m, 1H), 6.02 (br, 1H). $^{31}$P{$^1$H} NMR (202 MHz, CD$_2$Cl$_2$): $\delta$ 68.72 (minor species), 65.27 (major species). IR (CH$_2$Cl$_2$): $\nu$CO 2034, 1980 cm$^{-1}$.

[Fe(PPh$_2$P$_{C6H4}$)(amide)Ph(py)(CO)$_2$]BAr$_4$. Due to the instability of this complex, samples were prepared fresh and used immediately. A greenish-brown CH$_2$Cl$_2$ solution of FeBr(PPh$_2$P$_{C6H4}$)(amide)Ph(py)(CO)$_2$ (8.4 mg, 0.013 mmol) was added NaBAr$_4$ (11.7 mg, 0.013 mmol) to give a dark purple solution. After filtration, the sample was used in subsequent reactions without further purification. $^1$H NMR (499 MHz, CD$_2$Cl$_2$): $\delta$ 9.12 (d, $J = 5.8$ Hz, 1H), 7.90 (d, $J = 7.9$ Hz, 1H), 7.75 – 7.47 (m, 20H), 7.36 (dt, $J = 21.8, 6.8$ Hz, 7H), 7.26 – 7.12 (m, 6H), 5.89 (d, $J = 4.7$ Hz, 1H). $^{31}$P{$^1$H} NMR (202 MHz, CD$_2$Cl$_2$): $\delta$ 73.61 (s, 1P). IR (CH$_2$Cl$_2$): $\nu$CO 2141, 1991 cm$^{-1}$.

[Fe(PPh$_2$P$_{C6H4}$)(amide)Ph(py)(CO)(PMe$_3$)$_2$]Br. A CH$_2$Cl$_2$ solution (5 mL) of FeBr(PPh$_2$P$_{C6H4}$)(amide)Ph(py)(CO)(PMe$_3$)$_2$ (60 mg, 0.094 mmol) was added PMe$_3$ (0.1 mL, 0.983 mmol). The resulting solution turned from green-brown to bright orange and was stirred for 2 h, followed by filtration through celite. The filtrate was concentrated to ca. 1 mL, added pentane to precipitate the target compound as an orange powder, which was collected by filtration through a frit. Yield: 55 mg (77 %). $^1$H NMR (499 MHz, CD$_2$Cl$_2$): $\delta$ 8.98 (br, 1H), 8.01 (br, 2H), 7.72 (br, 3H), 7.65 – 7.05 (m, 14H), 6.98 (br, 1H), 6.58 (br, 1H), 6.40 (br, 1H), 5.81 (br, 1H), 0.73 (br, 9H), 0.45 (br, 9H). $^{31}$P{$^1$H} NMR (202 MHz, CD$_2$Cl$_2$): $\delta$ 63.49 (br, 1P), 17.03 (d, $J = 164$ Hz, 1P), 7.61 (d, $J = 164$ Hz, 1P). IR (THF): $\nu$CO 1932 cm$^{-1}$.

[Fe(PPh$_2$P$_{C6H4}$)(amide)Ph(py)(CO)(PMe$_3$)$_2$]BAr$_4$. This compound was characterized in-situ. A CD$_2$Cl$_2$ solution of [Fe(PPh$_2$P$_{C6H4}$)(amide)Ph(py)(CO)(PMe$_3$)$_2$]Br (6.5 mg, 0.008 mmol) was added NaBAr$_4$ (7.5 mg, 0.008 mmol). No color change was observed. After stirring for 1 h, the solution was filtered through a short plug of Celite, and the NMR spectra were recorded. $^1$H NMR (499 MHz, CD$_2$Cl$_2$): $\delta$ 8.95 (br, 1H), 8.03 (t, $J = 8.8$ Hz, 3H), 7.86 – 7.05 (m, 29H), 6.73 (br, 1H), 6.51 (br, 1H), 5.75 (d, $J = 3.6$ Hz,
1H), 0.73 (d, \( J = 8.6 \) Hz, 9H), 0.48 (d, \( J = 7.5 \), 9H). \(^{31}\)P\(^{1}\)H NMR (202 MHz, CD\(_2\)Cl\(_2\)): \( \delta \) 61.15, 14.74 (d, \( J = 186 \) Hz), 5.52 (d, \( J = 186 \) Hz). IR (CH\(_2\)Cl\(_2\)): \( \nu_{\text{CO}} \) 1936 cm\(^{-1}\).

\[\text{CoCl}_2(\text{Ph}_2\text{PC}_6\text{H}_4\text{NHPh}^\text{py})\]. A THF solution of \( \text{Ph}_2\text{PC}_6\text{H}_4\text{NHPh}^\text{py} \) (29.7 mg, 0.067 mmol) was added CoCl\(_2\) (9 mg, 0.069 mmol). Copious amount of a lavender solid precipitate formed immediately. The mixture was further stirred for 2 h, and the target compound was collected by filtration through a frit as a lavender powder. Yield: 35 mg (90 \%). \(^1\)H NMR (500 MHz, CD\(_2\)Cl\(_2\)): \( \delta \) 139, 56.5, 51.8, 29.3, 20.6, 19.5, 14.8, 13.9, 12.9, 12.2, 11.3, 9.35, 8.27, 5.33, 3.68, 1.48, 1.45, 0.50, –6.17, –7.85, –13.41.

\[\text{CoCl}_2(\text{Ph}_2\text{PC}_6\text{H}_4\text{NHPh}^\text{py})\]. Method A. A THF solution (10 mL) of Na[\( \text{Ph}_2\text{PC}_6\text{H}_4\text{(amide)Phpy} \)] (29 mg, 0.062 mmol) was added CoCl\(_2\) (10 mg, 0.077 mmol). An immediate color change from yellow to brown was observed. After stirring for 2.5 h, the solution was filtered through a short plug of Celite. Solvent was removed under reduced pressure to give a powder, which was redissolved in C\(_6\)D\(_6\) to give a brown solution, and the \(^1\)H NMR spectrum was recorded. \(^1\)H NMR (500 MHz, C\(_6\)D\(_6\)): \( \delta \) 31.7, 21.5, 19.1, 13.5, 12.0, 10.3, 9.920, 5.92, 5.58, 4.66, –3.23, –4.07, –8.32, –12.7. Method B. Alternatively, this compound was isolated as a byproduct in the synthesis of CoMe(\( \text{Ph}_2\text{PC}_6\text{H}_4\text{NHPh}^\text{py})(\text{PPh}_3)\) (see Chapter 5). X-ray diffraction quality single crystals were obtained by pentane diffusion into a THF solution. The compound CoCl(\( \text{Ph}_2\text{PC}_6\text{H}_4\text{(amide)Phpy} \)) was isolated as dark red crystals, and the \(^1\)H NMR spectrum in C\(_6\)D\(_6\) solution exhibited resonances similar to the compound obtained in method A. \(^1\)H NMR (500 MHz, C\(_6\)D\(_6\)): \( \delta \) 18.8, 13.3, 11.9, 10.3, 9.90, 5.88, 5.62, 4.67, –3.73.

\[\text{Co(Ph}_2\text{PC}_6\text{H}_4\text{(amide)Phpy})(\text{CO})\]. A round bottom Schlenk flask was loaded with CoCl\(_2\)(\( \text{Ph}_2\text{PC}_6\text{H}_4\text{NHPh}^\text{py} \)) (40 mg, 0.07 mmol) and added THF (50 mL). This suspension was purged with 1 atm CO and cooled in an acetone/CO\(_2\) bath. In a separate schlenk tube, a 1 M toluene solution of NaBEt\(_3\)H (150 mL, 0.15 mmol) was diluted with THF (10 mL). This solution was transferred to the cooled CoCl\(_2\)(\( \text{Ph}_2\text{PC}_6\text{H}_4\text{NHPh}^\text{py} \)) suspension under CO via canula. After the transfer was complete, the suspension was removed from the acetone/CO\(_2\) bath and allowed to warm to room temperature, during which time a red solution formed. This solution was further stirred for 16 h, and the solvent was evaporated.
under reduced pressure to give a dark red solid. The red compound was extracted with THF and filtered through a short plug of Celite. The filtrate was concentrated to ca. 2 mL, layered with pentane (10 mL), and stored under −35 °C for 48 h to give the target compound as dark red crystals. Yield: 18 mg (48 %). \(^1\)H NMR (499 MHz, C\(_6\)D\(_6\)): δ 8.98 (d, \(J = 5.7\) Hz, 1H), 8.14 − 7.95 (m, 4H), 7.46 (d, \(J = 7.5\) Hz, 2H), 7.22 (t, \(J = 9.2\) Hz, 1H), 7.09 − 6.97 (m, 9H), 6.94 − 6.86 (m, 1H), 6.64 − 6.54 (m, 2H), 6.43 (q, \(J = 7.3, 6.8\) Hz, 2H), 6.11 (t, \(J = 6.2\) Hz, 1H), 5.39 − 5.37 (m, 1H).

\(^{31}\)P\{\(^1\)H\} NMR (202 MHz, C\(_6\)D\(_6\)): δ 68.89 (s, 1P). IR (Et\(_2\)O): \(\nu\) CO 1909 cm\(^{-1}\).

NiBr\(_2\)(Ph\(_2\)P\(_6\)H\(_4\)NH\(_\text{Ph}p\)y). A THF solution (8 mL) of Ph\(_2\)P\(_6\)H\(_4\)NH\(_\text{Ph}p\)y (80 mg, 0.18 mmol) was added NiBr\(_2\)(thf)\(_2\) (65 mg, 0.18 mmol). Orange precipitates immediately formed. This mixture was further stirred for 2 h, followed by concentration to ca. 2 mL. The target compound was obtained via filtration through a frit as an orange powder. Yield: 120 mg (99 %). \(^1\)H NMR (499 MHz, CD\(_2\)Cl\(_2\)): δ 11.27 (br, 1H), 8.98 (br, 1H), 8.60 − 8.30 (m, 2H), 8.12 (d, \(J = 6.46\) Hz, 2H), 7.94 (t, \(J = 6.24\), 1H), 7.73 (d, \(J = 6.9\) Hz, 1H), 7.69 − 7.36 (m, 10H), 7.34 − 7.20 (m, 4H), 7.15 (m, 1H), 6.11 (s, 1H). \(^{31}\)P\{\(^1\)H\} NMR (202 MHz, CD\(_2\)Cl\(_2\)): δ 39.44 (br, 1P).

[NiBr(Ph\(_2\)P\(_6\)H\(_4\)NH\(_\text{Ph}p\)y)]BAr\(_F\)\(_4\). An orange CH\(_2\)Cl\(_2\) solution (10 mL) of NiBr\(_2\)(Ph\(_2\)P\(_6\)H\(_4\)NH\(_\text{Ph}p\)y) (120 mg, 0.18 mmol) was added a THF solution (2 mL) of NaBAr\(_F\)\(_4\) (160 mg, 0.18 mmol). No color change was observed. After stirring for 2 h, the solution was filtered through a short plug of Celite and concentrated to ca. 1 mL. Pentane (15 mL) was added to this solution to afford an orange oil. The solution was decanted, and the resulting oil subjected to vacuum until it solidified. The target compound was collected as a bright orange powder. Yield: 152 mg (58 %). Crystals suitable for X-ray diffraction were obtained by pentane vapor diffusion into a THF solution. \(^1\)H NMR (499 MHz, CD\(_2\)Cl\(_2\)): δ 9.06 (d, \(J = 5.6\) Hz, 1H), 8.38 (d, \(J = 7.2\) Hz, 2H), 8.07 (s, 1H), 8.05 − 8.01 (m, 1H), 7.98 (dd, \(J = 12.8, 7.4\) Hz, 2H), 7.74 (br, 8H), 7.68 − 7.61 (m, 2H), 7.57 (m, 10H), 7.44 (td, \(J = 7.8, 2.9\) Hz, 2H), 7.38 − 7.28 (m, 5H), 7.28 − 7.22 (m, 1H), 5.85 (d, \(J = 2.5\) Hz, 1H). \(^{31}\)P\{\(^1\)H\} NMR (202 MHz, CD\(_2\)Cl\(_2\)): δ 33.55 (s, 1P).

\textbf{Reaction of [Fe(Ph\(_2\)P\(_6\)H\(_4\)(amide)\(_\text{Ph}p\)y)(CO)\(_2\)]BAr\(_F\)\(_4\) with H\(_2\).} A J-Young NMR tube was loaded with FeBr(Ph\(_2\)P\(_6\)H\(_4\)(amide)\(_\text{Ph}p\)y)(CO)\(_2\) (5 mg, 0.008 mmol) and NaBAr\(_F\)\(_4\)
(7 mg, 0.008 mmol) and dissolved with CD$_2$Cl$_2$ (ca. 0.6 mL) to give a dark purple solution. The NMR tube was quickly frozen, the headspace evacuated and refilled with 1 atm H$_2$. The reaction was monitored by $^1$H and $^{31}$P NMR spectroscopy over the course of 16 h.

**General procedure for hydrosilylation catalysis using**

$[\text{NiBr}^{(\text{Ph}_2\text{P}_{\text{C}_6\text{H}_4}\text{NPhpy})}]\text{BAr}_4^+$. A scintillation vial was loaded with $[\text{NiBr}^{(\text{Ph}_2\text{P}_{\text{C}_6\text{H}_4}\text{NPhpy})}]\text{BAr}_4^+$ (6 mg, 0.004 mmol) and a stir bar. To this vial was added alkene (0.2 mmol, 1-octene: 22 mg, VPDMS: 35 mg), silane (0.24 mmol, Ph$_2$SiH$_2$: 45 mg, HMTS: 53mg ), and mesitylene (8mg, 0.066 mmol) to give a bright orange solution that was stirred constantly. The reaction was monitored by taking aliquots of the mixture, dissolving in CDCl$_3$, and $^1$H NMR spectra were recorded at specific time points. Yields were determined by integration of the SiH resonance with respect to mesitylene in the $^1$H NMR spectra. In reactions where NaBEt$_3$H was used as the activator, a 1 M toluene solution of NaBEt$_3$H (5 µL, 0.005 mmol) was injected via microsyringe as the last step to give a dark brown solution. Yields were determined as described above.

**7.9 Supporting Information**

![Figure 7.18 IR spectra of a CH$_2$Cl$_2$ solution sample of Fe($^{\text{Ph}_2\text{P}_{\text{C}_6\text{H}_4}\text{NPhpy}}$)(CO)$_2$]BAr$_4^+$ over 5 days.](image-url)
Figure 7.19  High field $^1$H NMR spectra of reaction of Fe[[Ph$_2$PPhC$_6$H$_4$(amide)Phpy](CO)$_2$]BAR$_4$ with H$_2$. Bottom: after 10 mins. Top: after 16 h.

Figure 7.20  IR spectrum of [Fe(Ph$_2$PPhC$_6$H$_4$(amide)Phpy)(CO)$_2$] in CD$_2$Cl$_2$. 
**Figure 7.21** $^1$H NMR spectra of [Fe($^{256}$P$_2$C$_6$H$_4$N$^{15}$Ph$^2$py)(CO)(PMe$_3$)$_2$]BAR$_4$ in CD$_2$Cl$_2$. Bottom: $^1$H NMR spectral. Middle: $^1$H{$^{31}$P} NMR spectrum selectively decoupled at $\delta$ 5.52. Top: $^1$H{$^{31}$P} NMR spectrum selectively decoupled at $\delta$ 14.74.

**Figure 7.22** $^1$H NMR spectra of crude CoCl($^{256}$P$_2$C$_6$H$_4$)(amide)$^{15}$Ph$^2$py) in C$_6$D$_6$. Bottom: obtained from addition of Na[$^{256}$P$_2$C$_6$H$_4$(amide)$^{15}$Ph$^2$py] to a THF solution of CoCl$_2$. Top: obtained from addition of MeLi to a Et$_2$O suspension of CoCl$_2$($^{256}$P$_2$C$_6$H$_4$N$^{15}$Ph$^2$py).
Figure 7.23 $^1$H NMR spectrum of $\text{Co(Ph}_2\text{P}_{\text{C}_6\text{H}_4}(\text{amide})\text{Ph}_\text{py})(\text{CO})$ in C$_6$D$_6$.

Figure 7.24 $^{31}$P NMR spectrum of $\text{Co(Ph}_2\text{P}_{\text{C}_6\text{H}_4}(\text{amide})\text{Ph}_\text{py})(\text{CO})$ in C$_6$D$_6$. 
Figure 7.25 $^1$H NMR spectra NiBr$_2$(Ph$_2$PCH$_2$NH$_2$Ph) in CD$_2$Cl$_2$.

7.10 References


(11) Fairweather, N. T.; Gibson, M. S.; Guan, H. *Organometallics* 2014, 34, 335.


