5072 *Organometallics* **2009,** *28,* 5072–5081
DOI: 10.1021/om900385a

ORGANOMETALLICS
Article

Synthesis and Reactivity of Iridium and Rhodium Silyl Complexes Supported by a Bipyridine Ligand

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Received May 12, 2009

The rhodium and iridium complexes $[(^t\text{Bu}_2\text{bpy})_2\text{M}(\mu\text{-Cl})]_2$ (M = Rh (**1**), Ir (**2**)) containing the bidentate $^t\text{Bu}_2$bpy (4,4′-di-*tert*-butyl-2,2′-bipyridyl) ligand were prepared. Dimeric complexes **1** and **2** react with HSiPh_3 to give $[(^t\text{Bu}_2\text{bpy})\text{MH}(\text{SiPh}_3)(\mu\text{-Cl})]_2$ in good yields (M = Rh (**3**) 92%, Ir (**4**) 90%). Addition of P^iPr_3 to **3** or **4** gave monomeric crystalline complexes of the type $(^t\text{Bu}_2\text{bpy})\text{MH}(\text{SiPh}_3)\text{Cl}(\text{P}^i\text{Pr}_3)$ (M = Rh (**7**) and Ir (**8**)), which adopt a slightly distorted octahedral coordination geometry with the $^t\text{Bu}_2$bpy ligand occupying sites *trans* to the hydride and chloride ligands, as determined by X-ray crystallography. Salt metathesis reactions of **7** and **8** produced $(^t\text{Bu}_2\text{bpy})\text{MH}(\text{SiPh}_3)(\text{R})\text{P}^i\text{Pr}_3$ as monomeric octahedral complexes with the $^t\text{Bu}_2$bpy ligand occupying sites *trans* to the hydride and R substituents (M = Rh, R = H (**11**) and M = Ir, R = H (**12**), Me (**14**), and Ph (**15**)). Salt metathesis reactions with **3** and **4** also generated the dimeric, dicationic complexes $[(^t\text{Bu}_2\text{bpy})\text{M}(\text{SiPh}_3)(\mu\text{-H})]_2[\text{B}(\text{C}_6\text{F}_5)_4]_2$, where M = Rh (**16**) or Ir (**17**). Thermolysis of **15** at 100 °C in C_6H_6 for 1 day produced **12** and Ph_4Si in 47% yield, and heating **15** in the presence of 1 equiv of HSiR_3 (R = Ph, Et) also gave **12**, as well as the Si−C coupled product PhSiR_3 in >95% yield.

Introduction

Transition metal complexes supported by the bpy (2,2′-bipyridyl) ligand play an important role in electronic applications,[1−7] supramolecular chemistry,[8] and catalysis.[9−17] Not surprisingly, bpy complexes have also been examined as catalysts for transformations involving organosilanes. Most notably, a bipyridyl-supported iridium catalyst generated by the combination of $[(\text{cod})\text{Ir}(\text{OMe})]_2$ (cod = 1,5-cyclooctadiene) and 2 equiv of $^t\text{Bu}_2$bpy (4,4′-di-*tert*-butyl-2,2′-bipyridine) has been found to catalyze the silylation of arenes under mild conditions; however, isolation of iridium silyl complexes from this system has not been reported.[12,13,17] This reaction mixture has also been found to catalyze silane borylation and the catalytic borylation of arenes.[16] More recently, the iridium silyl complex $(^t\text{Bu}_2\text{bpy})\text{Ir}(\text{Me})(\text{SiMe}_3)(\text{CH}_2\text{SiMe}_3)$ was isolated from reaction of $(^t\text{Bu}_2\text{bpy})\text{Ir}(\text{dmf})\text{Cl}_3$ with 3 equiv of $\text{Me}_3\text{SiCH}_2\text{MgCl}$. However, little is known about the chemistry of this interesting dialkyl silyl complex.[18]

Related research in these laboratories has shown that anionic ligands analogous to bpy support reactive rhodium and iridium complexes that engage in bond activation chemistry. The monoanionic, chelating 2-(2-pyridyl)indolide (PyInd) ligand has been found to stabilize coordinatively unsaturated Ir(V) and Rh(V) bis(silyl) dihydride complexes, one of which, the Rh(V) bis(silyl) dihydride $(\text{PyInd})\text{Rh}(\text{H})_2(\text{SiEt}_3)_2$, mediates the catalytic dehydrochlorinative coupling of chlorobenzene with triethylsilane.[19] A related system, derived from the monoanionic ligand, 3,5-diphenyl-2-(2-pyridyl)pyrrolide (PyPyr), supports analogous, coordinatively unsaturated Ir(V) and Rh(V) bis(silyl) dihydride complexes.[20] Interestingly, one of these Rh(V) bis(silyl) dihydrides, $(\text{PyPyr})\text{Rh}(\text{H})_2(\text{Si}^t\text{BuPh}_2)_2$, was found to undergo

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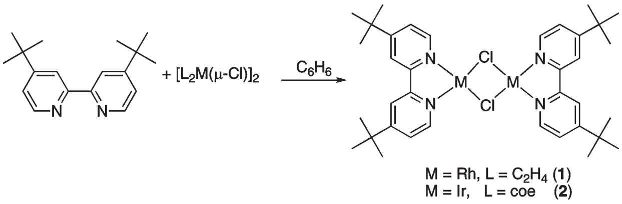
silane exchange through a 14-electron intermediate of the type (PyPyr)RhH(Si^{t}BuPh$_2$).

Given the observed bond activation chemistry for complexes of the type (N−N′)MH$_2$(SiR$_3$)$_2$ (where M = Rh, Ir, N−N′ = anionic ligand) and their unusual structural and electronic properties, it was of interest to investigate related complexes containing a neutral, chelating ligand with nitrogen donor atoms (N−N). Although it is difficult to envision pentavalent complexes supported by neutral N−N ligands, species of the type (N−N)MH$_2$(SiR$_3$)(L) and (N−N)MH(SiR$_3$)$_2$(L) should be accessible. Such complexes might be expected to react via dissociation of L, or by reductive elimination, to generate 16-electron intermediates. The purpose of the investigation described here is to define reactivity modes for rhodium and iridium complexes of the ^{t}Bu$_2$bpy ligand, in search of fundamental steps that may be of use in catalytic bond activation chemistry.

Results and Discussion

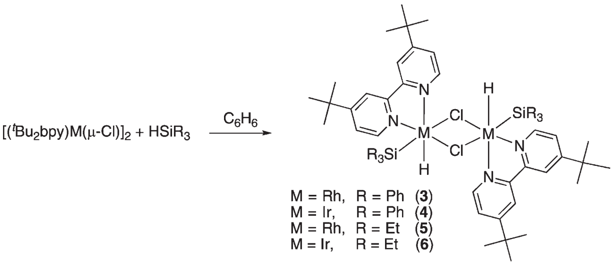
Synthesis of [(^{t}Bu$_2$bpy)M(μ-Cl)]$_2$ Complexes. Although the M(III) complexes (^{t}Bu$_2$bpy)M(dmf)Cl$_3$ have been reported,[18,21] M(I) precursors supported by ^{t}Bu$_2$bpy have not been described. To access Rh(I) and Ir(I) coordination complexes of ^{t}Bu$_2$bpy, the chloride-bridged precursors [(olefin)$_2$M(μ-Cl)]$_2$ were treated with ^{t}Bu$_2$bpy. A procedure analogous to that reported for the synthesis of [(bpy)M(μ-Cl)]$_2$ was used.[9,22] Addition of 2 equiv of ^{t}Bu$_2$bpy to [(C$_2$H$_4$)$_2$Rh(μ-Cl)]$_2$ in benzene, followed by stirring for 1 h at 25 °C, produced [(^{t}Bu$_2$bpy)Rh(μ-Cl)]$_2$ (**1**) as a purple powder in 95% yield (eq 1). In a similar manner, 2 equiv of ^{t}Bu$_2$bpy was added to [(coe)$_2$Ir(μ-Cl)]$_2$ (coe = cyclooctene) in C$_6$H$_6$ to obtain [(^{t}Bu$_2$bpy)Ir(μ-Cl)]$_2$ (**2**) as a red powder in 92% yield. The ^{1}H NMR spectra of **1** and **2** possess a downfield resonance, at 9.25 and 9.55 ppm, respectively, for the ^{t}Bu$_2$bpy proton nearest the metal center.



(1)

Reactions of [(^{t}Bu$_2$bpy)M(μ-Cl)]$_2$ with Silanes. Treatment of a benzene solution of **1** with 2 equiv of HSiPh$_3$ gave the maroon solid [(^{t}Bu$_2$bpy)RhH(SiPh$_3$)(μ-Cl)]$_2$ (**3**) in 92% yield after 1 h at 25 °C (eq 2). The ^{1}H NMR spectrum of **3** contains an upfield doublet at −14.80 ppm (J_{RhH} = 25 Hz) for the rhodium hydride ligand and six resonances for the ^{t}Bu$_2$bpy ligand, revealing that the pyridyl groups are in chemically different environments. A 2D NOESY experiment demonstrated that the hydride ligand is *trans* to a pyridine donor, while the silyl ligand occupies the position *trans* to a chloride ligand. A silyl resonance at 20.6 ppm in the ^{29}Si{^{1}H} NMR spectrum is consistent with a simple silyl ligand on rhodium.[23] The thermolysis of **3** at 60 °C for 8 h in C$_6$D$_6$ resulted in loss of 1 equiv of HSiPh$_3$ (and not ClSiPh$_3$) to give **1** (by ^{1}H NMR spectroscopy).

Similarly, reaction of 2 equiv of HSiPh$_3$ with **2** in benzene at 25 °C gave the red solid [(^{t}Bu$_2$bpy)IrH(SiPh$_3$)(μ-Cl)]$_2$ (**4**) in 90% yield. The ^{1}H NMR spectrum of **4** exhibits an upfield singlet at −17.21 ppm for the hydride ligand, and a silyl resonance at −20.5 ppm was observed in the ^{29}Si{^{1}H} NMR spectrum. Also, thermolysis of **4** at 60 °C for 8 h in C$_6$D$_6$ resulted in loss of 1 equiv of HSiPh$_3$ to regenerate **2** (by ^{1}H NMR spectroscopy).



(2)

Addition of HSiEt$_3$ to [(^{t}Bu$_2$bpy)M(μ-Cl)]$_2$ also resulted in oxidative addition of the Si−H bond to the metal center. Specifically, addition of 2 equiv of HSiEt$_3$ to a benzene-d_6 solution of [(^{t}Bu$_2$bpy)Rh(μ-Cl)]$_2$ in a J. Young NMR tube generated 1 equiv of [(^{t}Bu$_2$bpy)RhH(SiEt$_3$)(μ-Cl)]$_2$ (**5**) after 5 min at 25 °C (by NMR spectroscopy; eq 2). The ^{1}H NMR spectrum is consistent with the formation of **5**, which exhibits a resonance for a rhodium hydride ligand at −15.22 ppm, and a silyl resonance at 19.0 ppm was located in the ^{29}Si{^{1}H} NMR spectrum. However, [(^{t}Bu$_2$bpy)RhH(SiEt$_3$)(μ-Cl)]$_2$ loses HSiEt$_3$ at 25 °C over 4 h, leading to difficulties in its isolation. In comparison, loss of silane does not readily occur for the iridium analogue, and an analogous synthesis produces [(^{t}Bu$_2$bpy)IrH(SiEt$_3$)(μ-Cl)]$_2$ (**6**), which can be isolated as a red solid in 75% yield. The NMR shifts for **6** include an upfield singlet for the iridium hydride at −17.26 ppm in the ^{1}H NMR spectrum and a silyl resonance at −1.9 ppm in the ^{29}Si{^{1}H} NMR spectrum.

Synthesis and Characterization of Mononuclear (^{t}Bu$_2$bpy)MH(SiPh$_3$)Cl(PR$_3$) Complexes. To explore the chemistry of monomeric silyl hydride complexes, phosphines were added to complexes **3** and **4** to cleave the dimeric units. Reaction of P^{i}Pr$_3$ with **3** in benzene for 4 h at 25 °C gave (^{t}Bu$_2$bpy)RhH(SiPh$_3$)Cl(P^{i}Pr$_3$) (**7**) as a purple solid in 72% yield (eq 3). The ^{1}H NMR spectrum of **7** contains an upfield doublet of doublets at −16.00 ppm for the hydride ligand, with coupling to both rhodium (J_{RhH} = 10 Hz) and phosphorus (J_{HP} = 20.0 Hz). The ^{29}Si NMR spectrum of **7** possesses a silyl resonance at −9.3 ppm (J_{SiRh} = 20.0 Hz), which represents a 29 ppm upfield shift from that of **3**. A 2D NOESY spectrum of **7** confirms that the silyl and phosphine ligands are *trans* to each other, while the chloride, hydride, and ^{t}Bu$_2$bpy ligands adopt a *mer* arrangement. X-ray quality crystals of **7** were obtained by vapor diffusion of pentane into a THF solution at 25 °C (Figure 1). Compound **7** adopts a slightly distorted octahedral geometry, as indicated by the ∠SiRhP angle of 160.87(3)°. The silyl and phosphine groups are slightly bent toward the hydride ligand, resulting in a ∠SiRhH and ∠PRhH angle of 75(1)° and 86(1)°, respectively. For comparison, the ∠SiRhCl angle is 90.01(3)°.

The iridium analogue was synthesized by addition of 2 equiv of P^{i}Pr$_3$ to a solution of **4** in benzene to produce (^{t}Bu$_2$bpy)IrH(SiPh$_3$)Cl(P^{i}Pr$_3$) (**8**) as a red solid in 80% yield. The ^{1}H NMR spectrum of **8** contains an upfield doublet at −16.68 (J_{HP} = 15.0 Hz) for the iridium hydride ligand with a

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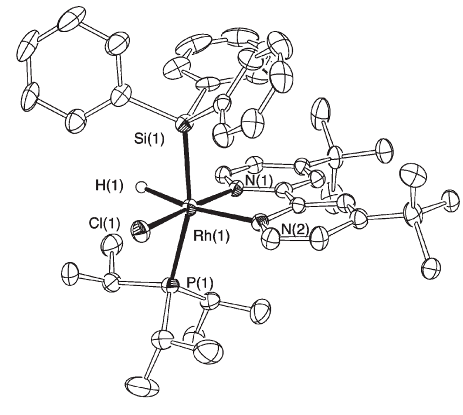
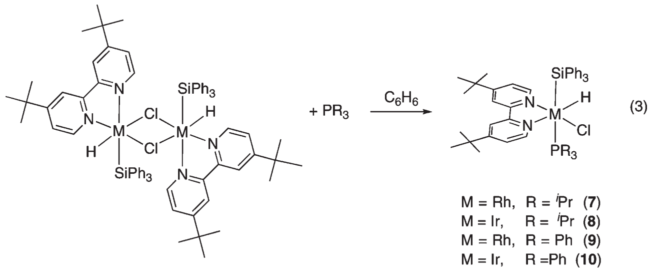


Figure 1. ORTEP diagram of **7** with thermal ellipsoids shown at the 50% probability level. Hydrogen atoms and the disordered *tert*-butyl groups are omitted for clarity. Selected bond lengths (Å): Rh1−N1 = 2.022(2), Rh1−N2 = 2.150(3), Rh1−Si1 = 2.362(1), Rh1−Cl1 = 2.3816(8), Rh1−P1 = 2.4817(9), and Rh1−H1 = 1.62(4). Selected bond angles (deg): N1−Rh1−N2 = 78.2(1), N1−Rh1−Si1 = 89.35(7), N2−Rh1−Si1 = 96.24(7), Si1−Rh1−Cl1 = 90.01(3), N1−Rh1−P1 = 93.04(7), N2−Rh1−P1 = 102.83(7), Si1−Rh1−P1 = 160.87(3), and Si1−Rh1−H1 = 75(1).

J_{SiH} coupling constant of 15.0 Hz, indicating little interaction between the silyl and hydride ligands. As with the rhodium analogue, the 2D NOESY spectrum of **8** is consistent with the geometry shown in eq 3. This is confirmed by the X-ray structure (Figure 2), where **8** exhibits a slight distortion from octahedral geometry as indicated by the ∠SiIrP angle of 164.52(2)° and small ∠SiIrH and ∠PIrH angles (80(1)°, 86(1)°). Interestingly, the ∠SiIrCl angle in **8** (83.85(2)°) is somewhat smaller than the comparable parameter in **7** (90.01(3)°).



Analogous compounds containing PPh_3 were synthesized in a similar manner and characterized as (^{t}Bu$_2$bpy)RhH($SiPh_3$)Cl(PPh_3) (**9**) (92%) and (^{t}Bu$_2$bpy)IrH($SiPh_3$)Cl(PPh_3) (**10**) (88%). However, these systems were found to be less useful, since it proved difficult to distinguish between the silicon and phosphorus atoms in X-ray crystal structures.

Synthesis of Dihydride, Alkyl Hydride, and Aryl Hydride Complexes. Silyl dihydride, alkylsilyl hydride, and arylsilyl hydride complexes of rhodium and iridium were targeted, since such species might represent products of various bond activations (e.g., C−H, Si−H, Si−C). In fact, the related complex (^{t}Bu$_2$bpy)Ir($SiMe_3$)Me(CH_2SiMe_3) is produced by Si−C cleavage.[18] These types of complexes also represent models for intermediates in catalytic processes, such as hydrosilylation and silane−hydrocarbon dehydrocoupling, that feature such bond activations.

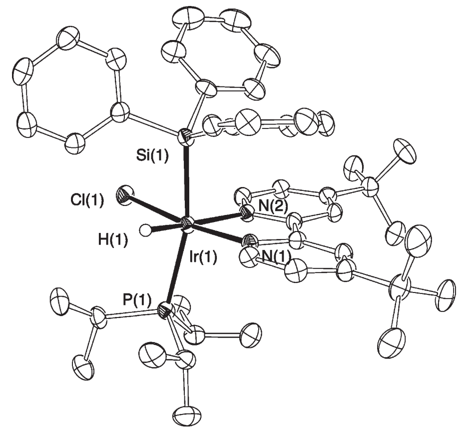


Figure 2. ORTEP diagram of **8** with thermal ellipsoids shown at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Ir1−N1 = 2.027(2), Ir1−N2 = 2.112(1), Ir1−Si1 = 2.3821(7), Ir1−Cl1 = 2.3959(7), Ir1−P1 = 2.4093(7), and Ir1−H1 = 1.55(3). Selected bond angles (deg): N1−Ir1−N2 = 78.05(8), N1−Ir1−Si1 = 92.22(6), N2−Ir1−Si1 = 95.10(5), Si1−Ir1−Cl1 = 83.85(2), N1−Ir1−P1 = 95.67(6), N2−Ir1−P1 = 99.54(5), Si1−Ir1−P1 = 164.52(2), and Si1−Ir1−H1 = 80(1).

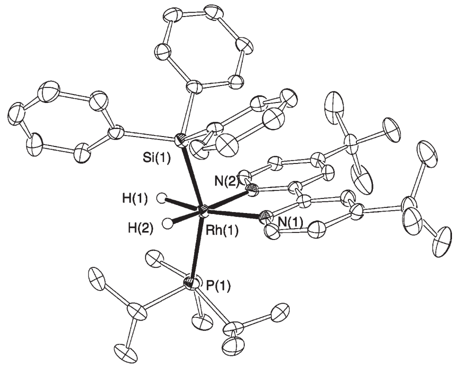


Figure 3. ORTEP diagram of **11** with thermal ellipsoids shown at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Rh1−N1 = 2.120(1), Rh1−N2 = 2.123(1), Rh1−Si1 = 2.3379(7), Rh1−P1 = 2.3596(7), Rh1−H1 = 1.50(2), and Rh1−H2 = 1.46(3). Selected bond angles (deg): N1−Rh1−N2 = 76.87(7), N1−Rh1−Si1 = 94.17(6), N2−Rh1−Si1 = 101.84(6), N1−Rh1−P1 = 104.06(6), N2−Rh1−P1 = 97.52(6), Si1−Rh1−P1 = 155.97(2), N1−Rh1−H1 = 170(1), N2−Rh1−H1 = 99.3(9), Si1−Rh1−H1 = 77.6(9), N1−Rh1−H2 = 102(1), N2−Rh1−H2 = 176.3(1), Si1−Rh1−H2 = 74(1), and H1−Rh1−H2 = 81(1).

Addition of 1 equiv of $LiBEt_3H$ to a −78 °C THF solution of **7** provided the purple solid (^{t}Bu$_2$bpy)Rh(H)$_2$($SiPh_3$)P^{i}Pr$_3$ (**11**) in 77% yield (eq 4). The ^1H NMR spectrum of **11** reveals an upfield resonance at −16.06 ppm (J_{HP} = 21.0 Hz, J_{RhH} = 13.5 Hz) that corresponds to two chemically equivalent hydride ligands. Furthermore, the ^1H NMR spectrum exhibits only three resonances for the pyridyl ring hydrogens of the ^{t}Bu$_2$bpy ligand, indicating the presence of a molecular plane of symmetry. A downfield shifted $^{29}Si\{^1H\}$ NMR resonance at 24.4 ppm (J_{SiP} = 173.0 Hz, J_{SiRh} = 11.4 Hz) and an upfield shifted $^{31}P\{^1H\}$ resonance at 44.9 ppm (J_{PRh} = 91.0 Hz) were also observed for **11**. Suitable crystals of **11** were grown for an X-ray crystallographic analysis by the slow evaporation of a THF solution at 25 °C, and the molecular structure (Figure 3) indicates that both hydrides

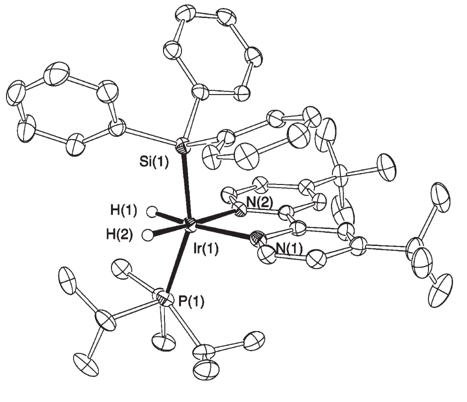
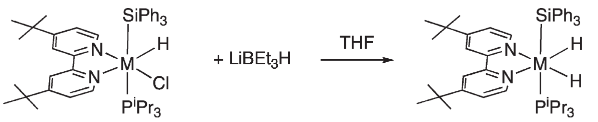


Figure 4. ORTEP diagram of **12** with thermal ellipsoids shown at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Ir1−N1 = 2.103(2), Ir1−N2 = 2.107(2), Ir1−P1 = 2.3326(8), and Ir1−Si1 = 2.3660(8). Selected bond angles (deg): N1−Ir1−N2 = 76.91(8), N1−Ir1−P1 = 104.60(6), N2−Ir1−P1 = 98.03(6), N1−Ir1−Si1 = 92.41(6), N2−Ir1−Si1 = 100.12(6), P1−Ir1−Si1 = 157.51(3), N1−Ir1−H1 = 174(1), N2−Ir1−H1 = 99(1), Si1−Ir1−H1 = 83(1), N1−Ir1−H2 = 97(1), N2−Ir1−H2 = 172(1), Si1−Ir1−H2 = 75(1), and H1−Ir1−H2 = 85(1).

lie in the plane of the ^{t}Bu$_2$bpy ligand, with Rh−H bond distances of 1.46(3) and 1.50(2) Å. Slight bending of the silyl and phoshine ligands toward the hydride is indicated by the ∠SiRhH angles of 77.6(9)° and 74(1)° and ∠PRhH angles of 85(1)° and 86(1)°. A small distortion from an ideal octahedral geometry is also evident in the ∠SiRhP bond angle of 155.97(2) Å.

A similar synthetic route was used to obtain the iridium analogue (^{t}Bu$_2$bpy)Ir(H)$_2$(SiPh$_3$)P^{i}Pr$_3$ (**12**) as a purple solid in 78% yield, via reaction of LiBEt$_3$H with **8** in THF. The ^{1}H NMR spectrum of **12** contains an upfield resonance at −18.93 ppm (J_{HP} = 16.8 Hz) for the hydride ligand, and the ^{29}Si{^{1}H} NMR resonance was observed at 6.65 ppm (J_{SiP} = 128.0 Hz). The X-ray structure of **12** confirmed the connectivity determined by NMR spectroscopy (Figure 4). Further distortion from an ideal octahedral geometry is indicated by the ∠SiRhP bond angle of 157.51(1) Å.



(4)

M = Rh (**11**)
M = Ir (**12**)

An attempt to prepare a methyl hydride complex of rhodium was based on reaction of 1 equiv of MeLi (1.6 M in Et$_2$O) with **7** at −78 °C in THF over 1 h. After warming to room temperature, the yellow, known complex (P^{i}Pr$_3$)$_2$-RhCl(C$_2$H$_4$)[24] (**13**) was isolated from the reaction mixture in 47% yield after crystallization from THF (eq 5). Compound **13** was characterized by ^{1}H and ^{31}P NMR spectroscopies and by X-ray crystallographic analysis. One equivalent of uncoordinated ^{t}Bu$_2$bpy was also formed during the course of the reaction. Since C$_2$H$_4$ extrusion from THF is known to occur in the presence of an alkyl lithium reagent,[25,26] the methylation was attempted in toluene and dioxane solvents; however, these reactions produced only intractable mixtures of products.

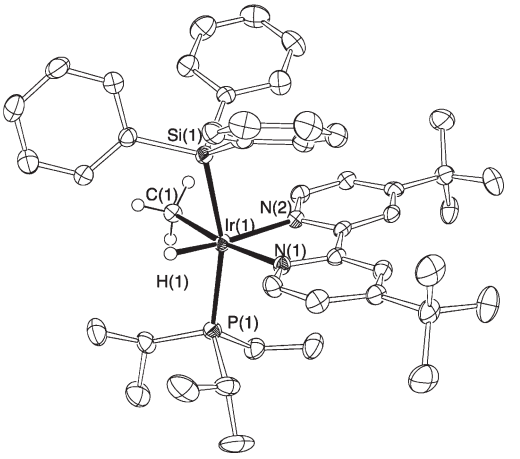
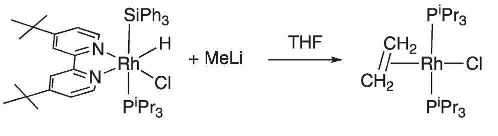


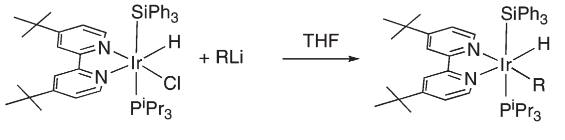
Figure 5. ORTEP diagram of **14** with thermal ellipsoids shown at the 50% probability level. Hydrogen atoms and the THF molecule are omitted for clarity. Selected bond lengths (Å): Ir1−N1 = 2.096(3), Ir1−N2 = 2.119(3), Ir1−C1 = 2.136(4), Ir1−P1 = 2.368(1), Ir1−Si1 = 2.370(1), and Ir1−H1 = 1.52(4). Selected bond angles (deg): N1−Ir1−N2 = 76.8(1), N1−Ir1−P1 = 95.19(9), N2−Ir1−P1 = 101.49(9), N1−Ir1−Si1 = 93.51(9), N2−Ir1−Si1 = 94.82(9), C1−Ir1−Si1 = 83.2(1), P1−Ir1−Si1 = 162.89(4), C1−Ir1−H1 = 88(1), and Si1−Ir1−H1 = 76(1).



(5)

7 **13**

An analogous alkylation procedure, involving addition of 1 equiv of MeLi (1.6 M in Et$_2$O) to **8** in THF at −78 °C, did not give an ethylene complex as observed for Rh. Instead, the expected methyl complex (^{t}Bu$_2$bpy)IrH(SiPh$_3$)(Me)P^{i}Pr$_3$ (**14**) was obtained as a purple solid in 82% yield (eq 6). The ^{1}H NMR spectrum of **14** possesses a broad doublet for the hydride ligand at −17.29 ppm (J_{HP} = 17.0 Hz) and a doublet of doublets at 1.02 ppm (J_{HP} = 12.0 Hz) for the iridium-bound methyl group. A ^{1}H,^{13}C{^{1}H} HSQC experiment with **14** reveals that the ^{13}C NMR resonance observed at −34.1 ppm correlates with the ^{1}H resonance at 1.02 ppm.



(6)

8

R = Me (**14**)
R = Ph (**15**)

Suitable crystals of **14** were grown by vapor diffusion of pentane into a THF solution at −30 °C, and the structure was determined by X-ray crystallography (Figure 5). Compound **14** adopts a slightly distorted octahedral geometry, with a ∠SiIrP bond angle of 162.89(4)°. The silyl group is slightly bent toward the hydride ligand, as indicated by the ∠SiIrH angle of 76(1)°. The Ir−Me bond distance for **14**

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(2.17(1) Å) and the ∠SiIrC bond angle of 82.5(3)° are comparable to the corresponding values found in $(PMe_3)_3$-$IrH(SiPh_3)(Me)$ (2.136(4) Å and ∠SiIrC of 83.2(1)°).[27] However, the Ir−C (2.17(1) Å) and Ir−Si (2.371(1) Å) bond distances for **14** are longer than those observed for the five-coordinate complex $(^tBu_2bpy)Ir(SiMe_3)(Me)(CH_2SiMe_3)$ (Ir−C: 2.069(5) Å, Ir−Si: 2.279(2) Å).[18] Complex **14** represents one of the few examples of an iridium hydridomethylsilyl derivative that is not supported by multiple phosphine ligands.[28−37]

An attempt to synthesize a rhodium phenylsilyl hydride complex was based on treatment of **7** with PhLi in C_6H_6 or THF. However, these reactions yielded intractable mixtures (by ^1H and ^{31}P NMR spectroscopies). Other phenyl transfer reagents such as $PhSnMe_3$ also gave complex mixtures by ^1H and ^{31}P NMR spectroscopies. In contrast, the isolation of an iridium phenyl compound was relatively straightforward. Addition of 1 equiv of PhLi to a THF solution of **8** at 25 °C produced $(^tBu_2bpy)IrH(SiPh_3)(Ph)P^iPr_3$ (**15**) as a purple-brown solid in 90% yield (eq 6). The ^1H NMR spectrum of **15** possesses a resonance at −17.48 (J_{HP} = 16.0 Hz) for the hydride ligand, while the ^{29}Si and $^{31}P\{^1H\}$ NMR resonances were observed at −3.42 and 19.36 ppm, respectively.

Synthesis of $[(^tBu_2bpy)M(SiPh_3)(\mu\text{-}H)]_2[B(C_6F_5)_4]_2$ Complexes. To access coordinatively unsaturated, electrophilic complexes related to those described above, attempts were made to exchange the chloride ligands in $[(^tBu_2bpy)$-$MH(SiPh_3)(\mu\text{-}Cl)]_2$ complexes with the weakly coordinating anion $B(C_6F_5)_4^-$.[30] Addition of 2 equiv of $LiB(C_6F_5)_4(Et_2O)_2$ to a solution of **3** in fluorobenzene gave $[(^tBu_2bpy)Rh$-$(SiPh_3)(\mu\text{-}H)]_2[B(C_6F_5)_4]_2$ (**16**) as a maroon solid in 90% yield (eq 7). The ^1H NMR spectrum of **16** indicates that the pyridyl groups are equivalent, and an upfield triplet is observed at −22.73 ppm with J_{RhH} = 33.5 Hz, indicating that the hydride ligand is bridging between two rhodium centers. A $^{29}Si\{^1H\}$ NMR resonance for **16** is observed at 24.1 ppm, verifying retention of the silyl ligand.

The iridium analogue of **16** can be prepared in a similar manner. A solution of **4** in CH_2Cl_2 was treated with 2 equiv of $LiB(C_6F_5)_4(Et_2O)_2$ over 2 h at 25 °C to generate $[(^tBu_2bpy)Ir(SiPh_3)(\mu\text{-}H)]_2[B(C_6F_5)_4]_2$ (**17**) as an orange solid in 92% yield. The ^1H NMR spectrum of **17** contains a singlet at −22.51 ppm for the iridium bridging hydride ligands, and the $^{29}Si\{^1H\}$ NMR resonance for **17** was located at −21.0 ppm. X-ray quality crystals of **17** were grown by vapor diffusion of pentane into a CH_2Cl_2 solution of **17** at 25 °C (Figure 6). The solid-state structure of **17** possesses half of the molecule in the asymmetric unit, with the two halves related by inversion, and an Ir−Si bond distance of 2.344(1) Å. Interestingly, one of the phenyl substituents of the silyl ligand is oriented such that it appears to be coordinated to the other iridium center. The resulting Ir−C_{ipso} distance of 2.87(1) Å is consistent with a weak bonding interaction between the iridium and the *ipso* carbon of the silyl ligand. No interaction is observed between the silyl groups and the hydride ligands, as indicated by the ∠SiIrH angle of 88(1)°.

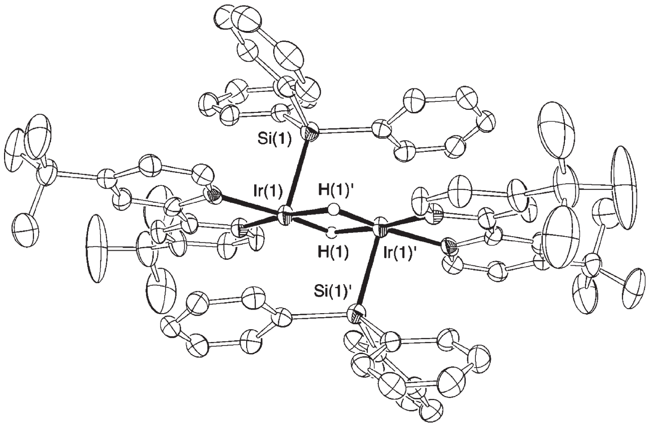
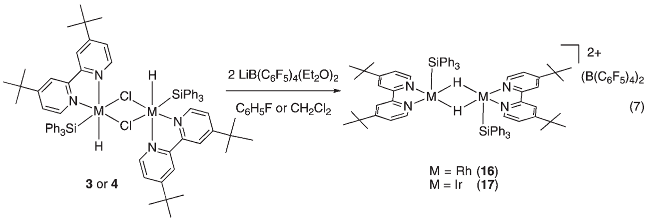


Figure 6. ORTEP diagram of **17** with thermal ellipsoids shown at the 50% probability level. Only one of the two independent molecules is shown. The hydrogen atoms (except for H(1) and H(1)′), the $B(C_6F_5)_4$ anions, and the CH_2Cl_2 molecule are omitted for clarity. Selected bond lengths (Å): Ir1−N1 = 2.034(4), Ir1−N2 = 2.074(4), Ir1−Si1 = 2.344(1), Ir1−H1 = 1.45(1), Ir1′−H1 = 1.78(1), and Ir1−C_{ipso} = 2.87(1). Selected bond angles (deg): N1−Ir1−N2 = 77.8(1), N1−Ir1−Si1 = 99.4(1), N2−Ir1−Si1 = 94.7(1), N1−Ir1−H1 = 96(1), N2−Ir1−H1 = 173(1), and Si1−Ir1−H1 = 88(1).



(7)

Additions of Lewis bases to **16** and **17** were explored to evaluate the accessibility of the coordination site that possesses the bonding interaction with the *ipso* carbon. Addition of 2 equiv of phosphine (PPh_3 or P^iPr_3) to **16** or **17** gave no reaction until decomposition after 16 h at 60 °C in CD_2Cl_2 (by ^1H NMR spectroscopy). Similarly, treatment of **16** or **17** with 2 equiv of tertiary silanes ($HSiEt_3$ or $HSiPh_3$) or 2 equiv of 1-hexene for 16 h at 60 °C in CD_2Cl_2 gave no reaction, and only decomposition was observed (by ^1H NMR spectroscopy).

An alternate path to **17** was achieved by addition of 1 equiv of $LiB(C_6F_5)_4(Et_2O)_2$ to the mononuclear P^iPr_3 complex **8** in CH_2Cl_2, which quantitatively produced **17** and 1 equiv of free P^iPr_3 (by ^1H and ^{31}P NMR spectroscopy).

Thermolysis of $(^tBu_2bpy)IrH(SiPh_3)(R)P^iPr_3$ Complexes. The thermolyses of iridium complexes **12**, **14**, and **15** were examined to characterize available reductive elimination pathways, which could serve as models for potential product-forming steps. Complexes of the type $L_2MH(SiR_3)R$

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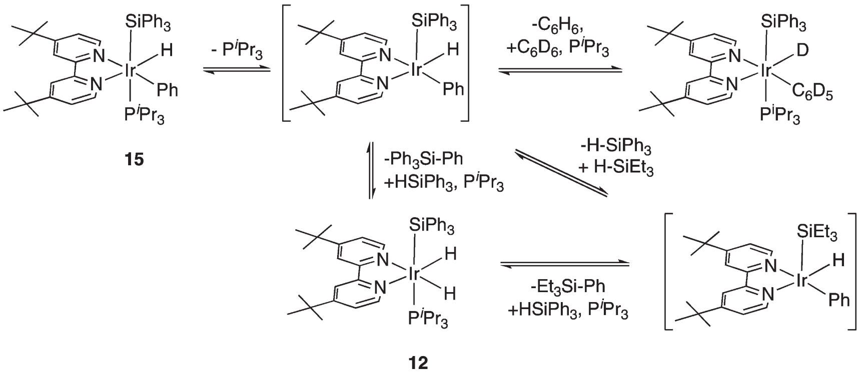
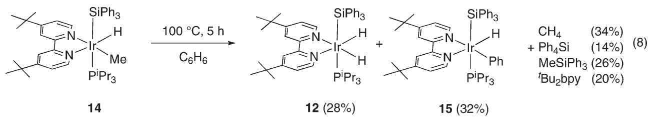
Scheme 1

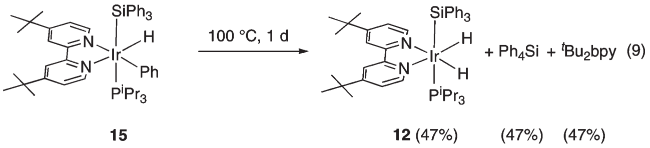


have been found to favor reductive eliminations to form C−H and Si−H bonds, with either very little or no Si−C bond formation.[36−38] Also, reductive eliminations from these complexes are expected to produce low-valent intermediates, which should engage in bond activation steps with appropriate substrates.

Heating a C_6D_6 solution of **12** to 180 °C for 2 days resulted in no H_2 evolution, and complete deuteration of the Ir−H positions was observed (by ^{1}H and ^{2}H NMR spectroscopy). After **12** was heated in C_6H_6 at 180 °C for 2 days, it was recovered in 95% yield (by ^{1}H NMR spectroscopy). The thermolysis of **14** was also examined by heating a solution of the complex in C_6D_6 to 100 °C. After 5 h, a complex mixture of products was observed (by ^{1}H and ^{2}H NMR spectroscopy), and the activation of C_6D_6 was indicated by the presence of multiple deuteride resonances in the ^{2}H NMR spectrum. The thermolysis of **14** in C_6H_6 at 100 °C over 5 h produced **12** and **15** in a 0.88:1 ratio, for a combined 60% yield (relative to a hexamethylbenzene internal standard), and CH_4 was also observed (eq 8).



The elimination of methane from **14** presumably generates a reactive Ir(I) silyl intermediate such as [(^{t}Bu$_2$bpy)-Ir(SiPh$_3$)P^{i}Pr$_3$], which then participates in bond activation reactions to give **12** and **15**. This intermediate could oxidatively add benzene to give one of the decomposition products (**15**). To examine the behavior of **15** under these reaction conditions, a solution of **15** in C_6H_6 was heated at 100 °C for 1 day. Workup of the reaction mixture provided **12**, free ^{t}Bu$_2$bpy, and Ph$_4$Si, each in 47% yield (eq 9), as confirmed by ^{1}H NMR spectroscopy and GC-MS of the organic compounds (integration values were calibrated to a known quantity of hexamethylbenzene as an internal standard). Addition of 1 equiv of P^{i}Pr$_3$ to a solution of **15** in C_6H_6 followed by heating at 100 °C for 4 days completely inhibited the thermolysis, and only **15** and P^{i}Pr$_3$ were observed (by ^{1}H NMR spectroscopy). The inhibition by added phosphine implies that phosphine dissociation is a key step in the thermolytic conversion of **15** to give **12**. Thermolysis of **15** in a solution of C_6D_6 for 1 day at 100 °C gave a mixture of **12**, **12**-d_1, and **12**-d_2 (1:2:1) with deuterium incorporation into the hydride positions (by ^{1}H and ^{2}H NMR spectroscopy). Addition of 1 equiv of HSiPh$_3$ to a C_6H_6 solution of **15** followed by heating to 100 °C for 1 day produced no free ^{t}Bu$_2$bpy, and **12** and Ph$_4$Si were produced in ≥95% yield (by ^{1}H NMR spectroscopy and GC-MS).



Addition of 1 equiv of HSiEt$_3$ to a solution of **15** at 100 °C produced **12** and PhSiEt$_3$ in ≥95% yield after 1 day, and no Ph$_4$Si was formed under these conditions. Interestingly, Si−C bond formation can also proceed under mild conditions upon reaction of HSiEt$_3$ with **15**. Addition of 10 equiv of HSiEt$_3$ to a benzene solution of **15** at 25 °C produced **12** and PhSiEt$_3$, both in ≥95% yield (based on Ir) after 1 day. Catalytic Si−C coupling to form PhSiEt$_3$ was not observed in this reaction, and when **15** was treated with 10 equiv of HSiPh$_3$ over 16 h at 100 °C, no catalysis was detected (**12** and Ph$_4$Si were both produced stoichiometrically and 9 equiv of HSiPh$_3$ remained, by ^{1}H NMR spectroscopy and GC-MS). Heating **12** or **15** in the presence of HSiPh$_3$ and 10 equiv of the hydrogen acceptor CH$_2$CH^{t}Bu did not facilitate catalytic turnover, and only 1 equiv of **12** was observed in both cases after 2 days at 100 °C (for the thermolysis of **15**, 1 equiv of Ph$_4$Si was also produced as determined by ^{1}H NMR spectroscopy and GC-MS).

Notably, the transformations described above provide evidence for C−H activation processes involving benzene. This was observed in the partial conversion of **14** to **15** in benzene and in the incorporation of deuterium into the hydride positions of **12** and **15** in the presence of benzene-d_6. The latter process implies C−H activation by an Ir(I) silyl complex supported by ^{t}Bu$_2$bpy (Scheme 1). The detailed nature of the low-valent species responsible for bond activations in this system is currently undefined, but related elimination−addition processes, involving preceding phosphine dissociation, have been the subject of mechanistic investigations.[39,40] The observed Si−C reductive elimination of arylsilanes is also noteworthy, in that it serves as a model for the product-forming step in catalytic silylations of arenes. Silyl-aryl reductive eliminations are observed in thermolyses of **14** and **15** and proceed cleanly in the presence of excess silane. This implies that silanes are efficient traps for an Ir(I) hydride intermediate in this system, which would be formed by the Si−C reductive elimination. A second type of Si−H activation appears to involve an intermediate Ir(I) phenyl

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species, since reaction of $HSiEt_3$ with **15** led to a high yield of $PhSiEt_3$, presumably via a preceding $HSiPh_3/HSiEt_3$ exchange process (Scheme 1). However, note that exchange of $HSiEt_3$ into the dihydride **12** is very slow, since addition of 10 equiv of $HSiEt_3$ to **12** in benzene resulted in no conversion after 12 days at 100 °C (by ^1H NMR spectroscopy).

An interesting comparison can be made with the thermolysis of $(PMe_3)_3IrH(SiPh_3)(Me)$ in benzene-d_6, which generates CH_4 by reductive elimination. Orthometalation of a phenyl substituent on the silyl ligand gives the final, isolated product, $(PMe_3)_3IrH(\kappa^2\text{-}o\text{-}C_6H_4SiMe_2)$ (48% yield after heating at 95 °C for 2 days).[36] A related complex, $(PMe_3)_3IrH(SiEt_3)(Me)$, gave both C−H and Si−C reductive elimination (80% CH_4, 20% $MeSiEt_3$) upon heating at 100 °C for 1 day, presumably via steps similar to those described in Scheme 1.[37] Furthermore, the related iridium complex (dppe)IrH($SiPh_2H$)(Mes)(CO) (dppe = bis(diphenylphosphino)ethane, Mes = 2,4,6-trimethylphenyl) readily undergoes reductive eliminations; however, only C−H and Si−H (and no Si−C) bond formations were observed.[38]

Given the observed Si−C reductive elimination for complex **15**, an attempt was made to observe the catalytic dehydrohalogenation of haloarenes. Reaction of 1 equiv of **15** with 10 equiv of $HSiEt_3$, 10 equiv of PhI (or PhCl), and 10 equiv of $LiN(SiMe_3)_2$ gave no coupling of the haloarene, and 1 equiv of **12** and $PhSiEt_3$ were observed after 8 h at 100 °C. No further change was observed after continued heating of the reaction mixture for 2 days at 120 °C (by ^1H NMR spectroscopy and GC-MS).

Concluding Remarks

The simple dimeric $[(^tBu_2bpy)M(\mu\text{-}Cl)]_2$ complexes allow synthetic access to monomeric group 9 chlorohydridosilyl complexes by facile Si−H oxidative addition followed by phosphine coordination. For iridium, rare examples of complexes containing hydride, silyl, and hydridocarbyl (phenyl or methyl) groups have been isolated. Interestingly, the thermolysis of **15** does not lead to an orthometalation product, as is observed for the related $(PMe_3)_3IrH(SiPh_3)(Me)$,[36] but rather to C−Si bond formation to produce Ph_4Si.

The reductive elimination pathways available to **15** are of relevance to catalytic aryl−Si bond-forming reactions, many of which employ rhodium-based catalysts. The intermediates proposed for these reactions often take the form $[M]H(SiR_3)Ar$. For (PyInd)Rh complexes that have been found to catalyze Si−C coupling reactions between hydrosilanes and aryl chlorides, a proposed intermediate is $(PyInd)RhHCl(SiEt_3)Ph$.[19] For the coupling of arenes with triethylsilane, the catalyst $Cp^*Rh(H)_2(SiEt_3)_2$ is proposed to go through an intermediate of the type $Cp^*RhH(SiEt_3)_2Ar$.[41] Furthermore, the intermediate $(dipphen)IrH(Si^sBuF_2)_n(Ar)$ (dipphen = 2,9-diisopropyl-1,10-phenanthroline, $n = 1$ or 3) has been proposed for the silylation of arenes with fluorodisilanes.[17] Although catalytic Si−C bond-forming reactions have yet to be observed in the $(^tBu_2bpy)M$ systems described here, it is hoped that these reactivity studies will serve as a basis for the development of such catalysis.

Experimental Section

General Procedures. All experiments were conducted under nitrogen using standard Schlenk techniques or in a Vacuum Atmospheres drybox. Nondeuterated solvents were distilled under N_2 from appropriate drying agents and stored in PTFE-valved flasks. Deuterated solvents (Cambridge Isotopes) were vacuum-transferred from appropriate drying agents.

The compounds $HSiPh_3$, $HSiEt_3$, PPh_3, MeLi (1.6 M in Et_2O), $LiBEt_3H$ (1.0 M in Et_2O), and $^tBu_2bpy$ were purchased from Aldrich and dried over appropriate drying agents. The compound P^iPr_3 was purchased from Strem and used without further purification. The compounds PhLi,[42] $[(coe)_2Ir(\mu\text{-}Cl)]_2$,[43] $[(C_2H_4)_2Rh(\mu\text{-}Cl)]_2$,[44] and $LiB(C_6F_5)_4(Et_2O)_2$[45] were synthesized according to literature procedures.

Analytical Methods. ^1H, ^2H, $^{29}Si\{^1H\}$, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectra were recorded using Bruker AVB 400, AV-500, or DRX 500 spectrometers equipped with a 5 mm BB probe. Spectra were recorded at room temperature and referenced to the residual protonated solvent for ^1H NMR spectrum or to tetramethylsilane for the ^{29}Si NMR spectrum. $^{31}P\{^1H\}$ NMR spectra were referenced relative to 85% H_3PO_4 external standard ($\delta = 0$). $^{13}C\{^1H\}$ NMR spectra were calibrated internally with the resonance for the solvent relative to tetramethylsilane. Coupling constants in the ^1H NMR spectrum (J_{RhH}, J_{PH}, and J_{SiH}) were determined by ^{31}P-filtered ^1H NMR spectroscopy, $^1H\{^{31}P\}$ NMR spectroscopy, and ^{29}Si-filtered ^1H NMR spectroscopy. Coupling constants in the ^{29}Si NMR spectrum (J_{SiRh} and J_{SiP}) were determined by comparing a ^1H, $^{29}Si\{^{31}P\}$ HMBC NMR spectrum to the ^{29}Si NMR spectrum. Elemental analyses were performed by the College of Chemistry Microanalytical Laboratory at the University of California, Berkeley. Identities of organic products were confirmed by ^1H NMR spectroscopy and by GC-MS, using an Agilent Technologies 6890N GC system with an HP-5MS column.

$[(^tBu_2bpy)RhCl]_2$ (1). A 5 mL benzene solution of $^tBu_2bpy$ (0.689 g, 2.57 mmol) was added to a 5 mL solution of $[(C_2H_4)_2Rh(\mu\text{-}Cl)]_2$ (0.500 g, 1.28 mmol) in benzene. The reaction mixture was stirred for 1 h, and the volatile compounds were removed *in vacuo*. The resulting purple solid was extracted with 5 mL of THF, and the volatile material was then removed *in vacuo*. The isolated purple solid was washed with 2 mL of pentane to give the pure product in 95% yield (0.992 g, 1.22 mmol). ^1H NMR (C_6D_6): δ 9.25 (d, $J_{HH} = 6.0$ Hz, 2H, Ar*H*), 7.98 (s, 2H, Ar*H*), 7.77 (s, 2H, Ar*H*), 7.63 (d, $J_{HH} = 6.0$ Hz, 2H, Ar*H*), 7.37 (d, $J_{HH} = 6.0$ Hz, 2H, Ar*H*), 7.22 (d, $J_{HH} = 6.0$ Hz, 2H, Ar*H*), 1.45 (s, 18H, CCH_3), 1.38 (s, 18H, CCH_3). $^{13}C\{^1H\}$ NMR: δ 158.5, 156.9, 150.4, 147.7, 123.7, 123.1, 118.7, 117.2, 35.5, 30.0. Anal. Calcd (%) for $C_{36}H_{48}Cl_2N_4Rh_2$: C, 53.15, H, 5.95, N, 6.89. Found: C, 52.81, H, 6.25, N, 6.74.

$[(^tBu_2bpy)IrCl]_2$ (2). A 5 mL benzene solution of $^tBu_2bpy$ (0.494 g, 1.84 mmol) was added to a 5 mL solution of $[(coe)_2Ir(\mu\text{-}Cl)]_2$ (0.500 g, 0.921 mmol) in benzene. The reaction mixture was stirred for 1 h, and the volatile compounds were removed *in vacuo*. The resulting red solid was extracted with 5 mL of THF, and the volatile material was then removed *in vacuo*. The isolated red solid was washed with 2 mL of pentane to give the pure product in 92% yield (0.839 g, 0.840 mmol). ^1H NMR (C_6D_6): δ 9.55 (d, $J_{HH} = 4.5$ Hz, 2H, Ar*H*), 8.10 (s, 2H, Ar*H*), 8.06 (d, $J_{HH} = 6.0$ Hz, 2H, Ar*H*), 7.87 (s, 2H, Ar*H*), 7.61 (d, $J_{HH} = 6.0$ Hz, 2H, Ar*H*), 7.37 (d, $J_{HH} = 4.5$ Hz, 2H, Ar*H*), 1.49

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(s, 18H, CCH_3), 1.43 (s, 18H, CCH_3). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): 170.0, 160.5, 157.5, 150.9, 123.1, 122.2, 118.9, 118.1, 35.0, 34.9. Anal. Calcd (%) for $C_{36}H_{48}Cl_2N_4Ir_2$: C, 43.58, H, 4.84, N, 5.65. Found: C, 39.26, H, 4.74, N, 5.39. This complex was recrystallized from THF, but this did not provide a better agreement for the combustion analysis. However, the complex is pure by NMR spectroscopy and proved to be a suitable starting material as described below.

$[(^t\mathrm{Bu_2bpy})\mathrm{RhH(SiPh_3)}(\mu\text{-}\mathrm{Cl})]_2$ (3). A 5 mL benzene solution of HSiPh$_3$ (0.320 g, 1.23 mmol) was added to a 5 mL solution of $[(^t\mathrm{Bu_2bpy})\mathrm{RhCl}]_2$ (0.500 g, 0.615 mmol) in benzene. The reaction mixture was stirred for 1 h, and the volatile compounds were removed *in vacuo*. The resulting maroon solid was dissolved with 5 mL of THF, and the reaction mixture was passed through Celite. The resulting solution was then evacuated to dryness. The isolated maroon solid was washed with 2 mL of pentane to give the pure product in 92% yield (0.750 g, 0.563 mmol). ^{1}H NMR (C$_6$D$_6$): δ 9.05 (d, J_{HH} = 5.0 Hz, 2H, ArH), 8.31 (d, J_{HH} = 6.5 Hz, 2H, ArH), 8.00 (s, 2H, ArH), 7.92 (s, 2H, ArH), 7.56 (d, J_{HH} = 6.5 Hz, 2H, ArH), 7.18 (d, J_{HH} = 7.5 Hz, 12H, SiArH), 7.05 (t, J_{HH} = 7.5 Hz, 6H, SiArH), 6.92 (t, J_{HH} = 7.5 Hz, 12H, SiArH), 6.72 (d, J_{HH} = 5.0 Hz, 2H, ArH), 1.54 (s, 18H, CCH_3), 1.46 (s, 18H, CCH_3), −14.80 (d, J_{RhH} = 25 Hz 2H, RhH). ^{13}C{^{1}H} NMR: δ 161.2, 159.5, 157.9, 156.4, 150.8, 142.3, 135.5, 129.3, 128.9, 127.8, 126.5, 126.3, 122.5, 117.9, 117.0, 35.1, 30.2. ^{29}Si{^{1}H} NMR: δ 20.6. Anal. Calcd (%) for $C_{72}H_{80}Cl_2Rh_2N_4Si_2$: C, 64.81, H, 6.04, N, 4.20. Found: C, 64.75, H, 6.19, N, 4.53.

$[(^t\mathrm{Bu_2bpy})\mathrm{IrH(SiPh_3)}(\mu\text{-}\mathrm{Cl})]_2$ (4). A 5 mL benzene solution of HSiPh$_3$ (0.262 g, 1.01 mmol) was added to a 5 mL solution of $[(^t\mathrm{Bu_2bpy})\mathrm{IrCl}]_2$ (0.500 g, 0.505 mmol) in benzene. The reaction mixture was stirred for 1 h, and the volatile compounds were removed *in vacuo*. The resulting red solid was dissolved with 5 mL of THF, and the reaction mixture was passed through Celite. The resulting solution was then evacuated to dryness. The isolated red solid was washed with 2 mL of pentane to give the product in 90% yield (0.686 g, 0.455 mmol). ^{1}H NMR (C$_6$D$_6$): δ 9.10 (d, J_{HH} = 6.5 Hz, 2H, ArH), 8.75 (d, J_{HH} = 4.5 Hz, 2H, ArH), 7.90 (s, 2H, ArH), 7.87 (s, 2H, ArH), 7.24 (d, J_{HH} = 4.5 Hz, 2H, ArH), 7.01 (ov m, 18H, SiArH), 6.86 (t, J_{HH} = 7.0 Hz, 12H, SiArH), 6.67 (d, J_{HH} = 6.5 Hz, 2H, ArH), 1.49 (s, 18H, CCH_3), 1.41 (s, 18H, CCH_3), −17.21 (s, 2H, IrH, T_1 = 0.432 s). ^{13}C{^{1}H} NMR: δ 151.7, 139.2, 135.7, 135.5, 133.4, 130.0, 129.8, 128.1, 127.8, 127.1, 124.5, 119.5, 30.1, 26.1. ^{29}Si{^{1}H} NMR: δ −20.5. Anal. Calcd (%) for $C_{72}H_{80}Cl_2Ir_2N_4Si_2$: C, 57.16, H, 5.33, N, 3.70. Found: C, 56.80, H, 5.43, N, 3.66.

$[(^t\mathrm{Bu_2bpy})\mathrm{RhH(SiEt_3)}(\mu\text{-}\mathrm{Cl})]_2$ (5). To an NMR tube were added $[(^t\mathrm{Bu_2bpy})\mathrm{RhCl}]_2$ (0.025 g, 0.062 mmol) and 0.5 mL of a C$_6$D$_6$ solution of HSiEt$_3$ (0.007 g, 0.060 mmol). The NMR tube was capped, inverted three times, and then placed into the NMR probe. ^{1}H NMR (C$_6$D$_6$): δ 9.52 (br s, 2H, ArH), 9.20 (br s, 2H, ArH), 7.86 (br s, 4H, ArH), 6.84 (br s, 2H, ArH), 6.74 (br s, 2H, ArH), 1.07 (s, 18H, CCH_3), 1.02 (s, 18H, CCH_3), 0.96 (t, J_{HH} = 7.0 Hz, 18H, SiCH$_2$CH_3), 0.52 (br m, 12H, SiCH_2CH$_3$), −15.22 (d, J_{RhH} = 20.0 Hz, 2H, RhH). ^{1}H, ^{29}Si{^{1}H} HMBC NMR: δ 19.0.

$[(^t\mathrm{Bu_2bpy})\mathrm{IrH(SiEt_3)}(\mu\text{-}\mathrm{Cl})]_2$ (6). A 5 mL benzene solution of HSiEt$_3$ (0.118 g, 1.02 mmol) was added to a 5 mL solution of $[(^t\mathrm{Bu_2bpy})\mathrm{IrCl}]_2$ (0.500 g, 0.505 mmol) in benzene. The reaction mixture was stirred for 1 h, and the volatile material was then removed under vacuum. The resulting red solid was dissolved in 5 mL of THF, the reaction mixture was passed through Celite, and the volatile material was then removed *in vacuo*. The isolated red solid was washed with 2 mL of pentane to give the pure product in 75% yield (0.569 g, 0.465 mmol). ^{1}H NMR (C$_6$D$_6$): δ 9.72 (d, J_{HH} = 4.0 Hz, 2H, ArH), 9.43 (d, J_{HH} = 5.5 Hz, 2H, ArH), 7.95 (s, 2H, ArH), 7.84 (s, 2H, ArH), 7.49 (d, J_{HH} = 5.5 Hz, 2H, ArH), 7.13 (d, J_{HH} = 4.0 Hz, 2H, ArH), 1.50 (s, 18H, CCH_3), 1.46 (s, 18H, CCH_3), 0.37 (t, J_{HH} = 8.0 Hz, 18H, SiCH$_2$CH_3), 0.21 (m, 12H, SiCH_2CH$_3$), −17.26 (s, 2H, IrH). ^{13}C{^{1}H} NMR: δ 160.2, 159.4, 157.9, 157.7, 150.0, 136.2, 128.9, 123.3, 122.1, 118.5, 117.5, 35.1, 30.1, 7.7, 6.4. ^{1}H, ^{29}Si{^{1}H} HMBC NMR: δ −1.9. Anal. Calcd (%) for $C_{48}H_{80}Cl_2Ir_2N_4Si_2$: C, 47.07, H, 6.58, N, 4.57. Found: C, 46.97, H, 6.38, N, 4.32.

$(^t\mathrm{Bu_2bpy})\mathrm{RhH(SiPh_3)Cl(P}^i\mathrm{Pr_3)}$ (7). A 5 mL benzene solution of P^{i}Pr$_3$ (0.0866 g, 0.541 mmol) was added to a 5 mL solution of $[(^t\mathrm{Bu_2bpy})\mathrm{RhH(SiPh_3)}(\mu\text{-}\mathrm{Cl})]_2$ (0.360 g, 0.270 mmol) in benzene. The reaction mixture was stirred for 4 h, and the volatile material was removed *in vacuo*. The resulting purple solid was crystallized by vapor diffusion of pentane into a THF solution to give purple crystals of the product in 72% yield (0.322 g, 0.390 mmol). ^{1}H NMR (C$_6$D$_6$): δ 10.67 (d, J_{HH} = 5.0 Hz, 1H, ArH), 8.69 (d, J_{HH} = 5.0 Hz, 1H, ArH), 7.75 (d, J_{HH} = 6.0 Hz, 6H, ArH), 7.39 (s, 1H, ArH), 7.28 (s, 1H, ArH), 7.16 (m overlapping with benzene-d_6, 9H, ArH), 6.90 (d, J_{HH} = 5.0 Hz, 1H, ArH), 6.37 (d, J_{HH} = 5.0 Hz, 1H, ArH), 2.79 (m, 3H, PCH), 1.53 (m, 18H, PCHCH_3), 1.08 (s, 9H, CCH_3), 0.95 (s, 9H, CCH_3), −16.00 (dd, J_{HP} = 20.0 Hz, J_{RhH} = 10.0 Hz, 1H, RhH). ^{13}C{^{1}H} NMR: δ 157.9, 156.3, 154.3, 150.8, 136.2, 135.3, 133.0, 130.5, 129.2, 128.2, 126.4, 125.5, 121.9, 118.8, 115.7, 34.8, 34.1, 23.6 (J_{CP} = 13.0 Hz), 19.8. ^{29}Si{^{1}H} NMR: δ −9.3 (m, J_{SiRh} = 20.0 Hz). ^{31}P{^{1}H} NMR: δ 54.5 (J_{RhP} = 88.0 Hz). Anal. Calcd (%) for $C_{45}H_{61}ClN_2PRhSi$: C, 65.32, H, 7.43, N, 3.39. Found: C, 65.06, H, 7.81, N, 3.48.

$(^t\mathrm{Bu_2bpy})\mathrm{IrH(SiPh_3)Cl(P}^i\mathrm{Pr_3)}$ (8). A 5 mL benzene solution of P^{i}Pr$_3$ (0.0530 g, 0.331 mmol) was added to a 5 mL solution of $[(^t\mathrm{Bu_2bpy})\mathrm{IrH(SiPh_3)}(\mu\text{-}\mathrm{Cl})]_2$ (0.250 g, 0.165 mmol) in benzene. The reaction mixture was stirred for 4 h, and the volatile compounds were removed *in vacuo*. The resulting red-orange solid was dissolved in 5 mL of THF, the reaction mixture was passed through Celite, and the volatile components were removed under vacuum. The isolated red-orange solid was crystallized by vapor diffusion of pentane into a THF solution to give red crystals of the product in 80% yield (0.243 g, 0.265 mmol). ^{1}H NMR (C$_6$D$_6$): δ 9.61 (d, J_{HH} = 5.0 Hz, 1H, ArH), 8.32 (d, J_{HH} = 5.0 Hz, 1H, ArH), 7.78 (s, 1H, ArH), 7.76 (d, J_{HH} = 6.0 Hz, 6H, ArH), 7.71 (s, 1H, ArH), 7.00 (m, 9H, ArH), 6.54 (d, J_{HH} = 5.0 Hz, 1H, ArH), 5.90 (d, J_{HH} = 5.0 Hz, 1H, ArH), 2.21 (m, 3H, PCH), 1.00 (m, 18H, PCHCH_3), 0.98 (s, 9H, CCH_3), 0.95 (s, 9H, CCH_3), −16.68 (d, J_{HP} = 15.0 Hz, 1H, IrH). ^{13}C{^{1}H} NMR: δ 158.2, 155.7, 149.8, 144.1, 136.5, 128.0, 126.4, 125.8, 123.8, 122.7, 117.2, 116.5, 34.24, 34.15, 31.5, 29.6 (J_{CP} = 19.4 Hz), 18.6 (J_{CP} = 8.5 Hz). ^{29}Si{^{1}H} HMBC NMR: δ −13.4 (d, J_{SiP} = 144.5, Hz, J_{SiH} = 15.0 Hz). ^{31}P{^{1}H} NMR: δ 4.35. Anal. Calcd (%) for $C_{45}H_{61}ClIrN_2PSi$: C, 58.96, H, 6.71, N, 3.06. Found: C, 59.03, H, 6.80, N, 2.99.

$(^t\mathrm{Bu_2bpy})\mathrm{RhH(SiPh_3)Cl(PPh_3)}$ (9). A 5 mL benzene solution of PPh$_3$ (0.0982 g, 0.378 mmol) was added to a 5 mL solution of $[(^t\mathrm{Bu_2bpy})\mathrm{RhH(SiPh_3)}(\mu\text{-}\mathrm{Cl})]_2$ (0.250 g, 0.188 mmol) in benzene. The reaction mixture was stirred for 4 h, and the volatile compounds were removed *in vacuo*. The resulting red solid was dissolved in 5 mL of THF, and the reaction mixture was passed through Celite. The volatile components were then removed under vacuum. The resulting red solid was crystallized by vapor diffusion of pentane into a THF solution to give purple crystals of the product in 92% yield (0.323 g, 0.347 mmol). ^{1}H NMR (C$_6$D$_6$): δ 10.55 (d, J_{HH} = 6.0 Hz, 1H, ArH), 9.06 (s, 1H, ArH), 8.31 (t, J_{HH} = 7.0 Hz, 6H, ArH), 8.17 (d, J_{HH} = 4.5 Hz, 1H, ArH), 7.84 (d, J_{HH} = 5.0 Hz, 1H, ArH), 7.66 (d, J_{HH} = 5.5 Hz, 3H, ArH), 7.56 (ov m, 7H, ArH), 7.15−6.87 (ov m, 9H, ArH), 6.16 (d, J_{HH} = 4.5 Hz, 1H, ArH), 1.16 (s, 9H, CCH_3), 1.00 (s, 9H, CCH_3), −15.15 (dd, J_{HP} = 20.0 Hz, J_{RhH} = 25.0 Hz, 1H, RhH). ^{13}C{^{1}H} NMR: δ 156.7, 155.1, 154.1, 153.0, 152.3, 137.1, 136.4, 135.8, 134.3, 133.0 (J_{CP} = 8.0 Hz), 132.6, 130.5, 129.8, 128.8, 128.3, 127.1, 126.5, 121.6, 121.3, 116.6, 34.0, 30.0. ^{1}H, ^{29}Si{^{1}H} HMBC NMR: δ −9.1 (dd, J_{SiP} = 151.0 Hz, J_{SiRh} = 40.0 Hz). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): δ 33.2 (d, J_{RhP} = 91.1 Hz). Anal. Calcd (%) for

$C_{54}H_{55}ClN_2RhPSi$: C, 69.78, H, 5.96, N, 3.01. Found: C, 69.60, H, 6.12, N, 3.30.

(^{t}Bu$_2$bpy)IrH(SiPh$_3$)Cl(PPh$_3$) (10). A 5 mL benzene solution of PPh$_3$ (0.0866 g, 0.330 mmol) was added to a 5 mL solution of [(^{t}Bu$_2$bpy)IrH(SiPh$_3$)(μ-Cl)]$_2$ (0.250 g, 0.165 mmol) in benzene. The reaction mixture was stirred for 4 h, and the volatile compounds were removed *in vacuo*. The resulting orange solid was dissolved in 5 mL of THF, the reaction mixture was passed through Celite, and the volatile material was removed under vacuum. The resulting orange solid was crystallized by vapor diffusion of pentane into a THF solution to give the product as orange crystals in 88% yield (0.148 g, 0.146 mmol). ^{1}H NMR (C_6D_6): δ 9.06 (d, J_{HH} = 6.0 Hz, 1H, Ar*H*), 7.77 (s, 1H, Ar*H*), 7.61 (d, J_{HH} = 6.4 Hz, 1H, Ar*H*), 7.55−7.34 (ov m, 23H, Ar*H*), 7.31 (d, J_{HH} = 6.4 Hz, 1H, Ar*H*), 7.26 (d, J_{HH} = 6.4 Hz, 1H, Ar*H*), 7.19 (t, J_{HH} = 2.4 Hz, 6H, Ar*H*), 7.05 (d, J_{HH} = 2.4 Hz, 1H, Ar*H*), 5.90 (d, J_{HH} = 6.4 Hz, 1H, Ar*H*), 1.45 (s, 9H, CC*H*$_3$), 1.28 (s, 9H, CC*H*$_3$), −16.87 (d, J_{HP} = 12.8 Hz, 1H, Ir*H*, T_1 = 0.547 s). ^{13}C{^{1}H} NMR: δ 160.6, 159.3, 158.3, 150.5, 141.5, 135.6 (J_{CP} = 8.8 Hz), 129.8, 128.0, 126.3 (J_{CP} = 21.1 Hz), 123.2, 122.2, 118.3, 117.3, 35.1, 30.1. ^{1}H, ^{29}Si{^{1}H} HMBC NMR: δ −9.2 (d, J_{SiP} = 121.7 Hz). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ −0.36. Anal. Calcd (%) for $C_{54}H_{55}ClIrN_2PSi$: C, 63.66, H, 5.44, N, 2.75. Found: C, 63.99, H, 5.40, N, 3.04.

(^{t}Bu$_2$bpy)Rh(H)$_2$(SiPh$_3$)P^{i}Pr$_3$ (11). A 5 mL THF solution of (^{t}Bu$_2$bpy)RhH(SiPh$_3$)Cl(P^{i}Pr$_3$) (0.200 g, 0.242 mmol) was cooled to −78 °C. To this solution was added LiBEt$_3$H (0.24 mL of 1.0 M in THF) via syringe, and the reaction mixture was allowed to stir for 1 h. The mixture was allowed to warm to room temperature and then stirred for an additional 1 h. The volatile compounds were removed under reduced pressure. Benzene (15 mL) was added to dissolve the resulting solid. The solution was filtered through Celite, and the volatile material was removed *in vacuo* to give a purple solid. The resulting purple solid was crystallized by vapor diffusion of pentane into a THF solution to give the product as purple crystals in 77% yield (0.147 g, 0.186 mmol). ^{1}H NMR (C_6D_6): δ 8.68 (d, J_{HH} = 5.6 Hz, 2H, Ar*H*), 7.83 (s, 2H, Ar*H*), 7.76 (d, J_{HH} = 6.5 Hz, 6H, Ar*H*), 7.15 (ov m, 9H, Ar*H*), 6.40 (d, J_{HH} = 6.5 Hz, 2H, Ar*H*), 1.93 (br d, J_{HH} = 6.8 Hz, 3H, PC*H*), 1.19 (s, 18H, CC*H*$_3$), 0.95 (m, 18H, PCHC*H*$_3$), −16.06 (dd, J_{HP} = 21.0 Hz, J_{RhH} = 13.5 Hz, 2H, Rh*H*). ^{13}C{^{1}H} NMR: δ 156.4, 154.3, 153.2, 136.2, 135.7, 129.4, 126.4, 125.5, 120.9, 117.0, 30.0, 26.3 (J_{CP} = 7.0 Hz), 19.6. ^{1}H, ^{29}Si{^{1}H} HMBC NMR: δ 24.4 (dd, J_{SiP} = 173.0 Hz, J_{SiRh} = 11.4 Hz). ^{31}P{^{1}H} NMR: δ 44.9 (d J_{PRh} = 91.0 Hz). Anal. Calcd (%) for $C_{45}H_{62}N_2PRhSi$: C, 68.16, H, 7.88, N, 3.53. Found: C, 68.06, H, 8.00, N, 3.64.

(^{t}Bu$_2$bpy)Ir(H)$_2$(SiPh$_3$)(P^{i}Pr$_3$) (12). A 5 mL THF solution of (^{t}Bu$_2$bpy)IrH(SiPh$_3$)Cl(P^{i}Pr$_3$) (0.100 g, 0.110 mmol) was cooled to −78 °C. To this solution was added LiBEt$_3$H (0.15 mL of 1.0 M in THF) via syringe, and the reaction mixture was allowed to stir for 1 h. The mixture was allowed to warm to room temperature and then stirred for an additional 1 h. The volatile compounds were then removed under reduced pressure, and 15 mL of benzene was added to dissolve the product. The resulting solution was filtered through Celite, and the volatile components were removed under vacuum. The resulting purple solid was crystallized by vapor diffusion of pentane into a THF solution to give purple crystals in 78% yield (0.075 g, 0.085 mmol). ^{1}H NMR (C_6D_6): δ 8.96 (d, J_{HH} = 5.6 Hz, 2H, Ar*H*), 7.78 (d, J_{HH} = 7.6 Hz, 6H, Ar*H*), 7.57 (s, 2H, Ar*H*), 7.06 (ov m, 9H, Ar*H*), 6.30 (d, J_{HH} = 5.6 Hz, 2H, Ar*H*), 1.99 (br d, J_{HH} = 6.8 Hz, 3H, PC*H*), 1.03 (s, 18H, CC*H*$_3$), 0.96 (q, J_{HH} = 6.8 Hz, 18H, PCHC*H*$_3$), −18.93 (d, J_{HP} = 16.8 Hz, 2H, Ir*H*). ^{13}C{^{1}H} NMR: δ 155.3, 154.9, 154.8, 144.5, 136.2, 127.9, 126.4, 125.5, 121.8, 117.8, 34.1, 27.6 (J_{CP} = 16.0 Hz), 19.4. ^{1}H, ^{29}Si{^{1}H} HMBC NMR: δ 6.65 (d, J_{SiP} = 128.0 Hz, J_{SiH} = 4.5 Hz). ^{31}P{^{1}H} NMR: δ 27.54. Anal. Calcd (%) for $C_{45}H_{62}IrN_2PSi$: C, 61.26, H, 7.08, N, 3.18. Found: C, 61.21, H, 7.14, N, 3.04.

(P^{i}Pr$_3$)$_2$RhCl(C$_2$H$_4$) (13). A 5 mL THF solution of (^{t}Bu$_2$bpy)RhH(SiPh$_3$)Cl(P^{i}Pr$_3$) (0.100 g, 0.121 mmol) was cooled to −78 °C. To this solution was added MeLi (0.08 mL of 1.6 M in Et_2O) via syringe, and the reaction mixture was allowed to stir for 1 h. The solution was allowed to warm to room temperature and then stirred for an additional 1 h. The volatile compounds were removed under reduced pressure, and 10 mL of benzene was added to dissolve the resulting solid. The solution was filtered through Celite, and the volatile material was removed under vacuum to give a purple solid. Slow evaporation from a THF solution produced yellow crystals of **13** in 47% yield (0.047 g, 0.097 mmol). NMR spectra and the X-ray structure are consistent with previously reported data.[24]

(^{t}Bu$_2$bpy)IrH(SiPh$_3$)(Me)P^{i}Pr$_3$ (14). A 5 mL THF solution of (^{t}Bu$_2$bpy)IrH(SiPh$_3$)Cl(P^{i}Pr$_3$) (0.100 g, 0.110 mmol) was cooled to −78 °C. To this solution was added MeLi (0.10 mL of 1.6 M in Et_2O) via syringe, and the reaction mixture was allowed to stir for 1 h. The reaction mixture was allowed to warm to room temperature and was then stirred for an additional 1 h. The volatile compounds were then removed under reduced pressure, and 10 mL of benzene was added to dissolve the product. The solvent was filtered through Celite, and the volatile material was removed under vacuum to give a purple solid in 82% yield (0.080 g, 0.090 mmol). ^{1}H NMR (C_6D_6): δ 8.70 (d, J_{HH} = 6.0 Hz, 1H, Ar*H*), 8.56 (d, J_{HH} = 6.0 Hz, 1H, Ar*H*), 7.91 (s, 1H, Ar*H*), 7.86 (s, 1H, Ar*H*), 7.65 (d, J_{HH} = 7.5 Hz, 6H, Ar*H*), 7.02 (m, 6H, Ar*H*), 6.42 (d, J_{HH} = 6.0 Hz, 1H, Ar*H*), 6.18 (d, J_{HH} = 6.0 Hz, 1H, Ar*H*), 2.08 (m, 3H, PC*H*), 1.06 (s, 9H, CC*H*$_3$), 1.02 (dd, J_{HH} = 7.5 Hz, J_{HP} = 12.0 Hz, 3H, IrC*H*$_3$), 1.00 (s, 9H, CC*H*$_3$), 0.83 (m, 9H, PCHC*H*$_3$), −17.29 (br d, J_{HP} = 17.0 Hz, 1H, Ir*H*). ^{13}C{^{1}H} NMR: δ 156.9, 155.8, 155.7, 148.3, 145.5, 136.2, 136.1, 135.3, 129.2, 126.4, 125.4, 122.9, 122.1, 117.4, 117.2, 38.2, 30.0, 29.4, 18.4 (J_{CP} = 12.5 Hz), −34.1. ^{1}H, ^{29}Si{^{1}H} HMBC NMR: δ −1.86 (d J_{SiP} = 163.0 Hz). ^{31}P{^{1}H} NMR: δ 6.46. Anal. Calcd (%) for $C_{46}H_{64}IrN_2PSi$: C, 61.64, H, 7.20, N, 3.13. Found: C, 61.62, H, 7.38, N, 3.10.

(^{t}Bu$_2$bpy)IrH(SiPh$_3$)(Ph)P^{i}Pr$_3$ (15). A 5 mL THF solution of (^{t}Bu$_2$bpy)IrH(SiPh$_3$)Cl(P^{i}Pr$_3$) (0.200 g, 0.218 mmol) was added to a flask equipped with a stir bar. To this solution was added PhLi (0.019 g, 0.226 mmol) in 5 mL of THF, and the reaction solution was allowed to stir for 10 h. The volatile material was removed under vacuum, and 5 mL of benzene was added to dissolve the remaining solid. The reaction mixture was filtered through Celite, and the volatile compounds were removed *in vacuo*. A purple-brown solid was isolated in 90% yield (0.189 g, 0.197 mmol). ^{1}H NMR (C_6D_6): δ 10.07 (d, J_{HH} = 6.0 Hz, 1H, Ar*H*), 8.89 (d, J_{HH} = 6.0 Hz, 1H, Ar*H*), 8.15 (d, J_{HH} = 7.0 Hz, 2H, Ar*H*), 7.67 (s, 1H, Ar*H*), 7.65 (s, 1H, Ar*H*), 7.52 (d, J_{HH} = 7.0 Hz, 6H, Ar*H*), 7.09 (br d, 9H, Ar*H*), 6.93 (t, J_{HH} = 7.0 Hz, 2H, Ar*H*), 6.63 (ov m, 2H, Ar*H*), 6.22 (d, J_{HH} = 6.0 Hz, 1H, Ar*H*), 2.07 (m, 3H, PC*H*), 1.09 (m, 18H, PCHC*H*$_3$), 0.94 (s, 9H, CC*H*$_3$), 0.57 (q, 9H, PCHC*H*$_3$), −17.48 (d, J_{HP} = 16.0 Hz, 1H, Ir*H*). ^{13}C{^{1}H} NMR: δ 157.2, 156.3, 155.7, 155.4, 153.9, 146.9, 141.3, 136.5, 128.6, 128.1, 127.7, 126.2, 125.1, 122.4, 122.1, 121.7, 120.5, 118.6, 118.0, 29.9, 29.7, 21.6 (J_{CP} = 18.0 Hz), 20.6 (J_{CP} = 13.0 Hz). ^{1}H, ^{29}Si{^{1}H} HMBC NMR: δ −3.42. ^{31}P{^{1}H} NMR: δ 19.36. Anal. Calcd (%) for $C_{51}H_{62}IrN_2PSi$: C64.19, H, 6.55, N, 2.94. Found: C, 63.84, H, 6.48, N, 3.14.

[(^{t}Bu$_2$bpy)Rh(SiPh$_3$)(μ-H)]$_2$[B(C$_6$F$_5$)$_4$]$_2$ (16). A 5 mL fluorobenzene solution of [(^{t}Bu$_2$bpy)RhH(SiPh$_3$)(μ-Cl)]$_2$ (0.132 g, 0.198 mmol) was added to a flask equipped with a stir bar. To this solution was added LiB(C_6F_5)$_4$(Et_2O)$_2$ (0.165 g, 0.198 mmol), and the reaction mixture was allowed to stir for 2 h. The mixture was filtered through Celite, and the volatile material was removed under vacuum to give a maroon solid in 90% yield (0.237 g, 0.178 mmol). ^{1}H NMR (CD_2Cl_2): δ 7.92 (d, J_{HH} = 6.0 Hz, 4H, Ar*H*), 7.81 (s, 4H, Ar*H*), 7.35 (d, J_{HH} = 7.0 Hz, 18H, Ar*H*), 7.24 (d, J_{HH} = 6.0 Hz, 4H, Ar*H*), 7.00 (t, J_{HH} = 7.0 Hz, 12H, Ar*H*), 1.47 (s, 36H, CC*H*$_3$), −22.73 (t, J_{RhH} = 33.5 Hz, 2H, Rh*H*). ^{13}C{^{1}H} NMR: δ 170.9, 154.2, 153.7, 147.2 (br), 137.2 (br), 135.9, 135.5, 135.3 (br), 131.6, 131.2, 128.3 (br), 127.8, 124.7, 120.1, 29.7. ^{1}H, ^{29}Si{^{1}H} HMBC NMR: δ 24.1. ^{19}F NMR: δ −131.4 (br s, 16F), −162.3 (br s, 8F), −166.3 (br s, 16F). Anal. Calcd (%) for $C_{120}H_{80}B_2F_{40}N_4Rh_2Si_2$: C, 54.98, H, 3.08, N, 2.14. Found: C, 54.71, H, 3.20, N, 2.14.

[(^{t}Bu$_2$bpy)Ir(SiPh$_3$)(μ-H)]$_2$[B(C$_6$F$_5$)$_4$]$_2$ (17). A 5 mL CH_2Cl_2 solution of [(^{t}Bu$_2$bpy)IrH(SiPh$_3$)(μ-Cl)]$_2$ (0.150 g, 0.199 mmol) was added to a flask equipped with a stir bar. To this solution was added $LiB(C_6F_5)_4(Et_2O)_2$ (0.166 g, 0.199 mmol), and the reaction mixture was allowed to stir for 2 h. The solution was filtered through Celite, and the volatile compounds were removed *in vacuo* to give an orange solid. The resulting orange solid was dissolved in 1 mL of CH_2Cl_2, and pentane was allowed to vapor-diffuse into the solution. Orange crystals of the product were isolated in 92% yield (0.256 g, 0.178 mmol). ^{1}H NMR (CD_2Cl_2): δ 8.28 (d, J_{HH} = 6.0 Hz, 4H, Ar*H*), 7.84 (s, 4H, Ar*H*), 7.25 (m, 18H, Ar*H*), 7.13 (d, J_{HH} = 6.0 Hz, 4H, Ar*H*), 6.93 (t, J_{HH} = 7.0 Hz, 12H, Ar*H*), 1.43 (s, 36H, CC*H*$_3$), −22.51 (s, 2H, Ir*H*). ^{13}C{^{1}H} NMR: δ 166.7, 154.9, 154.4, 149.1 (br), 147.1 (br), 137.2 (br), 135.4, 131.6, 131.0, 127.9, 125.3, 120.3, 29.7. ^{1}H, ^{29}Si{^{1}H} HMBC NMR: δ −21.0. ^{19}F NMR: δ −132.3 (br s, 16F), −162.7 (br s, 8F), −166.7 (br s, 16F). Anal. Calcd (%) for $C_{120}H_{80}B_2F_{40}Ir_2N_4Si_2$: C, 51.47, H, 2.88, N, 2.00. Found: C, 51.17, H, 2.92, N, 2.00.

X-ray Structure Determinations. The X-ray analyses of compounds **7**, **8**, **11**, **12**, **14**, and **17** were carried out at the UC Berkeley CHEXRAY crystallographic facility. Measurements were made with a Bruker SMART CCD area detector with graphite-monochromated Mo Ka radiation (λ = 0.71073 Å). Data were integrated by the program SAINT and analyzed for agreement using XPREP. Empirical absorption corrections were made using SADABS. Structures were solved by direct methods and expanded using Fourier techniques. All calculations were performed using the SHELXTL crystallographic package. All non-hydrogen atoms were refined anisotropically unless otherwise stated.

For **7**: Crystals were grown from vapor diffusion of pentane into THF at 25 °C.

For **8**: Crystals were grown from vapor diffusion of pentane into THF at 25 °C.

For **11**: Crystals were grown from slow evaporation of THF at 25 °C.

For **12**: Crystals were grown from slow evaporation of THF at 25 °C.

For **14**: Crystals were grown from vapor diffusion of pentane into THF at −30 °C.

For **17**: Crystals were grown from vapor diffusion of pentane into CH_2Cl_2 at 25 °C.

Acknowledgment. This work is supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division, of the U.S. Department of Energy under Contract DE-AC02-76SF0098. We thank Dr. Rudi Nunlist for NMR spectroscopy assistance and Dr. Frederick Hollander and Dr. Antonio diPasquale for X-ray crystallography assistance.

Supporting Information Available: Text describing complete experimental details for solutions of the X-ray structures, and structural data for **7**, **8**, **11**, **12**, **14**, and **17**. This material is available free of charge via the Internet at http://pubs.acs.org.