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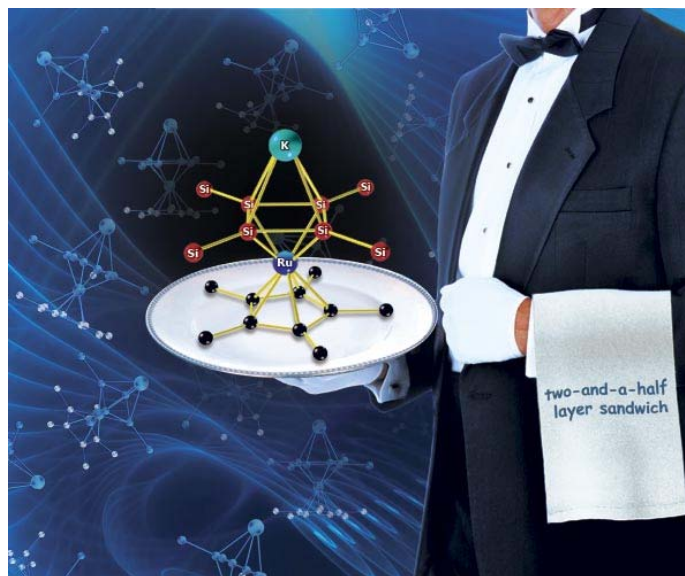


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Synthesis and reactivity of rhodium and iridium alkene, alkyl and silyl complexes supported by a phenyl-substituted PNP pincer ligand†‡

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New rhodium and iridium complexes supported by the phenyl-substituted PNP pincer ligand $\text{PNP}^{\text{Ph}}\text{H}$ ($\text{HN}(2\text{-PPh}_2\text{-4-Me-C}_6\text{H}_3)_2$) (**1**) were synthesized. The reaction of 2 equiv. of **1** with $[(\text{COD})\text{IrCl}]_2$ afforded the coordination complex $[(\text{PNP}^{\text{Ph}}\text{H})\text{Ir}(\text{COD})]\text{Cl}$ (**2**) featuring hydrogen bonding between the N–H group and the chloride anion, as characterized by NMR spectroscopy and X-ray crystallography. Reaction of **1** with $[(\text{COE})_2\text{IrCl}]_2$ or $[(\text{COE})_2\text{RhCl}]_2$ in benzene provided a mixture of complexes including $(\text{PNP}^{\text{Ph}}\text{H})\text{MHCl}_2$ ($\text{M} = \text{Ir}$ (**4**), $\text{M} = \text{Rh}$ (**7**)) and $(\text{PNP})\text{M}(\text{COE})$ ($\text{M} = \text{Ir}$ (**5**), $\text{M} = \text{Rh}$ (**8**)). Alkene complexes of the type $(\text{PNP}^{\text{Ph}})\text{M}(\text{L})$ ($\text{M} = \text{Ir}$, $\text{L} = \text{COD}$ (**3**) and COE (**5**); $\text{M} = \text{Rh}$, $\text{L} = \text{COE}$ (**8**) and $\text{L} = \text{ethylene}$ (**9**)) were synthesized by reaction of $(\text{PNP}^{\text{Ph}})\text{Li}$ with the appropriate alkene chloride complexes. Reactions of silanes with **5**, **8** or **9** produced silyl hydride complexes $(\text{PNP}^{\text{Ph}})\text{MH}(\text{SiR}_3)$ ($\text{M} = \text{Ir}$, $\text{R} = \text{Ph}$ (**16**) and $\text{R} = \text{Et}$ (**17**); $\text{M} = \text{Rh}$, $\text{R} = \text{Ph}$ (**18**), Et (**19**) and Ph_2Cl (**20**)) *via* Si–H oxidative addition. The J_{SiH} coupling constants for rhodium complexes **18**, **19** and **20** were determined to be *ca.* 35 Hz, while iridium complexes **16** and **17** exhibited coupling constants less than 10 Hz. X-Ray crystal structures of **16** and **18** reveal isostructural complexes featuring a trigonal bipyramidal geometry about iridium with a *mer* binding of the PNP^{Ph} ligand. A hydride ligand, located from the Fourier map for **18**, has a short contact of 1.83(3) Å with the silicon atom. Oxidative addition of iodomethane to **5** and **8** afforded $(\text{PNP}^{\text{Ph}})\text{M}(\text{Me})(\text{I})(\text{THF})$ ($\text{M} = \text{Rh}$ (**14**), $\text{M} = \text{Ir}$ (**12**)), respectively. Arene C–H activation upon thermolysis of **12** in benzene produced $(\text{PNP}^{\text{Ph}})\text{M}(\text{Ph})(\text{I})(\text{THF})$. Iridium silyl iodide complexes $(\text{PNP}^{\text{Ph}})\text{IrI}(\text{SiR}_3)$ ($\text{SiR}_3 = \text{SiPh}_3$ (**21**), SiH_2Mes (**22**) and SiH_2Xyl (**23**)) resulted from addition of organosilanes to **12**, *via* elimination of CH_4 .

Introduction

The activation of Si–H bonds by transition metal complexes is a fundamental step in various catalytic transformations of organosilanes.^{1,2,3} Within this context, research in this laboratory has focused on the study of fundamental reaction pathways involving Si–H bond activations *via* oxidative addition, σ -bond metathesis or α -hydrogen migration steps.^{2a,3e,4} These studies have led to progress in the field of organosilicon catalysis, and in the synthesis of novel transition metal–silicon species, including compounds that feature multiple bonds between a transition metal and silicon.⁵

The development of synthetic routes to compounds possessing a formal metal–silicon double bond (silylene complexes) has allowed their investigation as reagents and catalysts for new chemical transformations.^{5,6} Recently, efforts to develop new alkene hydrosilation catalysts based on transition metal silylene complexes led to discovery of a second example, with catalysts of the type $[(\text{PNP}^{\text{IPr}})(\text{H})\text{Ir}=\text{SiR}_2][\text{B}(\text{C}_6\text{F}_5)_4]$ ($\text{PNP}^{\text{IPr}} = [\text{N}(2\text{-P}^i\text{Pr}_2\text{-4-Me-C}_6\text{H}_3)_2]$).⁷

The electronic properties of the silylene catalyst appear to be crucial in this catalysis; in particular the cationic charge on the metal complex is necessary to render the silicon more Lewis acidic and reactive toward alkenes.⁸

A salient feature of the synthetic route to these PNP ancillary ligands is the potential to alter their steric and electronic characteristics through modification of the substituents on phosphorus.⁹ To investigate possible effects of ligand donor strength on the chemistry at the metal center, studies focused on rhodium and iridium complexes of PNP^{Ph} ($\text{PNP}^{\text{Ph}} = [\text{N}(2\text{-PPh}_2\text{-4-Me-C}_6\text{H}_3)_2]$) (**1**), and Si–H bond activation processes derived therefrom. Previously, Ozerov, Kiplinger and co-workers have reported the synthesis of $\text{PNP}^{\text{Ph}}\text{H}$ and have communicated its use in development of $(\text{PNP}^{\text{Ph}})\text{Lu}$ -phosphinidene chemistry,¹⁰ but the chemistry of late transition metals with this ligand has yet to be explored. In this contribution, the synthesis and characterization of rhodium and iridium alkene, alkyl and hydride complexes is described. Furthermore, Si–H activations of organosilanes by these rhodium and iridium complexes to produce new silyl complexes are discussed.

Results and discussion

Synthesis and characterization of $(\text{PNP}^{\text{Ph}})\text{Ir}$ alkene complexes

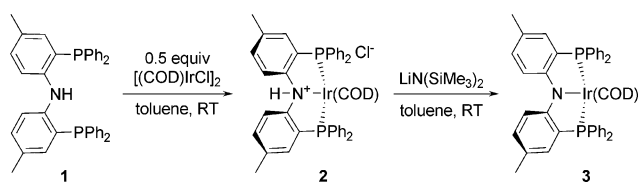
Addition of 2 equiv. of $(\text{PNP}^{\text{Ph}})\text{H}$ (**1**) to a solution of $[(\text{COD})\text{IrCl}]_2$ in toluene at room temperature afforded the single product

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† Dedicated to Uwe Rosenthal on the occasion of his 60th birthday.

‡ Electronic supplementary information (ESI) available: Tables of atomic coordinates, thermal displacement parameters, selected bond lengths and angles, and crystallographic information files for **2**, **3**, **16** and **18**. CCDC reference numbers 757516–757519. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b925856f

[(PNP^{Ph}H)Ir(COD)][Cl] (**2**), which precipitated out of the reaction mixture as a white powder in 91% yield (Scheme 1). The ¹H NMR resonance for the NH proton at 11.65 ppm in dichloromethane-*d*₂ is significantly downfield-shifted with respect to that for the free ligand (7.08 ppm in benzene-*d*₆),¹⁰ a feature that is consistent with the presence of a hydrogen bond between the NH and the outersphere chloride¹¹ (see structural discussion below). A broad singlet in the ¹H NMR spectrum for the olefinic protons suggests that the COD ligand is symmetrically bound in an η²,η² fashion to the iridium center. The ¹³C{¹H} NMR spectrum of **2** exhibits a resonance at 63.8 ppm attributed to the coordinated, olefinic carbon atoms. The phosphorus nuclei in the PNP^{Ph} ligand appear as a singlet at 13.7 ppm in the ³¹P{¹H} NMR spectrum of **2**. As determined by VT NMR spectroscopy, a dynamic process interconverts the vinylic COD hydrogens of **2** on the NMR time scale. Upon cooling a solution of **2** in dichloromethane-*d*₂ to –80 °C, the alkene resonances for the COD ligand in the ¹H NMR spectrum resolve into two separate signals at 3.56 and 3.48 ppm, consistent with the observed geometry in the crystal structure (see below). No N–H oxidative addition or loss of the COD ligand was observed, even after heating complex **2** to 60 °C for 26 h in bromobenzene-*d*₅. In contrast, addition of 2 equiv. of (PNP^{Pr})H to [CODIrCl]₂ affords (PNP^{Pr})IrH(Cl) after 18 h at ambient temperature.¹² This difference in reactivity can be attributed to the higher tendency for more electron-rich metal centers to undergo oxidative addition reactions and ascribed to the differences in donor properties of PNP^{Pr} and PNP^{Ph}, as phenyl-substituted phosphine ligands are less electron-donating than comparable alkyl-substituted phosphines.¹³



Scheme 1

Single crystals (colorless needles) for X-ray crystallography were obtained by vapor diffusion of heptane into a concentrated solution of **2** in *ortho*-dichlorobenzene at ambient temperature. Complex **2** crystallized in the *P* $\bar{1}$ space group with two molecules of *ortho*-dichlorobenzene in the unit cell (Fig. 1). Structural studies confirmed the cationic nature of **2** and the presence of an outersphere chloride anion. Notably, the chloride anion participates in hydrogen bonding with the hydrogen atom on the amine, as indicated by a Cl–H(N) distance of 2.31(5) Å. The geometry about iridium is a distorted trigonal bipyramid, with the phosphorus atoms and one alkene moiety of the COD ligand occupying the equatorial positions. The amido N and the second alkene arm of the COD ligand occupy the axial positions. Thus, the PNP ligand is bound in a *facial* manner to the iridium center, as further indicated by a P1–Ir1–P2 angle of 107.68(3) Å. The nitrogen atom of the PNP ligand exhibits a pyramidal bonding geometry, as illustrated by the bond angles around this atom (C(21)–N(1)–C(28) = 110.0(3)°, C(21)–N(1)–Ir(1) = 113.4(2)° and, C(28)–N(1)–Ir(1) = 115.5(2)°). Consistent with the low temperature solution NMR data, the solid

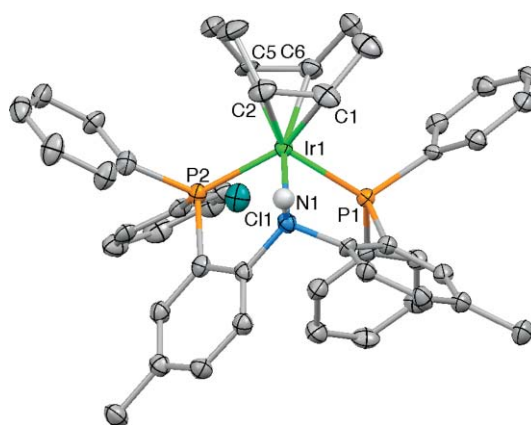


Fig. 1 Molecular structure of **2** displaying thermal ellipsoids at the 50% probability level. H-atoms, except for those attached to N(1), and disordered *ortho*-dichlorobenzene have been omitted for clarity. Selected bond lengths (Å): H(1)–Cl(1) = 2.31(5), C(1)–C(2) = 1.419(7), C(5)–C(6) = 1.404(6). Selected bond angles (°): P(1)–Ir(1)–P(2) = 107.68(3), P(1)–Ir(1)–N(1) = 82.04(9), P(2)–Ir(1)–N(1) = 84.05(9), P(1)–Ir(1)–C(1) = 101.74(13), P(1)–Ir(1)–C(6) = 87.55(12), P(2)–Ir(1)–C(2) = 109.91(13), P(2)–Ir(1)–C(5) = 83.92(11), N(1)–H(1)–Cl(1) = 139(4), C(21)–N(1)–C(28) = 110.0(3), C(21)–N(1)–Ir(1) = 113.4(2), C(28)–N(1)–Ir(1) = 115.5(2).

state structure of **2** reveals inequivalent positions for the two alkene groups of the cyclooctadiene ligand.

The synthesis of (PNP^{Ph})Ir(COD) (**3**) was achieved *via* deprotonation of **2** with LiN(SiMe₃)₂ in toluene to afford **3** as a bright yellow powder in moderate yield (69%, Scheme 1). In addition, complex **3** was synthesized by addition of 2 equiv. of (PNP^{Ph})Li (generated *in situ* by deprotonation of **1** with LiN(SiMe₃)₂) to [(COD)IrCl]₂ in toluene. The ¹H NMR spectrum of **3** in dichloromethane-*d*₂ contains two resonances for the olefinic protons on the cyclooctadiene ligand at 3.58 and 2.64 ppm. As these resonances are shifted upfield with respect to those of free cyclooctadiene, the NMR data support a bidentate coordination of COD to the iridium center and a 5-coordinate Ir(I) complex. Furthermore, the ³¹P{¹H} NMR spectrum in dichloromethane-*d*₂ contains a singlet at 13.5 ppm, for both phosphorus nuclei of the pincer ligand. The ¹³C{¹H} NMR spectrum contains two signals for the olefinic carbon nuclei at chemical shifts that are similar to those of **2**, a broad resonance at 66.1 ppm and a doublet of doublets at 60.3 ppm from coupling to magnetically inequivalent phosphorus nuclei.

Single crystals of **3** were obtained by vapor diffusion of pentane into a concentrated solution of **3** in CH₂Cl₂ at –35 °C. The X-ray structure of **3** reveals a distorted trigonal bipyramidal coordination geometry about the iridium atom (Fig. 2), similar to the geometry observed for **2**. The PNP ligand is bound in a *facial* manner with the P–Ir–P angle at 108.50(5)°, instead of the more common meridional binding usually observed with late metal complexes supported by this monoanionic ligand framework.¹⁴ The nitrogen atom is in a trigonal planar environment with the sum of the angles around N1 being 356.9(7)°. The alkene moieties of the cyclooctadiene ligand occupy different positions of the trigonal bipyramidal structure—one arm is in the axial position *trans* to the nitrogen atom while the other is in the equatorial plane. In this case, the unsymmetrical binding of the cyclooctadiene ligand is

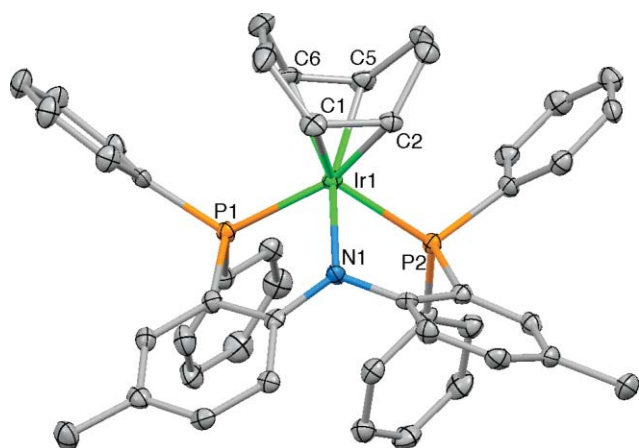
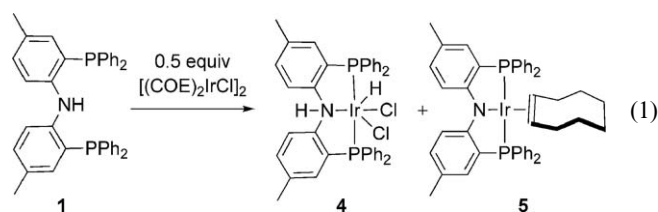


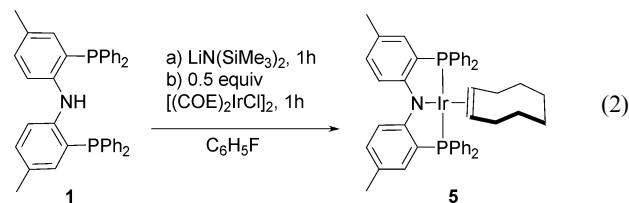
Fig. 2 Molecular structure of **3** displaying thermal ellipsoids at the 50% probability level. H-atoms have been omitted for clarity. Selected bond lengths (Å): C(1)–C(2) = 1.439(6), C(5)–C(6) = 1.400(6). Selected bond angles (°): P(1)–Ir(1)–P(2) = 108.50(5), P(1)–Ir(1)–N(1) = 82.25(9), P(2)–Ir(1)–N(1) = 78.54(9), P(1)–Ir(1)–C(1) = 109.91(12), P(1)–Ir(1)–C(6) = 86.79(11), P(2)–Ir(1)–C(2) = 98.53(11), P(2)–Ir(1)–C(5) = 90.39(11), C(29)–N(1)–C(26) = 121.4(3), C(29)–N(1)–Ir(1) = 119.9(2), C(26)–N(1)–Ir(1) = 115.6(2).

consistent with the appearance of two distinct resonances for the olefinic nuclei in the ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra.

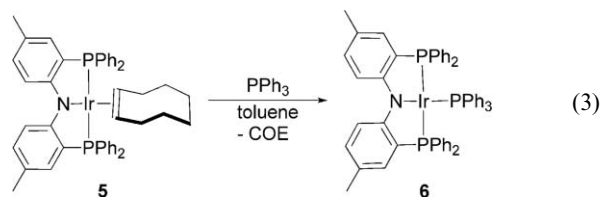
The synthesis of PNP^{Ph} iridium complexes from the chloride-bridged dimer $[(\text{COE})_2\text{IrCl}]_2$ was also explored. Addition of 2 equiv. of **1** to $[(\text{COE})_2\text{IrCl}]_2$ in bromobenzene- d_5 at ambient temperature over 18 h gave a mixture of compounds as determined by ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy (eqn (1)). When the reaction occurred in benzene, an off-white precipitate was observed after 18 h at ambient temperature. The isolated white precipitate was characterized by multinuclear NMR spectroscopy and combustion analysis as $(\text{PNP}^{\text{Ph}}\text{H})\text{IrHCl}_2$ (**4**), obtained in 33% yield. Complex **4** is insoluble in benzene, tetrahydrofuran and fluorobenzene, but exhibits high solubility in methylene chloride and *ortho*-dichlorobenzene. The ^1H NMR spectrum of **4** in dichloromethane- d_2 contains a resonance at 7.22 ppm for the N-H proton. Another resonance at -18.43 ppm, attributed to the Ir-H group, appears as a triplet of doublets from couplings to two equivalent phosphorus nuclei (J_{PH} 14.2 Hz) and to the NH (J_{HH} 2.1 Hz). The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum contains a single resonance at 15.4 ppm for both phosphorus nuclei of the pincer ligand. The remaining bright red solution of the reaction mixture contains two other complexes, as determined by NMR spectroscopy. One of these compounds was identified as $(\text{PNP}^{\text{Ph}})\text{Ir}(\text{COE})$ (**5**) by comparison with the independently synthesized complex (*vide infra*). Attempts to separate **5** from the unidentified minor product through fractional crystallizations were not successful, precluding the elucidation of the remaining unidentified iridium-containing species. Recently, Schneider *et al.* published a detailed analysis of a similar disproportionation reaction with iridium complexes of a different PNP ligand, $\text{HN}(\text{CH}_2\text{CH}_2\text{P}^i\text{Pr}_2)_2$, featuring ethylene spacers. In this related system, the reaction of $\text{HN}(\text{CH}_2\text{CH}_2\text{P}^i\text{Pr}_2)_2$ with $[(\text{COE})_2\text{IrCl}]_2$ in nonprotic solvents resulted in formation of a similar mixture of $(\text{PNP})\text{Ir}(\text{COE})$ and $(\text{PNP})\text{IrHCl}_2$.¹⁵



Treatment of a fluorobenzene solution of $[(\text{COE})_2\text{IrCl}]_2$ with 2 equiv. of $(\text{PNP}^{\text{Ph}})\text{Li}$ afforded $(\text{PNP}^{\text{Ph}})\text{Ir}(\text{COE})$ (**5**) after 1 h at ambient temperature (eqn (2)). Analytically pure **5** was obtained after removal of the LiCl salt by filtration, followed by washing the resulting bright orange powder with pentane. The olefinic nuclei for the cyclooctene ligand in **5** resonate at 2.98 ppm in the ^1H NMR spectrum and at 49.1 ppm in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (benzene- d_6). Furthermore, the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum exhibits two overlapping broad resonances at 28.9 and 27.8 ppm. The unique phosphorus resonances in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra are consistent with a square planar geometry at iridium, with the alkene bound perpendicular to the PNPIr plane. Similar $^{31}\text{P}\{^1\text{H}\}$ NMR features were observed for $(\text{PNP}^{\text{Pr}})\text{Ir}(\text{COE})$, which was structurally characterized by X-ray crystallography.^{7b}



Addition of a Lewis base to alkene complexes **3** and **5** was explored to evaluate the lability of the iridium-bound alkene ligands. Thus, the phosphine adduct $(\text{PNP}^{\text{Ph}})\text{Ir}(\text{PPh}_3)$ was obtained as a bright orange solid by addition of 1 equiv. of PPh_3 to **5** in toluene in an isolated yield of 73% yield (eqn (3)). The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum exhibits a doublet at 34.7 ppm corresponding to the PNP ligand, and a triplet at 19.6 ppm for the coordinated triphenylphosphine (J_{PP} 18.2 Hz). The displacement of COD by PPh_3 in **3** is slower and requires heating to 80 °C for 36 h. In contrast, the conversion of **5** to **6** in benzene is complete after 1 h at ambient temperature. Thus, as expected, 5-coordinate 18 electron complex **3** is more substitutionally inert than **5**.

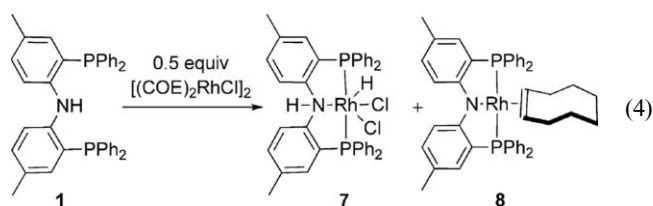


Synthesis and characterization of $(\text{PNP}^{\text{Ph}})\text{Rh}$ alkene complexes

The synthesis of $(\text{PNP}^{\text{Ph}})\text{Rh}(\text{L})$ complexes was achieved through synthetic routes that are analogous to those employed for iridium complexes $(\text{PNP}^{\text{Ph}})\text{Ir}(\text{L})$. Addition of 2 equiv. of **1** to $[(\text{COE})_2\text{RhCl}]_2$ in bromobenzene- d_5 resulted in a 1:1 mixture of two products after 1.5 h at ambient temperature. As with the analogous iridium reaction, the two products were identified as $(\text{PNP}^{\text{Ph}}\text{H})\text{RhHCl}_2$ (**7**) and $(\text{PNP}^{\text{Ph}})\text{Rh}(\text{COE})$ (**8**) (eqn (4)). Treatment of a benzene solution of $[(\text{COE})_2\text{RhCl}]_2$ with 2 equiv. of **1** resulted in precipitation of a white powder found to contain

7 (as a major product) and several minor species. Additionally, ^1H NMR spectroscopy of the reaction mixture resulting from 2 equiv. of **1** and $[(\text{COD})\text{RhCl}]_2$ in bromobenzene- d_5 at room temperature revealed formation of complex **7** as a minor product, along with several unidentified rhodium-containing species.

The ^1H NMR spectrum of **7** exhibits a complex multiplet at -14.00 ppm, due to couplings to Rh and P, and to the NH proton. The $^1\text{H}\{^{31}\text{P}\}$ NMR spectrum reveals a simple doublet of doublets for this signal, with couplings to Rh (J_{RhH} 11 Hz) and the NH group (J_{HH} 3 Hz). The NH group appears as a broad singlet at 7.00 ppm in the ^1H NMR spectrum, and exhibits a correlation peak with the hydride ligand in a 2D COSY experiment. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum contains a single resonance for phosphorus at 55.2 ppm, as a doublet with coupling to rhodium (J_{RhP} 131.7 Hz). Due to the minor products isolated with **7**, combustion analysis of this complex was not obtained.

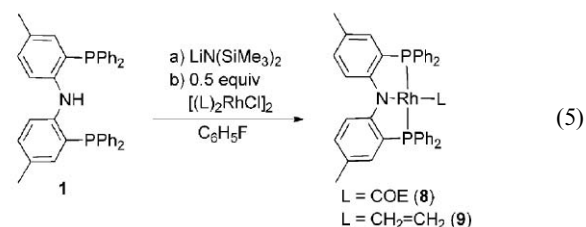


A higher yielding synthesis of $(\text{PNP}^{\text{Ph}})\text{Rh}(\text{COE})$ (**8**) was achieved by addition of 2 equiv. of $(\text{PNP}^{\text{Ph}})\text{Li}$ to $[(\text{COE})_2\text{RhCl}]_2$, to afford **8** as a light-orange solid in 83% yield (eqn (5)). The ^1H NMR spectrum of **8** reveals a broad doublet at 3.60 ppm, corresponding to the alkene protons of the cyclooctene ligand. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum contains a resonance for the PNP ligand, as a doublet at 38.5 ppm resulting from coupling to rhodium (J_{RhP} 149.0 Hz). Furthermore, the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum reveals a doublet resonance for the olefinic carbons at 68.5 ppm (J_{RhC} 11.5 Hz), which is significantly downfield from that of the iridium analog **5** (49.1 ppm).

In contrast to the iridium complex **5**, which exhibits inequivalent phosphorus signals, a single $^{31}\text{P}\{^1\text{H}\}$ NMR resonance is observed for **8**. The higher symmetry observed for **8** versus iridium alkene complex **5** is attributed to more rapid rotation about the rhodium–alkene bond in solution at room temperature. NMR studies at low temperatures were undertaken to confirm this. At -80°C , the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum in dichloromethane- d_2 revealed two doublets of doublets from two distinct phosphorus donors coupling to each other and to rhodium. Hence at -80°C , the NMR spectra exhibits unsymmetrical ligand resonances, which parallels the features observed at room temperature for **5**. The ^1H NMR spectrum of **8** at -80°C also revealed separate, broad signals for the olefinic protons at 3.47 and 2.87 ppm, further suggesting slow rotation about the rhodium–alkene bond at this temperature. The observed dynamic behavior at ambient temperature is attributed to weaker backbonding from the rhodium to the alkene in **8**, in comparison to that from iridium in **5**, which could result in a lower barrier for rotation about the transition metal alkene bond.

Similarly, addition of 2 equiv. of $(\text{PNP}^{\text{Ph}})\text{Li}$ to $[(\text{CH}_2=\text{CH}_2)_2\text{RhCl}]_2$ in toluene at room temperature afforded $(\text{PNP}^{\text{Ph}})\text{Rh}(\text{CH}_2=\text{CH}_2)$ (**9**) in 78% isolated yield (eqn (5)). The ethylene ligand exhibited a resonance at 3.08 ppm in the ^1H NMR spectrum and at 49.6 ppm (doublet with $J_{\text{RhC}} = 12.0$ Hz) in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of

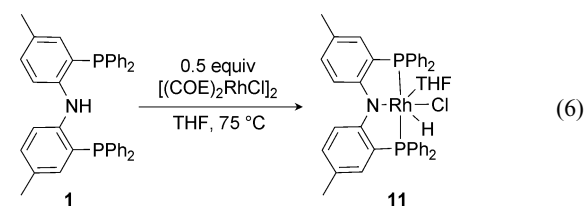
9 contains a single resonance at 35.7 ppm appearing as a doublet due to coupling to rhodium (J_{RhP} 139.0 Hz).



The lability of the alkene ligands in **8** and **9** was explored by substitution reactions employing PPh_3 . The synthesis of the PPh_3 adduct $(\text{PNP}^{\text{Ph}})\text{Rh}(\text{PPh}_3)$ (**10**), isolated as a bright orange powder in 97% yield, was achieved through an analogous protocol to that of eqn (3). The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **10** contains a doublet of triplets at 46.3 ppm corresponding to the triphenylphosphine ligand (J_{RhP} 158.1 Hz; J_{PP} 36.1 Hz). The PNP ligand exhibits a resonance at 40.5 ppm in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum appearing as a doublet of doublets. The difference in lability of the alkene in **8** and **9** was observed via small scale reactions with PPh_3 in benzene- d_6 . Addition of 1 equiv. of PPh_3 to ethylene complex **9** at room temperature resulted in complete conversion to **10** within 1 h. In contrast, displacement of the cyclooctene ligand of **8** by PPh_3 in benzene- d_6 at room temperature was only 75% complete after 2 h, as determined by NMR spectroscopy. The difference in lability between the cyclooctene and the ethylene ligands in **8** and **9** could be a result of the higher steric demand of the cyclooctene ligand, which might hamper association of PPh_3 in these substitution reactions.

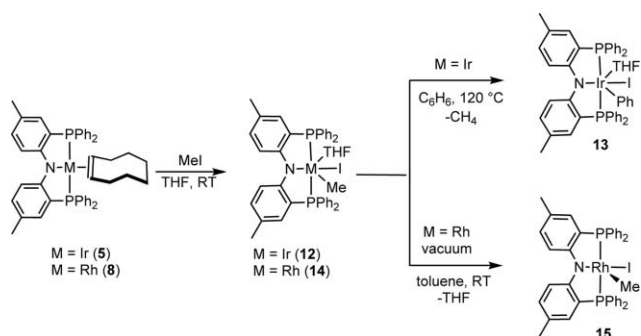
Synthesis and characterization of $(\text{PNP}^{\text{Ph}})\text{RhH}(\text{Cl})(\text{THF})$

Although N–H oxidative addition by group 9 complexes is facile for $(\text{PNP}^{\text{Ir}})\text{H}$,¹² analogous reactions for $(\text{PNP}^{\text{Ph}})\text{H}$ appear to be more difficult. The attempted synthesis of $(\text{PNP}^{\text{Ph}})\text{IrH}(\text{Cl})(\text{THF})$ by refluxing $[(\text{COE})_2\text{IrCl}]_2$ and **1** in THF resulted in an intractable mixture of products. Yet, following a synthesis modified from that published by Kaska *et al.*,¹⁶ synthesis of $(\text{PNP}^{\text{Ph}})\text{RhH}(\text{Cl})(\text{THF})$ (**11**) was achieved by refluxing **1** and $[(\text{COE})_2\text{RhCl}]_2$ in THF for 3 h at 75°C (eqn (6)). Complex **11** contains a coordinated THF molecule, as determined by ^1H NMR spectroscopy in benzene- d_6 . The resonances associated with THF appear at 3.14 and 0.78 ppm, shifted from 3.57 and 1.40 ppm for free THF.¹⁷ Structural analysis by a 2D NOESY NMR experiment indicates a *trans* arrangement between the THF and hydride ligands. The ^1H NMR spectrum of **11** reveals a resonance at -21.48 ppm attributed to the hydride ligand, appearing as overlapping doublets of triplets from coupling to phosphorus (J_{PH} 11.9 Hz) and rhodium (J_{RhH} 25.6 Hz). The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **11** contains a doublet at 34.7 ppm with a one-bond coupling to rhodium of 110.5 Hz.



Synthesis and characterization of (PNP^{Ph})MMe(I)(THF) (M = Rh, Ir) and (PNP)RhMe(I)

Methyl derivatives of the (PNP^{Ph})M fragment were obtained *via* oxidative addition of iodomethane to the corresponding iridium or rhodium alkene complexes. Addition of iodomethane to **5** in THF afforded (PNP^{Ph})IrMe(I)(THF) (**12**) after 30 min at room temperature (Scheme 2). The ¹H NMR spectrum of **12** in dichloromethane-*d*₂ contains resonances at 3.45 and 1.54 ppm for the THF ligand. In addition, a resonance at 0.83 ppm, appearing as a triplet due to coupling to phosphorus (6.5 Hz), confirms the presence of a methyl ligand on iridium. Structural analysis by 2D NOESY NMR spectroscopy indicates a *trans* relationship between the methyl and THF ligands (Scheme 2). Complex **12** also reveals an upfield ¹³C{¹H} resonance at −23.5 ppm, attributed to the iridium methyl group, and a ³¹P{¹H} NMR resonance at 9.7 ppm. No loss of THF was observed after exposure of solid **12** to vacuum for 2 h, or after removing the volatile materials under vacuum from a solution of **12** in benzene. However, when dark yellow **12** was dissolved in benzene, the solution acquired a faint green color. Upon heating this solution to 85 °C, the color of the solution changed to bright green. Furthermore, monitoring a solution of **12** in benzene-*d*₆ from 21 to 80 °C revealed a significant change in the ¹H chemical shift of the two THF signals from 0.87 to 1.24 ppm and from 3.12 to 3.57 ppm, respectively. The ¹H chemical shifts observed at 80 °C approximate those observed for free THF in benzene-*d*₆. The ³¹P{¹H} NMR resonance also undergoes a downfield shift from 13.5 to 23.9 ppm upon warming to 80 °C. The color change to green and the NMR data can be attributed to dissociation of the THF ligand to give rise to (PNP^{Ph})IrMe(I) *in situ* (similar PNP^{Ph} complexes with alkyl and halogen substituents exhibit a bright green color).^{12,18} The dissociation of the THF is reversible; upon cooling back to room temperature, the ¹H and ³¹P{¹H} NMR chemical shifts revert back to the initial values. Furthermore, the bright green color observed for the solution of **12** at higher temperatures changes to the initial yellow color.



Scheme 2

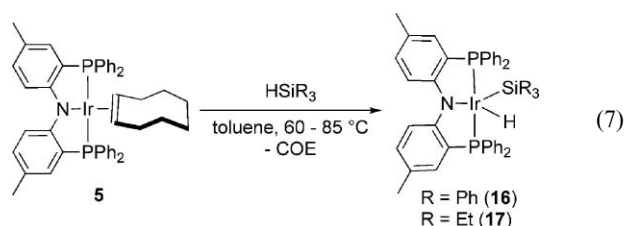
Notably, thermolysis of (PNP^{Ph})IrMe(I)(THF) in benzene to 120 °C for 20 h resulted in the formation of (PNP^{Ph})IrPh(I)(THF) (**13**) *via* C–H activation of the solvent. Compound **13** was isolated in 77% yield after precipitation from cold pentane (Scheme 2). A small-scale reaction in benzene-*d*₆ carried out in a Teflon-sealed J. Young tube at 120 °C and monitored by ¹H NMR spectroscopy indicated the formation of both CH₄ and CH₃D. The presence of CH₄ suggests that activation of the PNP ligand is also operative. Ligand activation was confirmed by the ²H NMR spectrum of

the reaction mixture, after removal of volatiles under vacuum, which revealed deuteration in the aromatic region for the PNP ligand. Previous work by Fryzuk *et al.* detailed C–H activation of arene solvents from thermolysis of [(PNP)IrMe(I)] (PNP = [−]N(SiMe₂CH₂PPh₂)₂).¹⁹ Similar to this system, C–H activation was observed only for the iridium analogs with the rhodium species not affording clean C–H activation products under these conditions (*vide infra*).

The synthesis of (PNP^{Ph})RhMe(I)(THF) (**14**) followed a procedure similar to that for **12**. Addition of iodomethane to **8** in THF at ambient temperature resulted in a color change to dark red. Isolation of **14** was achieved by removal of the volatile material under vacuum, followed by washing of the resulting red powder with pentane to give **14** in 83% yield. Interestingly, dissolution of **14** in benzene-*d*₆ at ambient temperature gave a color change to dark green indicating the presence of (PNP^{Ph})RhMe(I). In fact, THF-free (PNP^{Ph})RhMe(I) (**15**) was isolated by dissolving **14** in toluene and removing the volatiles under vacuum to give a dark green solid. The ¹H NMR spectrum of **15** contains a resonance at 2.01 ppm for the methyl ligand, appearing as a triplet of doublets due to couplings to phosphorus (*J*_{PH} 5.4 Hz) and rhodium (*J*_{RhH} 2.4 Hz). Notably, no loss of THF from (PNP^{Ph})RhH(Cl)(THF) (**11**) was observed in solution or under vacuum, despite the high *trans* effect of the hydride ligand. Furthermore, thermolyses of **11**, **14** or **15** in benzene produced intractable mixtures of products rather than a clean C–H activation product, as observed for iridium.

Reactions of silanes with (PNP^{Ph})IrL (L = COD and COE)

As part of an exploration of possible catalytic transformations of organosilanes mediated by PNP^{Ph}-supported iridium and rhodium complexes, stoichiometric reactions of Ir(I) complexes **3** and **5** with silanes were investigated. Initial efforts targeted the Si–H oxidative addition of organosilanes for the synthesis of iridium silyl hydride complexes. Heating 3.3 equiv. of Ph₃SiH with **5** in toluene to 60 °C for 20 h gave (PNP^{Ph})IrH(SiPh₃) (**16**) with the release of COE (eqn (7)). Addition of excess silane is necessary for the synthesis of **16**; reaction of a stoichiometric amount of Ph₃SiH with **5** resulted in a mixture of **5** and **16** after 20 h at 60 °C in benzene. No hydrosilation of the free alkene was observed even after heating the solution for 2 days at 100 °C, and the excess silane was not consumed in the reaction mixture. Multinuclear NMR spectroscopy verified the structure of **16** as an Ir(III) silyl hydride complex. The ²⁹Si NMR spectrum of **16** contains a resonance at −9.2 ppm, corroborating the presence of a silyl ligand.²⁰ The ¹H NMR spectrum exhibits a resonance at −19.25 ppm appearing as a triplet from coupling to phosphorus (*J*_{PH} 8.8 Hz), with a ²*J*_{SiH} coupling constant of 4 Hz for the iridium hydride. The IR spectrum of a Nujol mull of **16** contains a band at 1940 cm^{−1} attributed to the iridium hydride stretch.

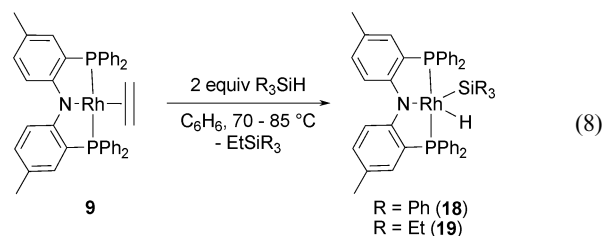


Similarly, addition of 3.5 equiv. of HSiEt_3 to **5** in toluene followed by heating in a sealed vessel for 4.5 h at 85 °C produced $(\text{PNP}^{\text{Ph}})\text{IrH}(\text{SiEt}_3)$ (**17**), isolated in 83% yield as a bright orange powder (eqn (7)). No hydrosilation of cyclooctene by the excess silane was observed after 18 h at 85 °C. The ^1H NMR spectrum of **17** contains a triplet at -18.93 ppm for the iridium hydride ligand with a $^2J_{\text{SiH}}$ coupling constant of 5.4 Hz that is similar to that of **16**. The ^{29}Si NMR resonance for the silyl ligand appears at 15.8 ppm. A weak absorbance at 1959 cm^{-1} in the IR spectrum is attributed to the Ir–H stretch.

Complex **3**, $(\text{PNP}^{\text{Ph}})\text{Ir}(\text{COD})$, also promotes the Si–H oxidative additions of tertiary silanes Ph_3SiH and Et_3SiH . However, these reactions to produce **16** and **17** require prolonged heating at 100 °C. Even at elevated temperatures, the yield of **16** and **17** remains at *ca.* 50% after 3 d at 100 °C. The more sluggish nature of these reactions results from the non-labile property of the chelating COD ligand.

Reactions of silanes with $(\text{PNP}^{\text{Ph}})\text{RhL}$ ($\text{L} = \text{COE}$ and $\text{CH}_2=\text{CH}_2$)

The synthesis of a rhodium silyl hydride complex was achieved by heating 2 equiv. of HSiPh_3 with $(\text{PNP}^{\text{Ph}})\text{Rh}(\text{CH}_2=\text{CH}_2)$ (**9**) at 85 °C in benzene. After 18 h, complete conversion to $(\text{PNP}^{\text{Ph}})\text{RhH}(\text{SiPh}_3)$ (**18**) was observed with the production of EtSiPh_3 from hydrosilation of ethylene, as confirmed by NMR spectroscopy and GC-MS (eqn (8)). Complex **18** was isolated in 72% yield after washing the resulting orange solid with pentane to remove the silane byproduct. The ^1H NMR spectrum of **18** exhibits a resonance for the Rh–H group at -13.91 ppm, appearing as a doublet of triplets due to couplings to rhodium (J_{RhH} 23.4 Hz) and phosphorus (J_{PH} 10.8 Hz). Compound **18** also exhibits a ^{29}Si NMR resonance at 17.8 ppm (J_{SiRh} 22 Hz) for the silyl ligand, and a $^{31}\text{P}\{^1\text{H}\}$ NMR peak as a doublet at 41.3 ppm (J_{RhP} 133.5 Hz). A ^{29}Si -filtered $^1\text{H}\{^{31}\text{P}\}$ NMR spectrum revealed a $^2J_{\text{SiH}}$ coupling constant of 35.9 Hz associated with the Rh–H resonance. This $^2J_{\text{SiH}}$ value suggests the presence of a weak interaction between the silyl and hydride ligands.^{20,21} The IR spectrum of **18** exhibits a peak at 1996 cm^{-1} for the Rh–H stretch, which is in the region expected for a terminal Rh–H bond.



Addition of 2 equiv. of Et_3SiH to **9** in benzene solution, followed by heating at 70 °C for 20 h, produced silyl complex $(\text{PNP}^{\text{Ph}})\text{RhH}(\text{SiEt}_3)$ (**19**), isolated in 90% yield as a brown powder (eqn (8)). A GC-MS of the reaction mixture confirmed the production of Et_4Si from the hydrosilation of ethylene. The ^1H NMR spectrum of **19** contains a resonance at -14.44 ppm for the rhodium hydride ligand appearing as an overlapping doublet of triplets (J_{RhH} 24.4 Hz; J_{PH} 11.5 Hz). Notably, the silicon satellites were observed for the hydride resonance *via* a ^{29}Si -filtered $^1\text{H}\{^{31}\text{P}\}$ NMR experiment ($^2J_{\text{SiH}}$ 33.5 Hz). The IR spectrum for **19** contains a peak at 2042 cm^{-1} attributed to the Rh–H stretching mode.

Table 1 Summary of NMR and IR data for complexes **16–20**

Compound	^1H NMR (δ M–H)	^{29}Si NMR (δ M–Si)	$^2J_{\text{SiH}}$ /Hz	IR ($\nu_{\text{M–H}}$ / cm^{-1})
$(\text{PNP})\text{IrH}(\text{SiPh}_3)$ (16)	–19.25	–9.2	4	1940
$(\text{PNP})\text{IrH}(\text{SiEt}_3)$ ^a (17)	–18.93	15.8	5.4	1959
$(\text{PNP})\text{RhH}(\text{SiPh}_3)$ (18)	–13.91	17.8	35.9	1996
$(\text{PNP})\text{RhH}(\text{SiEt}_3)$ (19)	–14.44	40.5	33.5	2042
$(\text{PNP})\text{RhH}(\text{SiPh}_2\text{Cl})$ (20)	–14.31	38.4	36.6	not observed

^a NMR acquired in CD_2Cl_2 .

Reaction of 1 equiv. of Ph_2SiHCl with **8** in benzene solution, followed by heating for 2 days at 75 °C, gave complete conversion to $(\text{PNP}^{\text{Ph}})\text{RhH}(\text{SiPh}_2\text{Cl})$ (**20**) with the release of cyclooctene. The ^1H NMR spectrum of **20** contains a resonance at -14.31 ppm appearing as an overlapping doublet of triplets, arising from coupling to rhodium (23.9 Hz) and phosphorus (10.3 Hz). Similar to **18** and **19**, a $^2J_{\text{SiH}}$ coupling constant of 36.6 Hz was determined *via* a ^{29}Si filtered $^1\text{H}\{^{31}\text{P}\}$ NMR experiment. The ^{29}Si NMR shift for the silyl ligand was observed at 38.4 ppm with a coupling to rhodium of 26 Hz. Selected NMR and IR data for silyl complexes **16–20** are summarized in Table 1.

The differences between the spectroscopic data for iridium *vs.* rhodium silyl hydride complexes warrant further discussion. Of notable interest is the difference in $^2J_{\text{SiH}}$ coupling constants between iridium complexes **16** and **17**, and rhodium complexes **18**, **19**, and **20**. Complexes **16** and **17** exhibit low coupling constants below 10 Hz, indicative of complete oxidative addition of the Si–H bond.^{20,21} In contrast, the larger coupling constants of *ca.* 35 Hz for **18**, **19** and **20**, suggest a weak Si–H interaction, although some caution should be used in interpreting observed coupling constants as these result from the addition of one- and two-bond couplings which are usually of opposite signs.^{21b,22} IR spectroscopy for the M–H stretches do not provide further evidence for non-classical Si–H interactions in the rhodium complexes, as $\nu(\text{MH})$ stretching frequencies of η^2 -silane late transition-metal complexes are usually red shifted to values *ca.* 200–400 cm^{-1} lower than those observed for **18** and **19**.^{20,22} In fact, comparison between the IR frequencies for the $\nu(\text{MH})$ stretches do not reveal any significant differences between the Ir and Rh complexes. However, a weak interaction between the silyl ligand and the rhodium hydride ligand in **18**, **19** and **20** is indicated by comparison of the NMR data of **18**, **19** and **20** with that of the iridium analogs **16** and **17**.

Non-classical Si–H interactions are sometimes described as arrested oxidative additions, and analogous interpretations have been used to describe dihydrogen complexes.²³ In general, the extent of oxidative addition is related to the electronic properties of the transition metal fragment, with electron deficient metal centers being less capable of full oxidative additions.^{23,24} Similar to the complexes supported by PNP^{Ph} , rhodium silyl hydride complexes supported by PNP^{IPr} exhibit $^2J_{\text{SiH}}$ coupling constants of *ca.* 30 Hz,²⁵ whereas analogous $(\text{PNP}^{\text{IPr}})\text{Ir}$ complexes possess coupling constants lower than 10 Hz.⁷ Hence, in the $(\text{PNP})\text{M}$ ($\text{M} = \text{Rh}, \text{Ir}$) systems investigated so far, the nature of the metal center appears to be more important than that of the PNP ligand (PNP^{IPr} *vs.* PNP^{Ph}). In several examples of complexes with similar ligands, non-classical dihydrogen complexes were more commonly found for the 2nd row transition metal analogs.²⁶ Limited examples of 4d

and 5d complexes containing non-classical Si–H interactions and supported by similar ancillary ligands are available for comparison. In one such example for group 9 metals, the orthometallated silyl hydride $[\text{Cp}^*(\text{PMe}_3)\text{Ir}(\text{H})(\text{SiPh}_2\text{C}_6\text{H}_4)][\text{B}(\text{C}_6\text{F}_5)_4]$ ²⁷ was better described as an Ir(v) silyl hydride complex whereas the rhodium analog was described as the Rh(III) species $[\text{Cp}^*(\text{PMe}_3)\text{Rh}(\eta^2\text{-HSiPh}_2\text{C}_6\text{H}_4)][\text{B}(\text{C}_6\text{F}_5)_4]$ ($^2J_{\text{SiH}} = 84 \text{ Hz}$),²⁸ from the features observed by NMR spectroscopy. Hence, the complexes presented in this contribution present another example of 2nd and 3rd row metals supported by the same ancillary ligand, in which only the 2nd row transition metal complex contains a non-classical interaction.

Structures of iridium and rhodium silyl hydride complexes

Further investigations of possible structural differences between PNP^{Ph} iridium and rhodium silyl hydride complexes included X-ray diffraction experiments. Crystals suitable for X-ray diffraction were obtained by vapor diffusion of pentane into a concentrated solution of $(\text{PNP}^{\text{Ph}})\text{IrH}(\text{SiPh}_3)$ (**16**) in $\text{C}_6\text{H}_5\text{F}$ at -30°C (Fig. 3). The geometry about the iridium atom is a distorted trigonal bipyramid with the phosphorus atoms occupying the apical positions, and a meridional binding of the PNP ligand to the iridium center as indicated by a P–Ir–P angle of $159.81(4)^\circ$. The iridium hydride was not located from the Fourier map, but is presumed to occupy the empty site in the equatorial plane. The Ir–Si distance at $2.322(1) \text{ \AA}$ is within the normal values reported for an iridium silyl bond.²⁹ The N–Ir–Si bond angle of $140.0(1)^\circ$ is widened from that of the ideal trigonal bipyramid structure, as previously documented for PNP-supported five-coordinate complexes with a d^6 electronic configuration.³⁰

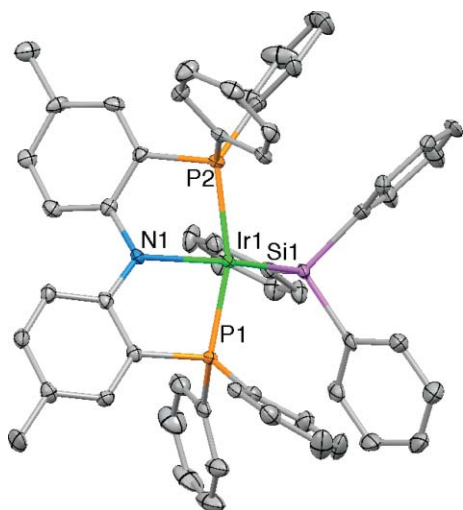


Fig. 3 Molecular structure of **16** displaying thermal ellipsoids at the 50% probability level. H-atoms, and the fluorobenzene molecule, have been omitted for clarity. Selected bond lengths (\AA): Ir(1)–Si(1) = $2.322(1)$, Ir(1)–P(1) = $2.280(1)$, Ir(1)–P(2) = $2.298(1)$, Ir(1)–N(1) = 2.067 . Selected bond angles ($^\circ$): P(1)–Ir(1)–P(2) = $159.81(4)$, N(1)–Ir(1)–Si(1) = $140.04(11)$.

Single crystals of $(\text{PNP}^{\text{Ph}})\text{RhH}(\text{SiPh}_3)$ (**18**) were obtained by vapor diffusion of pentane into a concentrated solution of **18** in toluene at -30°C . Crystals of **18** are isomorphous with **16** ($P2_1/c$ space group; similar lattice parameters, Fig. 4). The rhodium hydride was located and refined in the structure. The Rh–H bond

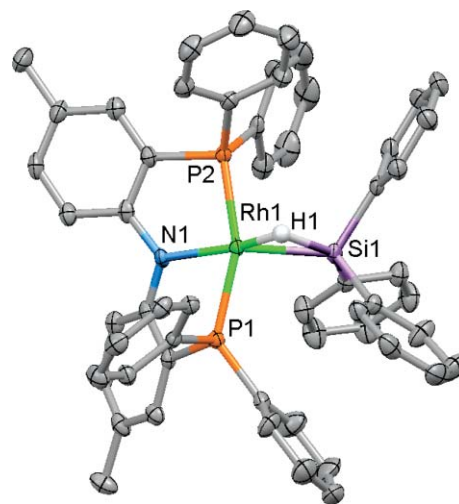


Fig. 4 Molecular structure of **18** displaying thermal ellipsoids at the 50% probability level. H-atoms except for H(1) have been omitted for clarity. Selected bond lengths (\AA): Si(1)–H(1) = $1.83(3)$, Rh(1)–H(1) = $1.49(3)$, Rh(1)–Si(1) = $2.315(1)$. Selected bond angles ($^\circ$): N(1)–Rh(1)–H(1) = $166.1(11)$, N(1)–Rh(1)–Si(1) = $141.65(7)$, P(1)–Rh(1)–P(2) = $159.68(3)$.

distance, $1.49(3) \text{ \AA}$, and the Rh–Si bond distance of $2.3148(8) \text{ \AA}$ are within normal bonding distances for rhodium hydride and silyl ligands.³¹ Interestingly, the crystal structure revealed a short Si–H distance of $1.83(3) \text{ \AA}$. A Si–H bond distance below 2.0 \AA is considered to be in the bonding range,^{20,21a} and the observed value is consistent with the $^2J_{\text{SiH}}$ coupling constant of 35.9 Hz and with the presence of a Si–H interaction. For comparison, transition-metal η^2 -silane complexes exhibit Si–H distances ranging between 1.6 and 1.9 \AA , whereas free silanes exhibit Si–H bond lengths of *ca.* 1.5 \AA .³² Furthermore, the N–Rh–H and N–Rh–Si bond angles are widened to $166.1(1)^\circ$ and $141.65(7)^\circ$, respectively. Comparisons of geometrical parameters for **18** with those for the structure of $(\text{PNP}^{\text{Ph}})\text{RhH}(\text{SiMe}_2\text{Cl})$, reported by Ozerov *et al.* reveal only small differences, since the latter complex possesses a slightly shorter Rh–Si bond length (2.26 \AA), a narrower N–Rh–Si bond angle ($136.83(4)^\circ$), and a slightly longer Si–H bond distance ($1.93(2) \text{ \AA}$).²⁵ Furthermore, only small structural differences are observed between **16** and **18**, despite the differences in observed $^2J_{\text{SiH}}$ coupling constants. However, it is difficult to conclusively address differences in Si–H distances between **16** and **18** without determination of accurate positions for both hydrides, or full computation analysis.

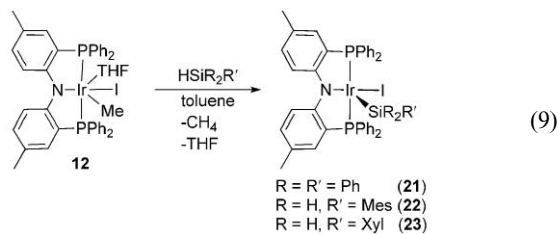
Correlations between structural parameters and $^2J_{\text{SiH}}$ coupling constants for rhodium and iridium complexes are hampered by the lack of availability of both Si–H distances from X-ray structures (as hydrides are often not located from the difference Fourier map) and $^2J_{\text{SiH}}$ coupling constants (as these are often not reported or obtained). Isostructural complexes for rhodium and iridium disilyl dihydrides $\text{Cp}^*\text{M}(\text{H})_2(\text{SiEt}_3)_2$ ³³ and $(\text{PSiP})\text{MHCl}$ ³⁴ ($\text{M} = \text{Rh}$ and Ir , $\text{PSiP} = [(2\text{-Cy}_2\text{PC}_6\text{H}_4)_2\text{SiMe}]$) have been reported. Neutron diffraction studies of both $\text{Cp}^*\text{Rh}(\text{H})_2(\text{SiEt}_3)_2$ and $\text{Cp}^*\text{Ir}(\text{H})_2(\text{SiEt}_3)_2$ indicated that these are M(v) silyl dihydride species, and this is consistent with the $^2J_{\text{SiH}}$ value for the rhodium analogue of 7.9 Hz . In addition, X-ray crystallography for the isostructural complexes $(\text{PSiP})\text{RhHCl}$ and $(\text{PSiP})\text{IrHCl}$ revealed

similar geometrical parameters with Si–H distances of 2.14(3) Å and 2.24(5) Å. These interatomic distances are usually assumed to indicate the lack of a significant non-classical interaction.³² The $^2J_{\text{SiH}}$ coupling constants for (PSiP)RhHCl and (PSiP)IrHCl are lower than 10 Hz, and consistent with long Si–H distances. Thus, the observed differences in coupling constants between **16** and **18**, and the short Si–H distance in the X-ray structure of **18**, suggest that the rhodium complex **18** contains a weak Si–H interaction that is absent in the iridium analogue.

Reactions of Rh(III) and Ir(III) complexes with silanes

Reactions of the Rh(III) complexes (PNP^{Ph})RhH(Cl)(THF) (**11**), (PNP^{Ph})RhMe(I)(THF) (**14**) and (PNP^{Ph})RhMe(I) (**15**) with a variety of silanes in benzene at room temperature, or with slight heating (to 75 °C), did not afford silyl complexes of the type (PNP^{Ph})RhX(SiR₃). Organosilanes employed in these reactions included HSiPh₃, H₂SiMes₂, H₂SiⁱBu₂, H₃SiPh, H₃SiXyl (Xyl = 3,5-dimethylphenyl), H₃SiMes and H₃SiDmp (Dmp = 2,6-dimesitylphenyl). The reaction mixtures typically included intractable mixtures of rhodium-containing complexes or decomposition products. Interestingly, the reaction of 1 equiv. of Ph₂SiH₂ with **11** in benzene for 24 h at ambient temperature produced complex (PNP^{Ph})RhH(SiPh₂Cl) (**20**) as a major product, with Si–Cl bond formation in this reaction. In addition, the ¹H NMR spectrum for the reaction mixture involving excess PhSiH₃ with **11** in benzene-*d*₆ revealed the formation of H₂SiPh₂, HSiPh₃, H₂, and SiH₄, among other unidentified silane species, suggesting that metal-catalyzed redistribution at silicon may readily complicate reaction mixtures of this kind.

In contrast, addition of 1 equiv. of HSiPh₃ to (PNP^{Ph})IrMe(I)(THF) (**12**) in toluene followed by heating at 60 °C for 18 h resulted in formation of (PNP^{Ph})IrI(SiPh₃) (**21**) with loss of CH₄ and THF (eqn (9)). Complex **21** can be isolated as a bright green powder in 85% yield, and is analytically pure by NMR spectroscopy and combustion analysis. Presumably, the strong *trans* effect of the silyl ligand³⁵ favors dissociation of THF and stabilizes the 5-coordinate structure. The resulting green complex is thermally stable, and does not decompose at ambient temperature or after heating at 60 °C for 18 h. Compound **21** exhibits a ²⁹Si NMR resonance at –1.5 ppm for the silyl ligand and a ³¹P{¹H} NMR resonance at 22.8 ppm for the PNP^{Ph} ligand.



Similarly, reactions of monosubstituted silane substrates H₃SiMes (Mes = 2,4,6-Me₃C₆H₃) and H₃SiXyl (Xyl = 3,5-Me₂C₆H₃) with **12** afforded (PNP^{Ph})IrI(SiH₂Mes) (**22**) and (PNP^{Ph})IrI(SiH₂Xyl) (**23**), respectively. In contrast to **21**, the reactions of the primary silanes and **12** are complete within 15 min at ambient temperature. The ¹H NMR spectrum of **22** exhibits a Si–H resonance appearing at 3.88 ppm ($^1J_{\text{SiH}}$ 199.7 Hz) and the ²⁹Si NMR shift is at –34.4 ppm. Similarly, complex **23** exhibits a resonance at 4.12 ppm in the ¹H NMR spectrum for the Si–H

group and a resonance at –23.2 ppm for the silyl ligand in the ²⁹Si NMR spectrum. Complexes **22** and **23** are thermally sensitive in solution and decompose to a complex mixture of products after 24 h at ambient temperature, as indicated by NMR spectroscopy. The structures of complexes **21**, **22** and **23** are believed to be square pyramidal (as depicted in eqn (9)) by analogy with other 5-coordinate complexes featuring halide and high *trans*-effect ligands (such as alkyl ligands).³⁰

Attempted synthesis of PNP^{Ph}-supported rhodium and iridium silylene complexes

Several established synthetic routes to transition metal silylene complexes involve chemical modification of silyl ligands.⁵ Two common routes feature abstraction of an anionic substituent (originally bound to silicon or the metal center). Abstraction from the metal may promote α -migration from silicon to the transition metal to produce silylene and hydride ligands. Several of the rhodium and iridium silyl complexes described above were envisioned as good precursors for the synthesis of silylene complexes analogous to those supported by PNP^{iPr}.⁷ For example, abstraction of a substituent on the silyl ligand of (PNP^{Ph})RhH(SiPh₂Cl) (**20**) appears to be a possible route to the silylene complex [(PNP^{Ph})(H)Rh=SiPh₂]⁺. However, attempts to prepare a silylene complex from **20** through this approach were not successful. For example, the combination of Li(OEt₂)₃B(C₆F₅)₄ and **20** in fluorobenzene at 60 °C gave no reaction (after 28 h). Furthermore, addition of [CPh₃][B(C₆F₅)₄] or AgOTf to **20** in bromobenzene-*d*₅ or fluorobenzene gave a mixture of complexes at ambient temperature.

Iridium was expected to better support a silylene ligand, due to the inherently stronger metal–ligand bonds for this 3rd row transition metal. In fact, rhodium silylene complexes are still quite rare, with no terminal silylene species known to date. Thus, the reactions of complexes (PNP^{Ph})IrI(SiPh₃) (**21**), (PNP^{Ph})IrI(SiH₂Mes) (**22**) and (PNP^{Ph})IrI(SiH₂Xyl) (**23**) were explored to determine whether these species could serve as precursors to iridium silylene complexes. Reactions of interest involved abstraction or chemical modification of a halide ligand on the metal center. Reagents for abstraction of anionic ligands from compounds **21**, **22** and **23** included AgOTf, AgB(C₆F₅)₄, B(C₆F₅)₃, Li(OEt₂)₃B(C₆F₅)₄, CPh₃OTf, and [CPh₃][B(C₆F₅)₄] but these attempts resulted in no conversion or a complex mixture of products. Reagents utilized to induce α -hydrogen eliminations³⁶ from **22** and **23** included LiN(SiMe₃)₂, LiNⁱPr₂, LiNp, LiCH₂SiMe₃, and MeLi, but these attempts resulted in intractable mixtures of products or lack of reaction under a variety of conditions (room temperature to 65 °C in fluorobenzene or bromobenzene-*d*₅). As further illustrated by difficulties encountered in the PNP^{Ph} system, the synthetic accessibility of transition metal silylene complexes depends strongly on the electronic and steric properties of the transition metal center and the silylene ligand.

Concluding remarks

Initial synthetic studies of rhodium and iridium complexes supported by the PNP^{Ph} ligand indicate that a number of clean transformations are possible. Notably, significant differences in reactivity and structure were observed between the rhodium and

iridium analogs. For example, thermolysis of (PNP^{Ph})IrMe(I)(THF) (**12**) in benzene resulted in the formation of (PNP^{Ph})IrPh(I)(THF) (**13**) *via* C–H activation of benzene, whereas thermolysis of rhodium(III) analogs **11**, **14** and **15** resulted in decomposition to multiple species. Further differences between rhodium and iridium complexes supported by the PNP^{Ph} ligand are observed in spectroscopic characteristics for silyl hydride analogs. The rhodium complexes exhibit J_{SiH} coupling constants of 35 Hz, whereas the iridium silyl hydride complexes contain small coupling constants of less than 10 Hz. X-Ray crystallography for silyl hydride complexes revealed similar structures for rhodium and iridium analogues, but the structure of the rhodium silyl hydride complex **18** contains a short Si–H distance that is consistent with a non-classical Si–H interaction.

This contribution also highlights the chemical differences that can result from altering the electronics at the transition metal center, by changing electron-donating phosphines containing isopropyl substituents by more electron-deficient phosphine donors containing phenyl substituents. Notably, attempts at the synthesis of rhodium or iridium silylene complexes supported by PNP^{Ph} ligands were unsuccessful, whereas a variety of iridium silylene complexes supported by PNP^{Pr} have been obtained.⁷ Current efforts include the exploration of other pincer systems amenable to the study of electronic and steric factors influencing the synthesis and reactivity of silyl and silylene species.

Experimental

General considerations

All experiments were carried out under a nitrogen atmosphere using standard Schlenk techniques or an inert atmosphere (N₂) glovebox. Olefin impurities were removed from pentane by treatment with concentrated H₂SO₄, 0.5 N KMnO₄ in 3 M H₂SO₄, and NaHCO₃. Pentane was then dried over MgSO₄ and stored over activated 4 Å molecular sieves, and dried over alumina. Thiophene impurities were removed from benzene and toluene by treatment with H₂SO₄ and saturated NaHCO₃. Benzene and toluene were then dried over CaCl₂ and further dried over alumina. Tetrahydrofuran, diethyl ether, dichloromethane, hexanes, benzene, toluene and pentane were dried using a VAC Atmospheres solvent purification system. Fluorobenzene was dried over P₂O₅, degassed and distilled under N₂. Benzene-*d*₆ was dried by vacuum distillation from Na/K alloy. C₆D₅Br was refluxed over CaH₂ for 20 h and then distilled under nitrogen. Dichloromethane-*d*₂ was dried by vacuum distillation from CaH₂. PNP^{Ph}H (**1**),¹⁰ [(COE)₂IrCl]₂,³⁷ [(COD)RhCl]₂,³⁸ [(COE)₂RhCl]₂³⁹ and [(CH₂=CH)₂RhCl]₂⁴⁰ were prepared according to literature methods. [(COD)IrCl]₂ was synthesized by refluxing [(COE)₂IrCl]₂ with excess COD in toluene for 18 h. All other chemicals were purchased from commercial sources, and used without further purification.

NMR spectra were recorded using Bruker AV-600, DRX-500, AV-500, AVB-400, and AVQ-400 spectrometers. ¹H NMR spectra were referenced internally by the residual solvent proton signal relative to tetramethylsilane. ¹³C{¹H} NMR spectra were referenced internally relative to the ¹³C signal of the NMR solvent relative to tetramethylsilane. ¹⁹F{¹H} spectra were referenced relative to a C₆F₆ external standard. ³¹P{¹H} spectra

were referenced relative to an 85% H₃PO₄ external standard. ²⁹Si NMR spectra were referenced relative to a tetramethylsilane standard and obtained *via* 2D ¹H ²⁹Si HMBC experiments unless specified otherwise. All spectra were recorded at room temperature unless otherwise noted. Virtual couplings are denoted by “v”, complex multiplets by “m” and broad resonances by “br”. In ¹³C{¹H} NMR spectra resonances obscured by the solvent signal are omitted. Elemental analyses were performed by the College of Chemistry Microanalytical Laboratory at the University of California, Berkeley. Infrared spectra were recorded on a Nicolet Nexus 6700 FTIR spectrometer with a liquid-nitrogen-cooled MCT-B detector. Measurements were made at a resolution of 4.0 cm^{−1}.

[(PNP^{Ph}H)Ir(COD)]Cl (2**).** A 50 mL Schlenk flask was loaded with **1** (0.20 g, 0.35 mmol), [(COD)IrCl]₂ (0.10 g, 0.15 mmol), and 30 mL of toluene. The reaction mixture was stirred at ambient temperature for 1 h after which a fine white precipitate formed, and then concentrated to *ca.* 10 mL and cooled to 0 °C. The resulting white solid was collected *via* filtration and washed with pentane to give **2** as a white powder. Yield: 0.27 g (91%). ¹H NMR (CD₂Cl₂, 500 MHz): δ 11.65 (1H, br s, NH), 8.01 (2H, dd, $J_{\text{PH}} = 8.3$ Hz, $J = 3.4$ Hz, ArH), 7.63 (4H, m, ArH), 7.46 (6H, m, ArH), 7.31 (2H, d, $J_{\text{PH}} = 6.1$ Hz, ArH), 7.25 (2H, t, $J = 7.5$ Hz, ArH), 7.14 (6H, m, ArH), 7.03 (4H, t, $J = 7.1$ Hz, ArH), 3.78 (4H, br s, HC=CH), 2.28 (6H, s, ArMe), 1.41 (4H, m, CH₂), 1.34 (4H, m, CH₂). ¹³C{¹H} NMR (CD₂Cl₂, 125.8 MHz): δ 155.4 (m), 138.7 (t, $J_{\text{CP}} = 2.2$ Hz), 136.8 (dd, $J_{\text{CP}} = 50.1$ Hz, $J_{\text{CP}} = 3.0$ Hz), 135.4 (dd, $J_{\text{CP}} = 46.2$ Hz, $J_{\text{CP}} = 3.0$ Hz), 134.0 (t, $J_{\text{CP}} = 6.3$ Hz), 133.3 (s), 132.5 (t, $J_{\text{CP}} = 5.6$ Hz), 132.0 (s), 131.6 (dd, $J_{\text{CP}} = 39.8$ Hz, $J_{\text{CP}} = 5.1$ Hz), 130.5 (s), 129.8 (s), 128.7 (t, $J_{\text{CP}} = 4.8$ Hz), 128.6 (t, $J_{\text{CP}} = 4.9$ Hz), 126.5 (t, $J_{\text{CP}} = 5.0$ Hz) (ArC), 63.8 (br, HC=CH), 31.7 (s, CH₂), 20.7 (s, ArMe). ³¹P{¹H} NMR (CD₂Cl₂, 202.5 MHz): δ 13.7 (s). Anal. Calcd for C₅₃H₅₃NClIrP₂ (includes one equivalent of toluene): C, 64.07; H, 5.38; N, 1.41. Found: C, 64.08; H, 5.46; N, 1.36.

(PNP^{Ph}H)Ir(COD) (3**).** A 50 mL Schlenk flask was loaded with **2** (0.200 g, 0.203 mmol), lithium bis(trimethylsilyl)amide (0.034 g, 0.203 mmol) and 20 mL of toluene. The reaction mixture was stirred for 45 min, and it was then filtered and dried under vacuum. The bright yellow solid was washed with pentane, collected by filtration and dried under vacuum. Yield: 0.120 g (69%). Alternative synthesis: A solution of lithium bis(trimethylsilyl)amide (0.03 g, 0.18 mmol) in toluene (2 mL) was added to a solution of **1** (0.10 g, 0.18 mmol) in toluene (7 mL) to afford a bright yellow solution. After 45 min, [(COD)IrCl]₂ (0.06 g, 0.18 mmol) was added to the stirred reaction mixture. After 1 h, the reaction mixture was filtered through Celite to remove all insoluble material. The supernatant was concentrated to *ca.* 2 mL of toluene, layered with *ca.* 10 mL of pentane and placed in a −25 °C freezer to afford a bright yellow solid. Yield: 0.11 g (72%). ¹H NMR (CD₂Cl₂, 500 MHz): δ 7.63 (4H, m, ArH), 7.42 (6H, m, ArH), 7.21–7.13 (8H, ov m, ArH), 7.10 (2H, t, $J = 7.2$ Hz, ArH), 6.93 (4H, t, $J = 7.2$ Hz, ArH), 6.81 (2H, d, $J = 8.2$ Hz, ArH), 3.58 (2H, m, CH=CH), 2.64 (2H, br m, CH=CH), 2.22 (6H, s, ArMe), (2H, spt, $J = 6.2$ Hz, CH₂), 1.34 (2H, m, CH₂), 1.10 (2H, m, CH₂), 0.83 (2H, spt, $J = 5.9$ Hz, CH₂). ¹³C{¹H} NMR (CD₂Cl₂, 125.8 MHz): δ 162.0 (d, $J_{\text{CP}} = 26.9$ Hz), 138.9 (d, $J_{\text{CP}} = 44.1$ Hz), 137.8 (d, $J_{\text{CP}} = 28.8$ Hz), 133.5 (m), 133.1 (s), 132.8 (m), 131. (d, $J_{\text{CP}} = 53.3$ Hz), 130.8 (s), 129.1 (d,

$J_{\text{CP}} = 29.2$ Hz), 128.4 (m), 128.2 (m), 126.8 (m), 119.2 (m) (ArC), 66.1 (br, CH=CH), 60.3 (dd, $J_{\text{CP}} = 27.8$ Hz, $J_{\text{CP}} = 5.4$ Hz, CH=CH), 32.3 (ov s, CH_2), 31.7 (ov s, CH_2), 20.6 (s, ArMe). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 202.5 MHz): δ 13.5 (s). Anal. Calcd for $\text{C}_{46}\text{H}_{44}\text{NiIrP}_2$: C, 63.87; H, 5.13; N, 1.62. Found: C, 63.48; H, 5.07; N, 1.69.

(PNP^{Ph}H)IrHCl₂ (4). A solution of **1** (0.10 g, 0.18 mmol) in 3 mL of benzene was added to a stirred suspension of $[(\text{COE})_2\text{IrCl}]_2$ (0.08 g, 0.09 mmol) in 1 mL of benzene. The reaction mixture was stirred at ambient temperature for 18 h. Afterward, a white precipitate was collected by filtration, washed sparingly with benzene, and dried under vacuum. Yield: 0.05 g (33%). ^1H NMR (CD_2Cl_2 , 500 MHz): δ 7.88 (2H, dd, $J = 8.2$ Hz, $J_{\text{PH}} = 3.5$ Hz, ArH), 7.56 (4H, vt, ArH), 7.46 (2H, d, $J = 8.2$ Hz, ArH), 7.37 (2H, m, ArH), 7.32 (6H, ov m, ArH), 7.22 (1H, br s, NH), 7.06 (2H, m, ArH), 6.73 (8H, m, ArH), 2.35 (6H, s, ArMe), -18.43 (1H, td, $^2J_{\text{PH}} = 14.2$ Hz, $J = 2.1$ Hz, IrH). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 150.9 MHz): δ 151.3 (dd, $J_{\text{CP}} = 8.2$ Hz, $J_{\text{CP}} = 4.1$ Hz), 138.8 (t, $J_{\text{CP}} = 3.3$ Hz), 136.2 (t, $J_{\text{CP}} = 5.1$ Hz), 135.0 (dd, $J_{\text{CP}} = 60.2$ Hz, $J_{\text{CP}} = 4.5$ Hz), 133.9 (s), 133.5 (s), 133.0 (t, $J_{\text{CP}} = 4.8$ Hz), 131.1 (br d, $J_{\text{CP}} = 62.6$ Hz), 131.1 (s), 130.6 (d, $J_{\text{CP}} = 7.8$ Hz), 130.4 (dd, $J_{\text{CP}} = 68.3$ Hz, $J_{\text{CP}} = 3.4$ Hz), 130.1 (s), 128.4 (t, $J_{\text{CP}} = 5.4$ Hz), 128.0 (t, $J_{\text{CP}} = 4.3$ Hz), 127.9 (t, $J_{\text{CP}} = 5.6$ Hz), 124.6 (d, $J_{\text{CP}} = 3.2$ Hz), 115.7 (d, $J_{\text{CP}} = 21.0$ Hz) (ArC), 21.16 (s, ArMe). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 202.5 MHz): δ 15.4 (s). Anal. Calcd for $\text{C}_{38}\text{H}_{34}\text{NCl}_2\text{IrP}_2$: C, 55.01; H, 4.13; N, 1.69. Found: C, 54.67; H, 4.05; N, 1.77.

(PNP^{Ph})Ir(COE) (5). A 100 mL Schlenk flask was loaded with **1** (1.81 g, 3.20 mmol), lithium bis(trimethylsilyl)amide (0.535 g, 3.20 mmol) and 50 mL of $\text{C}_6\text{H}_5\text{F}$. The reaction solution was stirred for 1 h at ambient temperature to give a bright yellow solution. The solution was added to a stirred suspension of $[(\text{COE})_2\text{IrCl}]_2$ (1.43 g, 1.60 mmol) in 20 mL of $\text{C}_6\text{H}_5\text{F}$ and stirring was continued for 1 h. The reaction mixture was filtered through Celite and the remaining salts were washed with CH_2Cl_2 (20 mL). The resulting bright red solution was concentrated to a thick slurry (10 mL) and washed with hexanes (50 mL). The resulting bright orange powder was collected by filtration and dried under vacuum to give a bright orange powder. Yield: 2.33 g (84%). ^1H NMR (C_6D_6 , 300 MHz): δ 8.03 (8H, br, ArH), 7.57 (2H, d, $J = 8.2$ Hz, ArH), 7.18 (2H, s, ArH), 7.04 (12H, m, ArH), 6.70 (2H, d, $J = 8.6$ Hz, ArH), 2.98 (2H, br m, HC=CH), 2.19 (2H, d, $J = 12.9$ Hz, CH_2), 2.01 (6H, s, ArMe), 1.43–1.07 (10H, ov m, CH_2). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 125.8 MHz): δ 162.8 (br m), 134.3 (br), 132.9 (s), 132.2 (s), 130.0 (s), 128.5 (s), 126.8 (t, $J_{\text{CP}} = 3.8$ Hz), 115.5 (br) (ArC), 49.13 (s, HC=CH), 32.4 (s, CH_2), 31.9 (s, CH_2), 26.9 (s, CH_2), 20.3 (s, ArMe). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 202.5 MHz): δ 28.9 (br), 27.8 (br). Anal. Calcd for $\text{C}_{46}\text{H}_{46}\text{NiIrP}_2$: C, 63.72; H, 5.35; N, 1.62. Found: C, 63.33; H, 5.50; N, 2.00.

(PNP^{Ph})Ir(PPh₃) (6). A solution of triphenylphosphine (0.018 g, 0.07 mmol) in 1 mL of toluene was added to a solution of **5** (0.060 g, 0.07 mmol) in 5 mL of toluene and the resulting solution was stirred for 20 h. The reaction mixture was filtered, and then concentrated to ca. 1 mL under vacuum. Bright orange crystals were obtained from a toluene (1 mL) and pentane (4 mL) mixture at -30 °C. Yield: 0.056 g (73%). ^1H NMR (C_6D_6 , 500 MHz): δ 7.81 (2H, dt, $J_{\text{PH}} = 6.2$ Hz, $J = 2.3$ Hz, ArH), 7.65 (8H, vq, ArH),

7.43 (6H, t, $J = 9.1$ Hz, ArH), 7.01 (2H, m, ArC), 6.94–6.87 (12H, ov m, ArH), 6.77–6.71 (5H, ov m, ArH), 6.66 (6H, td, $J = 7.8$ Hz, $J = 1.5$ Hz, ArH), 1.99 (6H, s, ArMe). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 125.8 MHz): δ 161.8 (t, $J_{\text{CP}} = 11.7$ Hz), 137.8 (dt, $J_{\text{CP}} = 48.4$ Hz, $J_{\text{CP}} = 2.31$ Hz), 135.1 (t, $J_{\text{CP}} = 24.5$ Hz), 134.8 (d, $J_{\text{CP}} = 11.1$ Hz), 133.9 (t, $J_{\text{CP}} = 6.3$ Hz), 133.2, 131.8, 129.0, 128.4 (d, $J_{\text{CP}} = 1.9$ Hz), 127.0 (d, $J_{\text{CP}} = 9.5$ Hz), 125.4 (t, $J_{\text{CP}} = 3.7$ Hz), 116.1 (br m) (ArC), 20.3 (s, ArMe). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 202.5 MHz): δ 34.7 (d, $^2J_{\text{PP}} = 18.2$ Hz, PNP), 19.6 (t, $^2J_{\text{PP}} = 18.2$ Hz, PPh₃). Anal. Calcd for $\text{C}_{63}\text{H}_{55}\text{NiIrP}_3$ (includes one equivalent of toluene, as evidenced by ^1H NMR spectroscopy): C, 68.09; H, 4.99; N, 1.26. Found: C, 67.86; H, 4.98; N, 1.48.

(PNP^{Ph}H)RhHCl₂ (7). A solution of **1** (0.10 g, 0.18 mmol) in 3 mL of benzene was added to a solution of $[(\text{COE})_2\text{RhCl}]_2$ (0.06 g, 0.09 mmol) in 1 mL of benzene. After 2 h, the white precipitate was collected by filtration, washed sparingly with benzene, and dried under vacuum. Yield: 0.05 g. The white powder was found to contain **7** as the major product. ^1H NMR (CD_2Cl_2 , 500 MHz): δ 7.86 (2H, dd, $J = 8.1$ Hz, $J_{\text{PH}} = 3.6$ Hz, ArH), 7.60 (4H, m, ArH), 7.46 (2H, d, $J = 9.0$ Hz, ArH), 7.39 (2H, d, $J = 6.9$ Hz, ArH), 7.32 (6H, m, ArH), 7.08 (2H, t, $J = 7.1$ Hz, ArH), 7.00 (1H, br s, NH), 6.75 (8H, ov m, ArH), 2.34 (6H, s, ArMe), -14.00 (1H, m, RhH), $J_{\text{PH}} = \text{ca. } 14$ Hz, $J_{\text{RHH}} = 11$ Hz, $J_{\text{HH}} = 3$ Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 150.9 MHz): δ 149.8 (m), 138.5 (t, $J_{\text{CP}} = 5.1$ Hz), 133.7 (s), 133.6 (s), 132.9 (t, $J_{\text{CP}} = 5.0$ Hz), 131.1 (s), 130.2 (s), 128.4 (t, $J_{\text{CP}} = 5.3$ Hz), 128.3 (t, $J_{\text{CP}} = 4.6$ Hz), 128.0 (t, $J_{\text{CP}} = 6.8$ Hz) (ArC), 21.2 (s, ArMe). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 202.5 MHz): δ 55.2 (d, $J_{\text{RHP}} = 131.7$ Hz).

(PNP^{Ph})Rh(COE) (8). A 100 mL Schlenk flask was loaded with **1** (1.16 g, 2.05 mmol), lithium bis(trimethylsilyl)amide (0.343 g, 2.05 mmol) and 40 mL of toluene. The reaction solution was stirred for 1 h at ambient temperature to produce a bright yellow solution. This solution was added to a stirred suspension of $[(\text{COE})_2\text{RhCl}]_2$ (0.736 g, 1.03 mmol) in 10 mL of toluene. After 30 min, the reaction mixture was filtered to remove the LiCl byproduct. The resulting red solution was taken to dryness under vacuum, and the resulting solid was washed with 30 mL of hexanes and collected by filtration to afford **8** as an orange powder. Yield: 1.30 g (83%). ^1H NMR (C_6D_6 , 500 MHz): δ 8.03 (8H, m, ArH), 7.54 (2H, dt, $J = 8.5$ Hz, $J = 2.3$ Hz, ArH), 7.09–7.01 (14H, ov m, ArH), 6.69 (2H, dd, $J = 8.5$ Hz, $J = 1.6$ Hz, ArH), 3.60 (2H, br d, $J = 5.8$ Hz, HC=CH), 2.25 (2H, d, $J = 13.0$ Hz, CH_2), 2.01 (6H, s, ArMe), 1.37–1.16 (8H, ov m, CH_2), 0.96 (2H, m, CH_2). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 125.8 MHz): δ 162.0 (t, $J_{\text{CP}} = 14.7$ Hz), 135.5 (t, $J_{\text{CP}} = 18.4$ Hz), 134.5 (t, $J_{\text{CP}} = 6.6$ Hz), 133.1 (s), 132.8 (s), 130.2 (s), 129.7 (s), 129.0 (t, $J_{\text{CP}} = 4.5$ Hz), 128.9 (s), 126.0 (t, $J_{\text{CP}} = 3.3$ Hz), 116.0 (t, $J_{\text{CP}} = 5.5$ Hz) (ArC), 68.5 (d, $J_{\text{RHC}} = 11.5$ Hz, HC=CH), 32.4 (br m, CH_2), 32.3 (s, CH_2), 27.0 (s, CH_2), 20.8 (s, ArMe). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 162.0 MHz): δ 38.5 (d, $J_{\text{RHP}} = 149.0$ Hz). Anal. Calcd for $\text{C}_{46}\text{H}_{46}\text{NiP}_2\text{Rh}$: C, 71.04; H, 5.96; N, 1.80. Found: C, 71.02; H, 5.95; N, 1.73.

(PNP^{Ph})Rh(CH₂=CH₂) (9). A 100 mL Schlenk flask was loaded with **1** (0.41 g, 0.72 mmol), lithium bis(trimethylsilyl)amide (0.12 g, 0.72 mmol) and 20 mL of toluene. The reaction solution was stirred for 1 h at ambient temperature to give a bright yellow solution. This solution was then added to a stirred suspension of $[(\text{CH}_2=\text{CH}_2)_2\text{RhCl}]_2$ (0.14 g, 0.36 mmol) in 10 mL of toluene.

After 1.5 h, the reaction mixture was filtered to remove the LiCl byproduct. The resulting red solution was evacuated to give an orange solid, which was washed with 30 mL of pentane and then dried under vacuum. Yield: 0.39 g (78%). ^1H NMR (C_6D_6 , 500 MHz): δ 7.84 (2H, d, J = 8.5 Hz, ArH), 7.73 (8H, br m, ArH), 7.06 (2H, br t, ArH), 7.00 (12H, br, ArH), 6.81 (2H, d, J = 8.4 Hz, ArH), 3.08 (4H, br, $\text{CH}_2=\text{CH}_2$), 1.99 (6H, s, ArMe). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 125.8 MHz): δ 162.6 (t, J_{CP} = 15.3 Hz), 134.4 (s), 133.9 (t, J_{CP} = 6.7 Hz), 133.0 (s), 130.1 (s), 129.2 (t, J_{CP} = 4.6 Hz), 128.7 (s), 126.6 (t, J_{CP} = 3.5 Hz), 126.1 (t, J_{CP} = 21.4 Hz), 116.0 (t, J_{CP} = 6.2 Hz) (ArC), 49.6 (d, J_{RhC} = 12.0 Hz, $\text{CH}_2=\text{CH}_2$), 20.7 (s, ArMe). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 162.0 MHz): δ 35.7 (d, J_{RhP} = 139.0 Hz). Anal. Calcd for $\text{C}_{40}\text{H}_{36}\text{NP}_2\text{Rh}$: C, 69.07; H, 5.22; N, 2.01. Found: C, 68.86; H, 5.00; N, 2.19.

(PNP^{Ph})Rh(PPh₃) (10). A solution of triphenylphosphine (0.034 g, 0.130 mmol) in 1 mL of toluene was added to a suspension of **8** (0.100 g, 0.129 mmol) in 3 mL of toluene. The resulting reaction mixture was then transferred to a flask equipped with a Teflon stopcock and a magnetic stirbar, and the flask was then placed in a 70 °C oil bath. After 5 h, the resulting homogenous solution was evaporated under vacuum leaving a bright orange powder. The powder was washed with 5 mL of pentane, collected by filtration and dried under vacuum. Yield: 0.116 g (97%). ^1H NMR (C_6D_6 , 500 MHz): δ 7.36 (10H, ov m, ArH), 7.26 (4H, t, J = 7.2 Hz, ArH), 7.15 (14H, ov m, ArH), 7.05 (3H, t, J = 7.2 Hz, ArH), 6.85 (6H, t, J = 7.2 Hz, ArH), 6.76 (2H, d, J = 8.4 Hz, ArH), 6.68 (2H, br m, ArH), 2.05 (6H, s, ArMe). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 125.8 MHz): δ 160.2 (t, J_{CP} = 15.0 Hz), 137.7 (t, J_{CP} = 2.6 Hz), 137.4 (t, J_{CP} = 2.4 Hz), 135.2 (t, J_{CP} = 19.8 Hz), 135.4 (s), 134.5 (s), 134.0 (t, J_{CP} = 6.6 Hz), 133.2 (s), 131.6 (s), 128.9 (s), 128.9 (s), 128.3 (t, J_{CP} = 4.6 Hz), 127.7 (s), 127.6 (s), 124.8 (t, J_{CP} = 3.3 Hz), 115.4 (t, J_{CP} = 5.9 Hz) (ArC), 20.5 (s, ArMe). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 202.5 MHz): δ 46.3 (1P, dt, J_{RhP} = 158.1 Hz, J_{PP} = 36.1 Hz), 40.5 (2P, dd, J_{RhP} = 118.8 Hz, J_{PP} = 36.4 Hz). Anal. Calcd for $\text{C}_{56}\text{H}_{47}\text{NP}_3\text{Rh}$: C, 72.34; H, 5.09; N, 1.51. Found: C, 72.61; H, 5.11; N, 1.83.

(PNP^{Ph})RhH(Cl)(THF) (11). A 100 mL round-bottom flask equipped with a magnetic stirbar was loaded with **1** (0.750 g, 1.33 mmol) and [(COE)₂RhCl] (0.473 g, 0.66 mmol). The solids were dissolved in 50 mL of THF and the resulting solution was stirred at ambient temperature. After 30 min, an insoluble brown precipitate formed. After 2 h at ambient temperature, a reflux condenser was attached to the flask and the reaction mixture was heated to 75 °C for another 3 h. After cooling to room temperature, the reaction mixture was dried under vacuum and triturated with 30 mL of hexanes to afford **11** as a bright orange powder. Yield: 0.860 g (84%). ^1H NMR (C_6D_6 , 500 MHz): δ 8.28 (4H, q, J = 5.9 Hz, ArH), 7.91 (2H, dt, J = 8.7 Hz, J_{PH} = 2.4 Hz, ArH), 7.87 (4H, m, ArH), 7.32 (2H, t, J_{PH} = 4.5 Hz, ArH), 7.07–7.00 (12 H, ov m, ArH), 6.77 (2H, dd, J = 8.7 Hz, J_{PH} = 1.3 Hz, ArH), 3.14 (4H, m, THF), 2.03 (6H, s, ArMe), 0.78 (4H, m, THF), -21.48 (1H, ov dt, J_{RhH} = 25.6 Hz, J_{PH} = 11.9 Hz, RhH). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 125.8 MHz): δ 162.6 (t, J_{CP} = 12.5 Hz), 135.4 (s), 135.3 (ov m), 135.0 (t, J_{CP} = 20.7 Hz), 134.5 (t, J_{CP} = 23.7 Hz), 132.5 (s), 130.8 (s), 129.9 (s), 129.1 (t, J_{CP} = 5.3 Hz), 126.5 (t, J_{CP} = 3.4 Hz), 122.0 (t, J_{CP} = 22.4 Hz), 118.0 (t, J_{CP} = 6.1 Hz) (ArC), 68.4 (s, THF), 25.5 (s, THF), 20.7 (s, ArMe). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 202.5 MHz):

δ 34.7 (d, J_{RhP} = 110.5 Hz). Anal. Calcd for $\text{C}_{42}\text{H}_{41}\text{NClOP}_2\text{Rh}$: C, 65.00; H, 5.32; N, 1.80. Found: C, 65.14; H, 5.15; N, 1.87.

(PNP^{Ph})IrMe(I)(THF) (12). A solution of iodomethane (0.12 g, 0.85 mmol) in THF (3 mL) was added to a stirred suspension of **5** (0.51 g, 0.59 mmol) in THF (20 mL). A gradual color change from bright orange to dark yellow was observed. After 1 h at ambient temperature, the solution was filtered and then evaporated to dryness under vacuum. The resulting yellow-brown solid was crystallized by diffusion of pentane (10 mL) into a concentrated solution of **12** in CH_2Cl_2 at -30 °C, to afford yellow orange crystals. Yield: 0.36 g (64%). ^1H NMR (CD_2Cl_2 , 500 MHz): δ 7.84 (8H, ov m, ArH), 7.80 (2H, dt, J = 8.7 Hz, J_{PH} = 2.5 Hz, ArH), 7.41–7.39 (12H, ov m, ArH), 7.18 (2H, br m, ArH), 6.96 (2H, d, J = 8.5 Hz, ArH), 3.45 (4H, br m, THF), 2.27 (6H, s, ArMe), 1.54 (4H, ov m, THF), 0.83 (3H, t, J_{PH} = 6.5 Hz, IrMe). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 125.8 MHz): δ 161.2 (t, J_{CP} = 10.7 Hz), 136.3 (s), 134.7 (t, J_{CP} = 5.1 Hz), 134.2 (t, J_{CP} = 5.3 Hz), 133.9 (t, J_{CP} = 25.7 Hz), 132.7 (s), 130.6 (s), 130.5 (s), 129.0 (t, J_{CP} = 27.0 Hz), 128.7 (t, J_{CP} = 4.8 Hz), 128.5 (t, J_{CP} = 5.0 Hz), 127.6 (t, J_{CP} = 4.3 Hz), 120.4 (t, J_{CP} = 26.0 Hz), 118.4 (t, J_{CP} = 5.8 Hz) (ArC), 68.83 (s, THF), 25.9 (s, THF), 20.5 (s, ArMe), -23.5 (br, IrMe). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 202.5 MHz): δ 9.7 (s). Anal. Calcd for $\text{C}_{43}\text{H}_{43}\text{NIrOP}_2$: C, 53.20; H, 4.46; N, 1.44. Found: C, 53.32; H, 4.39; N, 1.51.

(PNP^{Ph})IrPh(I)(THF) (13). A 50 mL thick walled flask with a Teflon stopcock was loaded with a solution of **12** (0.100 g, 0.11 mmol) in 10 mL of C_6H_6 . The flask was placed in a 120 °C oil bath for 20 h. The resulting brown solution was evaporated to dryness, and the resulting solid was redissolved in 2 mL of toluene. Then, 10 mL of pentane was added to the toluene solution and the resulting solution was placed in the -20 °C freezer for 20 h. The resulting brown solid is collected by filtration and dried under vacuum to give **13**. Yield: 0.089 g (77%). ^1H NMR (C_6D_6 , 400 MHz): δ 8.09 (6H, ov m, ArH), 7.62 (4H, m, ArH), 7.24 (2H, br t, J_{PH} = 4.8 Hz, ArH), 7.08 (2H, d, J = 8.3 Hz, ArH), 7.01 (6H, m, ArH), 6.88 (6H, m, ArH), 6.81 (d, J = 8.8 Hz), 6.40 (1H, t, J = 7.1 Hz), 6.17 (2H, d, J = 7.4 Hz, ArH), 3.13 (4H, m, THF), 2.03 (6H, s, ArMe), 0.59 (4H, m, THF). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 125.8 MHz): δ 162.2 (t, J_{CP} = 10.4 Hz), 142.8 (br), 137.1 (s), 134.7 (t, J_{CP} = 5.3 Hz), 134.6 (t, J_{CP} = 5.1 Hz), 134.2 (t, J_{CP} = 25.6 Hz), 132.9 (s), 130.3 (s), 128.9 (s), 127.7 (s), 126.0 (s), 122.4 (s), 121.7 (t, J_{CP} = 25.6 Hz), 119.0 (t, J_{CP} = 5.8 Hz) (ArC), 70.9 (s, THF), 25.4 (s, THF), 20.5 (s, ArMe). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 162.0 MHz): δ 12.5 (s). Anal. Calcd for $\text{C}_{48}\text{H}_{45}\text{NIrOP}_2$: C, 55.81; H, 4.39; N, 1.36. Found: C, 55.63; H, 4.07; N, 1.70.

(PNP^{Ph})RhMe(I)(THF) (14). Iodomethane (0.06 g, 0.42 mmol) was dissolved in 2 mL of THF and the resulting solution was added *via* cannula to a stirred solution of **8** (0.30 g, 0.39 mmol) in 20 mL of THF. After addition of iodomethane, the solution turned dark red. The reaction mixture was then evaporated to dryness under vacuum and the resulting solid was washed with 10 mL of pentane to afford a red powder. Yield: 0.29 g (83%). ^1H NMR (C_6D_6 , 400 MHz): δ 7.96 (10H, ov m, ArH), 7.35 (2H, br m, ArH), 7.02 (6H, ov m, ArH), 6.99 (6H, br m, ArH), 6.76 (2H, d, J = 8.6 Hz, ArH), 3.46 (4H, br m, THF), 1.97 (6H, s, ArMe), 1.87 (3H, br m, RhMe), 0.87 (4H, br m, THF). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 162 MHz): δ 37.0 (d, J_{RhP} = 111.1 Hz).

(PNP^{Ph})RhMe(I) (15). Complex **14** (0.29 g, 0.33 mmol) was dissolved in 5 mL of toluene, resulting in a color change from red to green. Removal of the volatile material under vacuum afforded the THF-free complex **15** as a dark green solid. Yield: 0.26 g (quant.). ¹H NMR (C₆D₆, 500 MHz): δ 7.94 (10H, ov m, ArH), 7.03 (8H, ov m, ArH), 6.96 (6H, ov m, ArH), 6.75 (2H, d, *J* = 7.3 Hz, ArH), 2.01 (3H, td, *J*_{PH} = 5.4 Hz, *J*_{RhH} = 2.4 Hz, RhMe), 1.96 (6H, s, ArMe). ¹³C{¹H} NMR (C₆D₆, 150.9 MHz): δ 161.2 (t, *J*_{CP} = 11.3 Hz), 135.8 (s), 135.0 (t, *J*_{CP} = 6.6 Hz), 134.8 (t, *J*_{CP} = 5.6 Hz), 132.9 (s), 130.9 (s), 129.3 (t, *J*_{CP} = 5.0 Hz), 129.1 (t, *J*_{CP} = 4.9 Hz), 122.8 (t, *J*_{CP} = 22.3 Hz), 118.8 (t, *J*_{CP} = 6.1 Hz) (ArC), 20.6 (s, ArMe), 6.6 (dm, *J*_{CRh} = 26.4 Hz, RhMe). ³¹P{¹H} NMR (C₆D₆, 202.5 MHz): δ 38.0 (d, *J*_{RhP} = 111.1 Hz). Anal. Calcd for C₃₉H₃₅NiP₂Rh: C, 57.87; H, 4.36; N, 1.73. Found: C, 58.15; H, 4.71; N, 1.91.

(PNP^{Ph})IrH(SiPh₃) (16). A solution of triphenylsilane (0.078 g, 0.300 mmol) in 1 mL of toluene was added to a solution of **5** (0.075 g, 0.087 mmol) in 5 mL of toluene. The reaction solution was transferred to a 25 mL Teflon-sealed reaction flask equipped with a magnetic stirbar which was then placed in a 60 °C oil bath for 20 h. After 20 h, the solution was evaporated under vacuum to give a bright orange oily residue. Crystallization from toluene (*ca.* 1.5 mL) layered with pentane (*ca.* 10 mL) gave pure **16** as a bright orange-red solid. Yield: 0.071 g (75%). ¹H NMR (C₆D₆, 500 MHz): δ 7.86–7.80 (6H, ov m, ArH), 7.69 (6H, d, *J* = 7.1 Hz, ArH), 7.01 (11H, ov m, ArH), 6.93 (2H, t, *J* = 7.1 Hz, ArH), 6.88 (6H, t, *J* = 7.2 Hz, ArH), 6.77 (6H, ov m, ArH), 6.63 (4H, t, *J* = 7.4 Hz, ArH), 1.86 (6H, s, ArMe), -19.25 (t, *J*_{PH} = 8.8 Hz, ²*J*_{SiH} = 4 Hz, IrH). ¹³C{¹H} NMR (C₆D₆, 125.8 MHz): δ 161.7 (t, *J*_{CP} = 11.2 Hz), 142.8 (br), 137.0 (s), 134.7 (s), 134.6 (t, *J*_{CP} = 6.5 Hz), 133.3 (t, *J*_{CP} = 6. Hz), 132.4 (s), 132.4 (t, *J*_{CP} = 26.7 Hz), 130.5 (s), 129.4 (s), 128.5 (m), 127.3 (s), 126.8 (s), 116.0 (t, *J*_{CP} = 5.5 Hz) (ArC), 20.1 (s, ArMe). ³¹P{¹H} NMR (C₆D₆, 202.5 MHz): δ 32.0 (s). ²⁹Si NMR (C₆D₆, 99.4 MHz): δ -9.2. IR: 1940 (νIr–H). Anal. Calcd for C₅₆H₄₈NiP₂Si: C, 66.12; H, 4.76; N, 1.38. Found: C, 66.00; H, 4.96; N, 1.28.

(PNP^{Ph})IrH(SiEt₃) (17). A solution of triethylsilane (0.05 g, 0.40 mmol) in 1 mL of toluene was added to a solution of **5** (0.10 g, 0.12 mmol) in 5 mL of toluene. The reaction solution was then transferred to a 25 mL Teflon-sealed reaction flask equipped with a magnetic stirbar, which was then placed in an 80 °C oil bath for 4.5 h. After 4.5 h, the solution was evaporated under vacuum to give a bright orange solid. Crystallization by diffusion of pentane into a CH₂Cl₂ solution (*ca.* 1 mL) of **5** afforded a bright orange-red solid. Yield (total from two crystallizations): 0.08 g (83%). ¹H NMR (CD₂Cl₂, 500 MHz): δ 8.23 (4H, q, *J*_{CP} = 5.7 Hz, ArH), 7.53–7.47 (8H, ov m, ArH), 7.44–7.39 (6H, ov m, ArH), 7.36–7.32 (4H, ov m, ArH), 6.93 (2H, d, *J* = 8.6 Hz, ArH), 6.87 (2H, t, *J* = 4.4 Hz, ArH), 2.14 (6H, s, ArMe), 0.50 (9H, t, *J* = 7.8 Hz, CH₃), -0.07 (6H, q, *J* = 7.8 Hz, CH₂), -18.93 (1H, t, *J*_{PH} = 9.4 Hz, ²*J*_{SiH} = 5.4 Hz, IrH). ¹³C{¹H} NMR (CD₂Cl₂, 125.8 MHz): δ 161.6 (t, *J*_{CP} = 11.3 Hz), 136.0 (t, *J*_{CP} = 7.1 Hz), 135.1 (t, *J*_{CP} = 25.0 Hz), 134.3 (s), 133.71 (t, *J*_{CP} = 8.8 Hz), 132.5 (t, *J*_{CP} = 26.9 Hz), 132.4 (s), 131.4 (s), 130.3 (s), 129.0 (t, *J*_{CP} = 5.4 Hz), 128.9 (s), 128.5 (t, *J*_{CP} = 4.8 Hz), 128.3 (m), 127.6 (t, *J*_{CP} = 3.7 Hz), 115.7 (t, *J*_{CP} = 5.4 Hz) (ArC), 20.4 (s, ArMe), 10.8 (s, CH₂), 10.4 (s, CH₃). ³¹P{¹H} NMR (CD₂Cl₂, 202.5 MHz): δ 33.7 (s). ²⁹Si NMR (CD₂Cl₂, 99.4 MHz): δ 15.8. IR: 1959 (νIr–H).

Anal. Calcd for C₄₄H₄₈NiP₂Si: C, 60.53; H, 5.54; N, 1.60. Found: C, 60.19; H, 5.47; N, 1.42.

(PNP^{Ph})RhH(SiPh₃) (18). A solution of triphenylsilane (0.094 g, 0.36 mmol) in 1 mL of benzene was added to **9** (0.125 g, 0.18 mmol) in 5 mL of benzene. This solution was then transferred to a 25 mL Teflon-sealed flask equipped with a magnetic stirbar. This flask was then placed in an 85 °C oil bath. After 18 h, the reaction mixture was cooled to room temperature and lyophilized with benzene to leave a fine orange powder. The powder was washed with 5 mL of pentane, and then collected by filtration. Yield: 0.120 g (72%). ¹H NMR (C₆D₆, 500 MHz): δ 8.1–7.6 (br, 5H, ArH), 7.79 (2H, br d, *J* = 7.5 Hz, ArH), 7.71 (6H, d, *J* = 7.0 Hz, ArH), 7.0–6.7 (7H, ov m, ArH), 6.95 (6H, ov m, ArH), 6.88 (9H, ov m, ArH), 6.78 (6H, ov m, ArH), 1.88 (6H, s, ArMe), -13.91 (1H, dt, *J*_{RhH} = 23.4 Hz, *J*_{PH} = 10.8 Hz, ²*J*_{SiH} = 35.9 Hz, RhH). ¹³C{¹H} NMR (C₆D₆, 125.8 MHz): δ 160.9 (t, *J*_{CP} = 13.1 Hz), 142.5 (s), 137.2 (s), 136.4 (s), 134.6 (s), 134.3 (br m), 133.3 (br m), 133.0 (s), 130.1 (br m), 130.0 (s), 128.9 (s), 127.5 (s), 127.3 (s), 127.1 (s), 126.9 (t, *J*_{CP} = 3.6 Hz), 116.2 (t, *J*_{CP} = 5.2 Hz) (ArC), 20.6 (s, ArMe). ³¹P{¹H} NMR (C₆D₆, 202.5 MHz): δ 41.3 (d, *J*_{RhP} = 133.5 Hz). ²⁹Si NMR (C₆D₆, 99.4 MHz): δ 17.8 (*J*_{SiRh} = 22 Hz). IR: 1996 (νRh–H). Anal. Calcd for C₅₆H₄₈NiP₂RhSi: C, 72.48; H, 5.21; N, 1.51. Found: C, 72.18; H, 5.34; N, 1.43.

(PNP^{Ph})RhH(SiEt₃) (19). A solution of Et₃SiH (0.030 g, 0.26 mmol) in 1 mL of benzene was added to **9** (0.089 g, 0.13 mmol) in 3 mL of benzene. The solution was then transferred to a 25 mL Teflon-sealed flask equipped with a magnetic stirbar. This flask was then placed in a 70 °C oil bath. After 20 h, the reaction mixture was cooled to room temperature, and lyophilized with benzene to leave a fine brown powder. The powder was washed with 5 mL of pentane, and then collected by filtration. Yield: 0.090 g (90%). ¹H NMR (C₆D₆, 500 MHz): δ 7.96 (8H, br, ArH), 7.79 (2H, d, *J* = 8.3 Hz, ArH), 7.04 (14H, ov br, ArH), 6.78 (2H, d, *J* = 8.2 Hz, ArH), 1.99 (6H, s, ArMe), 0.96 (9H, t, *J* = 7.7 Hz, SiCH₂CH₃), 0.47 (6H, q, *J* = 7.7 Hz, SiCH₂CH₃), -14.44 (1H, ov dt, *J*_{RhH} = 24.4 Hz, *J*_{PH} = 11.5 Hz, ²*J*_{SiH} = 33.5 Hz, RhH). ¹³C{¹H} NMR (C₆D₆, 150.9 MHz): δ 160.7 (t, *J*_{CP} = 14.1 Hz), 134.1 (br), 133.6 (s), 132.3 (s), 129.8 (s), 128.2 (s), 128.1 (s), 128.1 (s), 125.8 (t, *J*_{CP} = 21.6 Hz), 125.7 (t, *J*_{CP} = 3.6 Hz), 115.6 (t, *J*_{CP} = 6.1 Hz) (ArC), 20.0 (s, ArMe), 10.8 (t, *J*_{CP} = 2.6 Hz, SiCH₂CH₃), 9.9 (s, SiCH₂CH₃). ³¹P{¹H} NMR (C₆D₆, 202.5 MHz): δ 41.8 (d, *J*_{RhP} = 138.7 Hz). ²⁹Si NMR (C₆D₆, 99.4 MHz): δ 40.5 (*J*_{RhSi} = 20 Hz). IR: 2042 (νRh–H). Anal. Calcd for C₄₄H₄₈NiP₂RhSi: C, 67.42; H, 6.17; N, 1.79. Found: C, 67.32; H, 6.31; N, 1.85.

(PNP^{Ph})RhH(SiPh₂Cl) (20). A solution of Ph₂SiHCl (0.085 g, 0.39 mmol) in 1 mL of benzene was added to **8** (0.300 g, 0.39 mmol) in 5 mL of benzene. This solution was then transferred to a 50 mL Teflon-sealed flask equipped with a magnetic stirbar. This flask was then placed in a 75 °C oil bath. After 18 h, the reaction mixture was cooled to room temperature, and lyophilized with benzene to leave a fine orange powder. The powder was washed with 5 mL of pentane, and then collected by filtration. Yield: 0.260 g (76%). The IR stretch for the Rh–H of **20** was not observed using the standard procedure detailed previously. ¹H NMR (C₆D₆, 500 MHz): δ 8.09 (4H, br, ArH), 7.78 (2H, br d, *J* = 8.3 Hz, ArH), 7.62 (4H, d, *J* = 7.1 Hz), 7.12–7.02 (10H, ov m, ArH), 6.88 (4H, m, ArH), 6.81–6.76 (12H, ov m, ArH), 1.88 (6H, s, ArMe), -14.31

(1H, dt, $J_{\text{RhH}} = 23.9$ Hz, $J_{\text{PH}} = 10.3$ Hz, $^2J_{\text{SiH}} = 36.6$ Hz, RhH). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 125.8 MHz): δ 161.2 (t, $J_{\text{CP}} = 12.1$ Hz), 142.6 (s), 135.6 (s), 135.2 (br m), 135.0 (s), 133.8 (br m), 133.3 (s), 131.1 (br), 130.0 (br), 129.4 (br), 129.2 (s), 127.6 (s), 126.2 (t, $J_{\text{CP}} = 22.6$ Hz), 116.2 (t, $J_{\text{CP}} = 6.1$ Hz) (ArC), 20.6 (s, ArMe). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 202.5 MHz): δ 42.7 (d, $J_{\text{RHP}} = 129.3$ Hz). ^{29}Si NMR (C_6D_6 , 99.4 MHz): δ 38.4 ($J_{\text{RHSi}} = 26$ Hz). Anal. Calcd for $\text{C}_{50}\text{H}_{43}\text{NCIP}_2\text{RhSi}$: C, 67.76; H, 4.89; N, 1.58. Found: C, 67.64; H, 4.76; N, 1.49.

(PNP^{Ph})IrI(SiPh₃) (21). A solution of HSiPh_3 (0.05 g, 0.17 mmol) in 1 mL of toluene was added to a stirred solution of **12** (0.15 g, 0.17 mmol) in 10 mL of toluene. This reaction mixture was transferred to a 50 mL Teflon-sealed flask equipped with a magnetic stirbar. This flask was then placed in a 60 °C oil bath for 18 h. The volatile materials were removed under vacuum. The resulting green solid was washed twice with 5 mL of cold pentane and then collected by filtration. The collected solids were dried under vacuum to give **21** as a green powder. Yield: 0.17 g (85%). ^1H NMR (C_6D_6 , 500 MHz): δ 7.69 (4H, q, ArH), 7.61 (6H, d, $J = 7.3$ Hz, ArH), 7.41 (2H, br dt, $J = 8.4$ Hz, ArH), 7.37 (4H, q, ArH), 7.23 (2H, $J_{\text{PH}} = 4.3$ Hz, ArH), 6.94 (5H, q, ArH), 6.88–6.77 (16H, ov m, ArH), 6.69 (2H, d, $J = 7.7$ Hz), 1.99 (6H, s, ArMe). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 125.8 MHz): δ 160.8 (t, $J_{\text{CP}} = 9.6$ Hz), 139.7 (s), 138.0 (s), 135.9 (t, $J_{\text{CP}} = 6.0$ Hz), 134.6 (t, $J_{\text{CP}} = 26.5$ Hz), 134.3 (t, $J_{\text{CP}} = 5.7$ Hz), 133.9 (s), 132.28 (s), 130.8 (s), 130.0 (s), 128.9 (s), 127.2 (s), 126.4 (dt, $J_{\text{CP}} = 27.3$ Hz, $J_{\text{CP}} = 5.7$ Hz), 118.2 (t, $J_{\text{CP}} = 6.4$ Hz) (ArC), 20.6 (s, ArMe). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 202.5 MHz): δ 22.8 (s). ^{29}Si NMR (C_6D_6 , 99.4 MHz): δ -1.5. Anal. Calcd for $\text{C}_{56}\text{H}_{47}\text{NIrP}_2\text{Si}$: C, 58.84; H, 4.14; N, 1.23. Found: C, 59.14; H, 4.16; N, 1.32.

(PNP^{Ph})IrI(SiH₂Mes) (22). A solution of H_3SiMes (0.03 g, 0.17 mmol) in 1 mL of toluene was added to a stirred solution of **12** (0.15 g, 0.17 mmol) in 10 mL of toluene. The reaction mixture turned bright green after 20 min at ambient temperature. After 1 h, the volatile materials were removed under vacuum. The resulting green solid was washed with 20 mL of cold pentane and dried under vacuum to give **22** as a green powder. Yield: 0.11 g (63%). ^1H NMR (CD_2Cl_2 , 500 MHz): δ 7.81 (2H, dt, $J = 8.7$ Hz, ArH), 7.58 (4H, br q, $J = 5.9$ Hz, ArH), 7.49 (2H, br q, $J = 6.4$ Hz, ArH), 7.44–7.37 (4H, ov m, ArH), 7.29 (4H, t, $J = 7.8$ Hz, ArH), 7.25 (4H, t, $J = 7.6$ Hz, ArH), 7.02 (2H, t, $J = 5.1$ Hz, ArH), 6.98 (2H, d, $J = 8.7$ Hz, ArH), 6.23 (2H, s, ArH), 3.88 (2H, br t, $^1J_{\text{SiH}} = 199.7$ Hz, SiH), 2.21 (6H, s, ArMe), 2.08 (3H, s, ArMe), 1.90 (6H, s, ArMe). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 125.8 MHz): δ 160.0 (t, $J_{\text{CP}} = 20.2$ Hz), 144.5 (s), 139.3 (s), 134.4 (s), 133.9 (ov m), 132.1 (s), 132.0 (t, $J_{\text{CP}} = 4.0$ Hz), 130.7 (s), 130.6 (s), 129.0 (t, $J_{\text{CP}} = 5.1$ Hz), 128.3 (t, $J_{\text{CP}} = 5.3$ Hz), 128.2 (s), 126.9 (t, $J_{\text{CP}} = 28.7$ Hz), 124.0 (t, $J_{\text{CP}} = 26.1$ Hz), 118.3 (t, $J_{\text{CP}} = 5.6$ Hz) (ArC), 23.2 (s, ArMe), 21.3 (s, ArMe), 20.3 (s, ArMe). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 202.5 MHz): δ 25.3 (br s). ^{29}Si NMR (CD_2Cl_2 , 99.4 MHz): δ -34.4. Anal. Calcd for $\text{C}_{47}\text{H}_{45}\text{NIrP}_2\text{Si}$: C, 54.65; H, 4.39; N, 1.36. Found: C, 54.26; H, 4.26; N, 1.32.

(PNP^{Ph})IrI(SiH₂Xyl) (23). A solution of H_3SiXyl (0.02 g, 0.11 mmol) in toluene (3 mL) was added to a stirred solution of **12** (0.10 g, 0.11 mmol) in toluene (7 mL). The resulting solution was stirred for 30 min at ambient temperature and then evaporated to dryness to give a bright green solid. The solid was recrystallized

from a mixture of $\text{C}_6\text{H}_5\text{F}$ (ca. 1 mL) and pentane (ca. 7 mL) at -10 °C to afford **23** as a bright green solid. Yield = 0.05 g (48%). ^1H NMR (C_6D_6 , 400 MHz): δ 7.97 (2H, dt, $J = 8.6$ Hz, $J = 2.3$ Hz, ArH), 7.82 (4H, m, ArH), 7.75 (4H, m, ArH), 7.03 (7H, ov m, ArH), 6.92 (7H, br m, ArH), 6.79 (2H, s, ArH), 6.75 (2H, d, $J = 8.7$ Hz, ArH), 6.48 (1H, s, ArH), 4.12 (2H, t, $J_{\text{PH}} = 5.2$ Hz, $^1J_{\text{SiH}} = 202.8$ Hz, SiH), 2.00 (6H, s, ArMe), 1.92 (6H, s, ArMe). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 150.9 MHz): δ 161.1 (t, $J_{\text{CP}} = 10.1$ Hz), 136.8 (s), 135.6 (t, $J_{\text{CP}} = 5.8$ Hz), 134.7 (s), 134.6 (t, $J_{\text{CP}} = 6.2$ Hz), 133.8 (s), 133.5 (t, $J_{\text{CP}} = 26.4$ Hz), 132.7 (s), 131.3 (s), 131.2 (s), 130.7 (s), 129.3 (t, $J_{\text{CP}} = 5$ Hz), 128.8 (t, $J_{\text{CP}} = 5.3$ Hz), 126.7 (t, $J_{\text{CP}} = 28.8$ Hz), 124.8 (t, $J_{\text{CP}} = 27.2$ Hz), 118.4 (t, $J_{\text{CP}} = 5.6$ Hz) (ArC), 29.6 (s, ArMe), 21.5 (s, ArMe). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 162 MHz): δ 30.2 (br s). ^{29}Si NMR (C_6D_6 , 99.4 MHz): δ -23.2. Anal. Calcd for $\text{C}_{46}\text{H}_{43}\text{NIrP}_2\text{Si}$: C, 54.22; H, 4.25; N, 1.37. Found: C, 54.15; H, 4.34; N, 1.23.

X-Ray crystallography. General considerations

The single-crystal X-ray analyses of compounds **2**, **3**, **16** and **18** were carried out at the UC Berkeley CHEXRAY crystallographic facility. Measurements for **3** were made on a Bruker SMART 1000 area detector with graphite-monochromated Mo-K α radiation ($\lambda = 0.71069$ Å). Measurements for **2**, **16** and **18** were made on an APEX-II CCD area detector with a HELIOS multilayer mirrors monochromating device using Cu-K α radiation ($\lambda = 1.54184$ Å). Data for **3** was integrated by the program SAINT and analyzed for agreement using XPREP. Data for **2**, **16**, and **18** was integrated using the APEX2 program package. Empirical absorption corrections for **2** and **3** were made using SADABS or APEX2 programs. Analytical absorption corrections through face-indexing methods for **16** and **18** were made using APEX2 software package. Structures were solved by direct methods or Patterson methods using SHELX program package. For **18**, PLATON SQUEEZE⁴¹ was used to treat disordered toluene (see ESI). Crystallographic data are summarized in the ESI and CIF files for all structures are also included.†

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