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Synthesis and Structure of PNP-Supported Iridium Silyl and Silylene Complexes: Catalytic Hydrosilation of Alkenes

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Abstract: Oxidative addition of bulky primary, secondary, and tertiary silanes to PNP (PNP = $[N(2\text{-}P^iPr_2\text{-}4\text{-}Me\text{-}C_6H_3)_2]^-$) iridium complexes $(PNP)IrH_2$ and (PNP)Ir(COE) (**11**) afforded iridium silyl hydride complexes (PNP)Ir(H)(SiRR′R″) (**3**−**8**). Addition of 2 equiv of $PhSiH_3$ or $(3,5\text{-}Me_2C_6H_3)SiH_3$ to $(PNP)IrH_2$ or **11** yielded disilyl complexes $(PNP)Ir(SiH_2R)_2$ (R = Ph (**9**), $3,5\text{-}Me_2C_6H_3$ (**10**)). Hydride abstraction from $(PNP)Ir(H)(SiH_2R)$ (R = Trip (**5**), Dmp (**6**)) by $[Ph_3C][B(C_6F_5)_4]$ afforded iridium silylene complexes $[(PNP)(H)Ir{=}SiR(H)][B(C_6F_5)_4]$ (R = Trip (**12**), Dmp (**13**)) exhibiting downfield ^{29}Si NMR resonances (234 ppm (**12**), 226 ppm (**13**)) and downfield ^1H NMR resonances for the Si−H group (10.76 ppm (**12**), 9.76 ppm (**13**)). Thermally stable disubstituted silylene complexes $[(PNP)(H)Ir{=}SiPh_2][A]$ (A = $^-B(C_6F_5)_4$ (**14**), $^-CB_{11}H_6Br_6$ (**16**)) were isolated via hydride abstraction from $(PNP)Ir(H)(SiHPh_2)$. The X-ray structure of **16** confirmed sp^2 hybridization at silicon and revealed a short Ir−Si bond of 2.210(2) Å. Catalytic hydrosilation of alkenes by hydrogen-substituted silylene complexes $[(PNP)(H)Ir{=}SiMes(H)][B(C_6F_5)_4]$ (**1**) and **14** exhibited anti-Markovnikov regioselectivity with an array of alkene substrates. Addition of H_3SiMes to complex **1** afforded $[(PNP)(SiH(Mes)(Hex))IrH(SiH_2Mes)][B(C_6F_5)_4]$ (**19**), featuring a β-agostic interaction demonstrated by a J_{SiH} of 102 Hz for the N−SiH hydrogen. Similarly, addition of H_2SiPh_2 to **16** afforded the structurally characterized Ir(V) disilyl complex $[(PNP)(SiPh_2)Ir(SiPh_2H)(H)_2][CB_{11}H_6Br_6]$ (**20**). Complex **20** was found to be catalytically active for the hydrosilation of alkenes, which is consistent with its intermediacy in the catalytic cycle.

Introduction

Transition metal silylene complexes are of interest for their potential role in catalytic transformations involving organosilanes, such as the synthesis of chlorosilanes by the Direct Process[1] and the redistribution of organosilanes.[2] Research on transition metal silylene complexes has led to the development of several synthetic strategies for accessing these previously elusive species.[3] Established, general synthetic strategies are based on the chemical modification of silyl ligands by abstraction of an anionic substituent on the silyl ligand[4] or by α-hydrogen migration of a group from the silyl ligand to an unsaturated transition metal center.[5] These synthetic routes have provided a variety of transition metal silylene complexes,[3,6] and investigations on their stoichiometric reactivity have revealed unusual transformations with small molecules such as chlorinated hydrocarbons,[7] epoxides,[8] nitriles,[9] isocyanates,[10] and carbonyl compounds.[5e,11]

Thus, transition metal silylene complexes would seem to offer the potential for a number of new, metal-mediated transformations of organosilicon compounds, but so far only a handful of catalytic reactions have been shown to involve metal silylene

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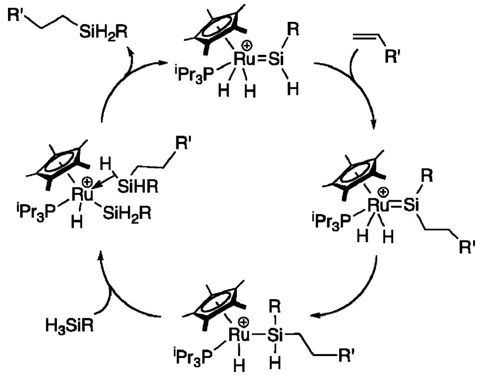
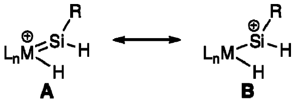
Scheme 1



complexes.[12,13] A striking recent example involves the ruthenium silylene complex [Cp*(P^{i}Pr$_3$)(H)$_2$Ru=SiH(Ph)][B(C$_6$F$_5$)$_4$], which is a catalyst for the regioselective hydrosilation of alkenes. Notably, this catalysis proceeds by a previously unknown mechanism and provides strictly anti-Markovnikov regioselectivity for a variety of olefin substrates. This catalyst is also highly selective for primary silane substrates and affords only secondary silane products. Mechanistic investigations implicate a reaction pathway involving the direct insertion of an alkene into the Si−H bond of an H-substituted silylene complex,[14] rather than a more traditional Chalk−Harrod cycle (Scheme 1).[15] Additional experimental and computational studies suggest that this reactivity is strongly correlated with a positive charge on the silylene complex, and in particular with a high degree of silylenium character (resonance form **B**). Computational studies suggest that electrophilicity at silicon promotes alkene binding to the silylene ligand and subsequent insertion of the alkene into the Si−H bond.[16] This crucial Si−C bond-forming step produces a new silylene ligand, and subsequent steps lead to release of product and activation of the primary silane to produce another H-substituted silylene ligand (Scheme 1). However, it should be noted that, whereas the Si−H addition step has been independently observed, little is known about the subsequent steps in the catalytic cycle, and none have been observed.

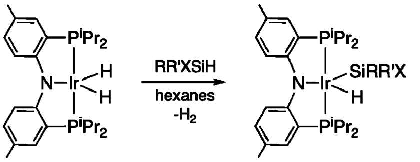


To better understand this new type of hydrosilation reaction, it is of interest to develop a variety of catalysts that function in a similar manner, to further probe steric, electronic, and mechanistic factors that are associated with this reactivity. Recently, this effort has targeted cationic, H-substituted silylene complexes such as the iridium silylene complex [(PNP)(H)Ir=SiMes(H)][B(C$_6$F$_5$)$_4$][17] (**1**, PNP = [$^-$N(2-P^{i}Pr$_2$-4-Me-C$_6$H$_3$)$_2$],[18] Mes = 2,4,6-Me$_3$C$_6$H$_2$), which was recently communicated. This complex has provided a second example of a silylene-mediated, highly regioselective hydrosilation catalyst. In this contribution, synthetic pathways to a variety of PNP-supported iridium silyl and silylene complexes are presented, along with detailed spectroscopic and structural characterizations of these species. A more complete description of the hydrosilation catalysis has been developed, and notably, complexes resulting from addition of the silane substrate to a cationic iridium silylene species have been characterized. These species appear to represent the resting state of the hydrosilation catalyst and provide insight into how the nitrogen donor atom of the PNP ligand may play a role in bond activations and product formation in (PNP)M complexes.

Results and Discussion

Synthesis and Characterization of (PNP)IrH(SiR$_3$) Complexes from (PNP)IrH$_2$. Several synthetic routes to silylene complexes are based on chemical transformations of transition metal silyl precursors. A convenient route to silyl complexes utilizes the oxidative addition of an Si−H bond to a transition metal.[19,20] This approach permits access to a variety of substituents on the resulting silyl ligands due to the commercial and synthetic availability of a range of organosilane substrates. Previous reports of bond activations by (PNP)IrH$_2$ describe facile oxidative additions of sp^2 C−H bonds upon addition of norbornene as a dihydrogen acceptor.[21] Hence, (PNP)IrH$_2$ was envisioned as a good starting point for Si−H bond activation routes to iridium silyl complexes, which might then serve as precursors to cationic iridium silylene complexes.

The synthesis of (PNP)IrH(SiH$_2$Mes) (**2**) from the reaction of (PNP)IrH$_2$ with MesSiH$_3$ has been previously reported.[17] Similarly, additions of silanes CySiH$_3$, (C$_6$F$_5$)SiH$_3$, TripSiH$_3$ (Trip = 2,4,6-^{i}Pr$_3$C$_6$H$_2$), DmpSiH$_3$ (Dmp = 2,6-dimesitylphenyl), Ph$_2$SiH$_2$, and Ph$_2$SiHCl to (PNP)IrH$_2$ in hexanes afforded the iridium silyl hydride complexes **3**−**8**, with the concomitant evolution of dihydrogen gas (eq 1). The formation of these Ir(III) silyl hydrides is quantitative by ^{1}H NMR spectroscopy, and these complexes can be crystallized from pentane or hexanes at −30 °C. In contrast to C−H activations, activations of Si−H bonds by (PNP)IrH$_2$ do not require a hydrogen acceptor.



(1)

R = Cy, X = R' = H **(3)**
R = C$_6$F$_5$, X = R' = H **(4)**
R = Trip, X = R' = H **(5)**
R = Dmp, X = R' = H **(6)**
R = R' = Ph, X = H **(7)**
R = R' = Ph, X = Cl **(8)**

Complexes **3**−**8** exhibit spectroscopic characteristics consistent with the proposed structures in eq 1. The ^{1}H NMR spectra for **3**−**8** feature two methine resonances and four methyl resonances for the isopropyl groups, indicating C_s symmetry.

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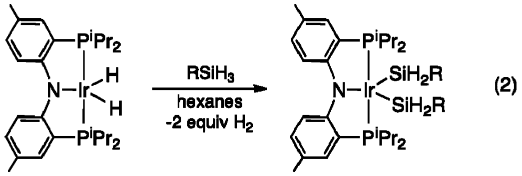
Table 1. NMR Data for Complexes **3**−**8**

complex	δ ^{1}H (Si*H*)	δ ^{29}Si (Ir*Si*)	δ ^{1}H (Ir*H*)
(PNP)IrH(SiH_2Cy) (**3**)	4.07	−27.3	−20.76
(PNP)IrH($SiH_2(C_6F_5)$) (**4**)	4.60	−79.0	−21.67
(PNP)IrH(SiH_2Trip) (**5**)	5.02	−74.1	−21.24
(PNP)IrH(SiH_2Dmp) (**6**)	4.39	−50.9	−20.21
(PNP)IrH($SiHPh_2$) (**7**)	6.28	−21.0	−19.83
(PNP)IrH($SiPh_2Cl$) (**8**)	N/A	10.8	−19.59

The ^{31}P{^{1}H} NMR spectra for these complexes reveal a single resonance for the PNP ligand at 47−49 ppm. The ^{29}Si NMR shifts for **3**−**8** are indicative of the presence of a silyl ligand[19] (Table 1). The ^{1}H NMR shifts for the Si−H and Ir−H groups are also tabulated in Table 1. Coupling between the iridium hydride and the silicon atom was found to result in $^2J_{SiH}$ values of less than 4 Hz for **4** and **8**, and this is consistent with complete oxidative addition of the Si−H bond.[19]

Single crystals of **6** were obtained by cooling a concentrated hexanes solution to −30 °C. The X-ray structure of **6** reveals a distorted trigonal bipyramid geometry about iridium with the phosphorus atoms in the apical positions (Figure 1). The P1−Ir1−P2 angle of 161.73(6)° is similar to those of other iridium complexes with this rigid ligand framework.[21] The Ir−Si distance of 2.323(2) Å is comparable to the corresponding distances in other structurally characterized iridium silyl complexes.[22] The hydride ligand was not located but is presumed to occupy the remaining equatorial position of the trigonal bipyramid. The N−Ir−Si angle of 140.1(2)° is wider than expected for a trigonal bipyramid, as has been documented for other PNP five-coordinate d^6 complexes.[23]

Synthesis and Characterization of (PNP)Ir($SiH_2R)_2$ Complexes from (PNP)IrH$_2$. Addition of 2 equiv of PhSiH$_3$ to (PNP)IrH$_2$ in hexane led to the formation of disilyl iridium complex (PNP)Ir($SiH_2Ph)_2$ (**9**) as burgundy microcystals in 79% yield (eq 2). The ^{1}H NMR spectrum of **9** exhibits only one resonance for the methine C*H* group and two resonances for the CH*Me*$_2$ methyls, indicating the presence of two equivalent silyl groups at iridium. The ^{29}Si NMR spectrum features a single resonance at −37.5 ppm for the silyl ligands. Similarly, (PNP)IrH$_2$ reacted with an excess of XylSiH$_3$ (Xyl = 3,5-Me$_2$C$_6$H$_3$) to give the disilyl iridium complex (PNP)Ir(SiH$_2$Xyl)$_2$ (**10**) in good yield as a dark red solid (eq 2). ^{1}H and ^{29}Si NMR spectra for **10** reveal features similar to those of **9**, including a ^{29}Si NMR resonance at −38.2 ppm for the silyl ligands.

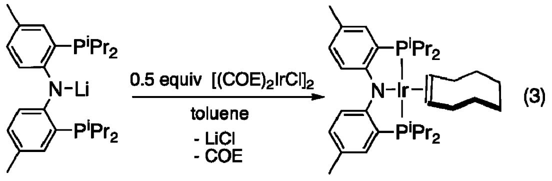


(2)

R = Ph (**9**)
R = 3,5-C$_6$H$_3$ (**10**)

The steric properties of the silane substrate dictate whether a complex of the type (PNP)Ir($SiR_3)_2$ or (PNP)IrH(SiR_3) is obtained from the reaction of excess silane with (PNP)IrH$_2$ or (PNP)IrCOE (*vide infra*). The silyl hydride products are obtained when the silane substrate used is di- or trisubstituted, or for monosubstituted silanes containing a bulky substituent. Attempts to isolate the silyl hydride complexes by dropwise addition of 1 equiv of PhSiH$_3$ or XylSiH$_3$ to (PNP)IrH$_2$ in hexanes gave a mixture of the disilyl and silyl hydride complexes. However, the reaction of (PNP)IrH$_2$ with an excess of the more sterically encumbered H$_3$SiMes exclusively afforded silyl hydride complex **2**. Similarly, reaction of the primary silane H$_3$SiPh produced disilyl complex **9**, whereas the disubstituted silane H$_2$SiPh$_2$ exclusively gave silyl hydride species **7**, even in the presence of excess silane.

Synthesis of (PNP)IrH(SiR$_3$) and (PNP)Ir(SiH$_2$R)$_2$ Complexes from (PNP)IrCOE. Synthesis of an iridium(I) complex for use in Si−H bond activations was achieved by addition of (PNP)Li[24] to [(COE)$_2$IrCl]$_2$ in toluene, to produce the alkene complex (PNP)IrCOE (**11**) in 64% yield (eq 3).



(3)

11

At ambient temperature, the ^{1}H NMR spectrum of **11** exhibits two distinct resonances for the methyl substituents on the aromatic rings of the ligand backbone, inequivalent aromatic proton resonances for the ligand backbone, and broadened resonances for the PCH*Me*$_2$ groups. The ^{1}H NMR spectrum of **11** at room temperature exhibits a resonance at 3.01 ppm, identified as the alkene hydrogen of the cyclooctene ligand. Variable-temperature NMR studies of **11** in toluene-*d*$_8$ indicated coalescence of these ligand resonances at 90 °C. The ^{31}P{^{1}H} NMR spectrum of **11** gives rise to an AB quartet pattern, and the observed J_{PP} coupling constant of 351 Hz supports a *trans* arrangement for the phosphorus nuclei. The ^{13}C{^{1}H} NMR shift for the alkenyl carbon at 41.1 ppm is indicative of a π-basic iridium center and a considerable amount of metallocyclopropane character.[25]

Complex **11** crystallizes in the $P2_1/n$ space group from a concentrated pentane solution to −30 °C. The X-ray structure depicts a slightly distorted square planar geometry about iridium and a perpendicular binding of the cyclooctene ligand with respect to the P−Ir−P−N plane (Figure 2). The distortion from square planar geometry results from the rigidity of the coordination of the PNP ligand and leads to a P−Ir−P bond angle (161.86(7)°) that is slightly reduced from linearity.

Addition of H$_3$SiMes and H$_2$SiPh$_2$ to **11** in hexanes at ambient temperature resulted in the formation of **1** and **7**, respectively, and the release of cyclooctene. Similarly, addition of 1 equiv of XylSiH$_3$ to complex **11** in benzene-*d*$_6$ afforded a mixture of the corresponding silyl hydride species and disilyl complex **10**. Thus, complex **11** is similar to (PNP)IrH$_2$ in its behavior as a precursor to a variety of iridium silyl complexes. Furthermore, no hydrosilation of

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(22) A search of the Cambridge Crystallographic Structure Database revealed a range of 2.29−2.41 Å for Ir−Si bond lengths for iridium silyl complexes.

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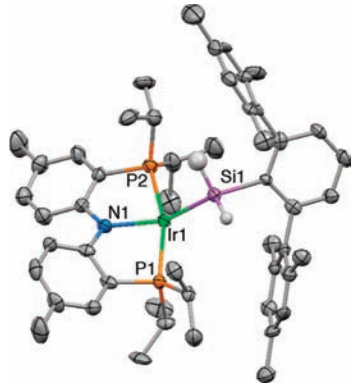


Figure 1. Molecular structure of **6** displaying thermal ellipsoids at the 50% probability level. H-atoms except for those attached to Si1 and disordered hexanes have been omitted for clarity. Selected bond lengths (Å): Ir1−Si1 = 2.323(2), Ir1−N1 = 2.060(6). Selected bond angles (deg): N1−Ir1−Si1 = 140.1(2), P1−Ir1−P2 = 161.73(6).

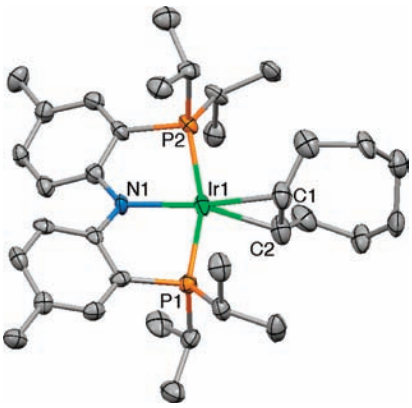


Figure 2. Molecular structure of **11** displaying thermal ellipsoids at the 50% probability level. H-atoms have been omitted for clarity. Selected bond lengths (Å): C1−C2 = 1.43(1), N1−Ir1 = 2.067(5). Selected bond angles (deg): P1−Ir1−P2 = 161.86(7).

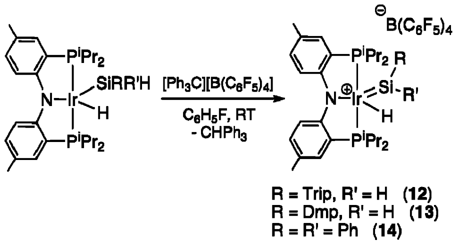
cyclooctene was observed at room temperature after formation of the silyl hydride or disilyl complexes.

Synthesis and Characterization of Iridium Silylene Complexes [(PNP)(H)Ir═SiRR′][B(C$_6$F$_5$)$_4$]. Treatment of (PNP)IrH(SiH$_2$Mes) (**2**) with 1 equiv of [Ph$_3$C][B(C$_6$F$_5$)$_4$] afforded a cationic, hydrogen-substituted silylene complex **1** via a hydride abstraction pathway, as previously communicated.[17] Several attempts to synthesize a larger family of PNP-supported iridium silylene complexes via treatment of complexes **3** and **4** with [Ph$_3$C][B(C$_6$F$_5$)$_4$] afforded intractable mixtures of products. For these mixtures, ^{1}H NMR spectroscopy indicated the absence of the characteristic downfield resonance associated with a hydrogen-substituted silylene complex.[26]

Addition of [Ph$_3$C][B(C$_6$F$_5$)$_4$] to complex **5** in bromobenzene-d_5 initially produced a bright blue-green solution. Initial decomposition was observed, as indicated by a color change to brown within 10 min at ambient temperature. One of the species in solution was identified by ^{1}H and ^{29}Si NMR spectroscopy as the hydrogen-substituted silylene complex [(PNP)(H)Ir═SiH(Trip)][B(C$_6$F$_5$)$_4$] (**12**). The silylene ligand exhibits a ^{1}H NMR shift of 10.76 ppm ($^1J_{\mathrm{SiH}}$ = 206.2 Hz) for the Si−*H* group and a ^{29}Si NMR resonance at 233.9 ppm (obtained by correlation to the Si−*H* resonance via a 2D ^{1}H,^{29}Si HMBC NMR experiment). Isolation of complex **12** was not successful due to its rapid decomposition to a mixture of intractable products within 45 min at ambient temperature.

Table 2. NMR Data for Iridium Silylene Complexes **12**−**14**

complex	δ ^{29}Si (Ir═*Si*)	δ ^{1}H (Si*H*)	δ ^{1}H (Ir*H*)
[(PNP)(H)Ir═SiH(Trip)][B(C$_6$F$_5$)$_4$] (**12**)	233.9	10.76	−18.4
[(PNP)(H)Ir═SiH(Dmp)][B(C$_6$F$_5$)$_4$] (**13**)	226.6	9.75	−20.4
[(PNP)(H)Ir═SiPh$_2$][B(C$_6$F$_5$)$_4$] (**14**)	264.8	N/A	−20.6



(4)

Reaction of **6** with 1 equiv of [Ph$_3$C][B(C$_6$F$_5$)$_4$] in bromobenzene-d_5 gave an intense blue-green solution, which contained [(PNP)(H)Ir═SiH(Dmp)][B(C$_6$F$_5$)$_4$] (**13**) in 65% yield (by integration of the Ir−*H* and Si−*H* signals in the ^{1}H NMR spectrum). Isolation of this compound was achieved by reaction of **6** with 1 equiv of [Ph$_3$C][B(C$_6$F$_5$)$_4$] in fluorobenzene, and the resulting blue-green solution was added to pentane at −30 °C to remove the triphenylmethane byproduct to give a blue solid. Complex **13** is thermally sensitive and was observed to undergo extensive decomposition over 19 h at −30 °C in fluorobenzene. It is therefore difficult to isolate in pure form.

The ^{1}H NMR spectrum of **13** exhibits complicated overlapping signals with several diagnostic resonances that support the formation of a hydrogen-substituted silylene complex. These overlapping signals can be attributed to two rotamers of **13**, most likely arising from hindered rotation around the Ir−Si bond due to steric constraints imposed by the bulky terphenyl substituent. Two overlapping triplets at 9.75 ppm ($^1J_{\mathrm{SiH}}$ = 206 Hz) are assigned to the Si−*H* group of **13** and correlate (by a 2D ^{1}H,^{29}Si HMBC NMR experiment) to a broad ^{29}Si NMR resonance at 226.6 ppm. The iridium hydrides give rise to a second pair of overlapping peaks in the ^{1}H NMR spectrum at −20.49 and −20.43 ppm. The ^{31}P{^{1}H} NMR spectrum also exhibits two overlapping signals at 54.6 and 54.4 ppm in a 2:1 ratio. Similarly, rotamers were observed for aryl complexes of the type (PNP)IrH(Ar) (where Ar = 2,5-Me$_2$C$_6$H$_3$, 2-C$_6$H$_4$F, and 2-C$_6$H$_4$Cl).[21]

Synthesis of a disubstituted iridium silylene complex was achieved by a hydride abstraction from **7** by [Ph$_3$C][B(C$_6$F$_5$)$_4$] to afford [(PNP)(H)Ir═SiPh$_2$][B(C$_6$F$_5$)$_4$] (**14**) as a violet solid in 97% yield after precipitation from pentane at −30 °C. The ^{1}H NMR spectrum of **14** exhibits a hydride resonance at −20.6 ppm and no resonance for a Si−*H* group. The ^{29}Si{^{1}H} NMR resonance at 264.8 ppm is indicative of a silylene ligand. Furthermore, the coupling constant between the silicon center and the iridium hydride ligand (~10 Hz) is consistent with the absence of a strong interaction between the hydride and silylene ligands. Complex **14** is thermally stable in fluorobenzene at ambient temperature for at least 3 weeks, unlike the hydrogen-substituted analogues. The NMR data for complexes **12**−**14** are summarized in Table 2.

A common synthetic route to cationic transition metal silylene complexes involves the abstraction of an anionic substituent on

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a silyl ligand, such a chloride or triflate.[3] However, treatment of **8** with $\mathrm{Li(Et_2O)_2B(C_6F_5)_4}$ in bromobenzene-d_5 at room temperature gave no reaction, and heating to 75 °C gave an intractable mixture of products rather than **14**. Similarly, efforts to facilitate anion exchange by treatment of **8** with AgOTf in either dichloromethane-d_2 or bromobenzene-d_5 gave a complex mixture of products, rather than the desired $\mathrm{(PNP)IrH(SiPh_2OTf)}$. Thus, interestingly, the preferred method for synthesis of $\mathrm{[(PNP)(H)Ir{=}SiRR']^+}$ silylene complexes involves hydride abstraction. Hydride abstractions with $\mathrm{[Ph_3C][PF_6]}$ have been employed for the synthesis of base-stabilized iron silylene complexes $\mathrm{Cp(CO)_2Fe{=}SiMe(Ar_N)}$ ($\mathrm{Ar_N = 2\text{-}(Me_2NCH_2)C_6H_4}$)[27] and $\mathrm{Cp(CO)_2Fe{=}SiMe_2{\cdot}HMPA}$,[28] but this synthetic route has not been used to obtain base-free silylene complexes.

Previously reported examples of iridium silylene complexes are limited to $\mathrm{[Cp^*(PMe_3)(H)Ir{=}SiR_2][B(C_6F_5)_4]}$,[29] $\mathrm{[(PMe_3)_3(H)_2Ir{=}SiMes_2][MeB(C_6F_5)_3]}$,[5b] $\mathrm{[(PEt_3)_3(H)_2Ir{=}SiH(Dmp)][B(C_6F_5)_4]}$,[26b] and $\mathrm{[PhB(CH_2PPh_2)_3](H)_2Ir{=}SiR_2}$.[5b] Complexes **1**, **12**, and **13** represent a significant contribution to the synthetic accessibility of these rare hydrogen-substituted silylene complexes, which include $\mathrm{[Cp^*(H)_2Os{=}SiR(H)][B(C_6F_5)_4]}$ (R = Trip, Dipp, $\mathrm{Si(SiMe_3)_3}$, $\mathrm{C_6F_5}$, H),[30] $\mathrm{[(PEt_3)_3(H)_2Ir{=}SiH(Dmp)][B(C_6F_5)_4]}$,[26b] $\mathrm{Cp^*(dmpe)(H)Mo{=}SiR(H)}$ (R = Ph, Mes, Bn),[5d] $\mathrm{[Cp^*(dmpe)(H)_2W{=}SiDipp(H)][B(C_6F_5)_4]}$,[5c] $\mathrm{Cp^*(CO)(H)Ru{=}SiH(C(SiMe_3)_3)}$,[31] and $\mathrm{Cp^*(CO)_2(H)W{=}SiH(C(SiMe_3)_3)}$.[5e] It is apparent that the nature of the substituent on silicon has a large effect on the stability of these complexes, and this is possibly related to steric constraints imposed by the bulky PNP ligand.

Synthesis and Structure of $\mathrm{[(PNP)(H)Ir{=}SiRR'][CB_{11}H_6Br_6]}$ Complexes. Attempts to crystallize iridium silylene complexes **1** and **14** from a variety of solvents were unsuccessful and led to viscous oils instead of crystalline material. To improve the crystallinity of these complexes, substitution of the tetrakis(pentafluorophenyl)borate counteranion with other weakly coordinating anions was explored.[32] The use of carborane anions was encouraged by the reports of their utility in the crystallization of silicon-based cations and their compatibility with cations containing electrophilic silicon.[33]

Use of $\mathrm{[Ph_3C][CB_{11}H_6Br_6]}$ rather than $\mathrm{[Ph_3C][B(C_6F_5)_4]}$ in the synthetic method of eq 4 allowed access to $\mathrm{[(PNP)(H)Ir{=}SiH(Mes)][CB_{11}H_6Br_6]}$ (**15**) and $\mathrm{[(PNP)(H)Ir{=}SiPh_2][CB_{11}H_6Br_6]}$ (**16**). The change in anion does not lead to significant differences in the NMR spectroscopy of the complexes. Notably, no significant shift was observed in the ^{29}Si NMR resonances of the silylene ligands for **15** and **16** versus **1** and **14**, indicating that in both cases there is little interaction between the anion and the silicon center in solution. Furthermore, these compounds are readily isolated as solids after multiple pentane washes, whereas the analogous $\mathrm{B(C_6F_5)_4^-}$ salts gave foams after similar procedures.

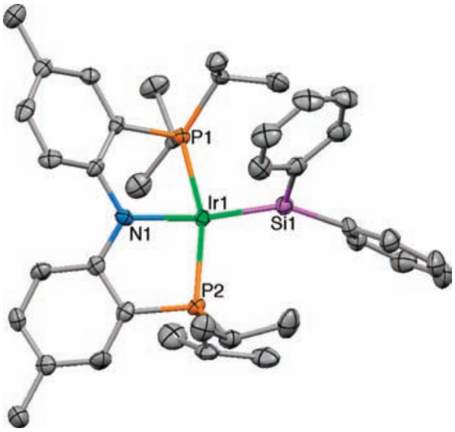

Figure 3. Molecular structure of the cation in **16** displaying thermal ellipsoids at the 50% probability level. H-atoms, carborane anion, and fluorobenzene molecule have been omitted for clarity. Selected bond lengths (Å): Ir1−Si1 = 2.210(2), Ir1−N1 = 2.022(5). Selected angles (deg): Ir1−Si1−C1 = 131.5(3), C1−Si1−C7 = 108.3(3), C7−Si1−Ir1 = 120.2(2), N1−Ir1−Si1 = 146.6(2).

X-ray-quality crystals of **16** were obtained from a concentrated solution of fluorobenzene via slow solvent evaporation (Figure 3). Complex **16** cocrystallized with one disordered molecule of fluorobenzene centered on an inversion center. The crystal structure reveals no interaction between the $\mathrm{CB_{11}H_6Br_6}$ anion and the unsaturated silicon center. The Ir−Si bond distance of 2.210(2) Å for **16** is very close to that observed for structurally characterized silylene complexes of the type $\mathrm{[PhB(CH_2PPh_2)_3](H)_2Ir{=}SiR_2}$ (2.250(3) and 2.260(3) Å).[5b] The sum of the bond angles about silicon is 360.0(8)°, a value that is quite consistent with sp^2 hybridization. The N−Ir−Si bond angle of 146.6(4)° indicates a substantial distortion from a trigonal bipyramidal coordination geometry, as observed for the silyl hydride complex **6**. Although the Ir−H hydrogen atom was not located during the structure refinement, it would presumably occupy the empty coordination site in the equatorial plane of the distorted trigonal pyramid. In addition, the $\mathrm{P_2NIr}$ and $\mathrm{SiC_2Ir}$ least-squares planes are nearly perpendicular; the angle between these planes is 79.4°.

Stoichiometric and Catalytic Reactions of Alkenes with Iridium Silylene Complexes. Addition of cyclooctene, 1-hexene, or styrene to a solution of complex **1** resulted in rapid addition of the alkene to the silylene ligand to produce disubstituted silylene complexes $\mathrm{[(PNP)(H)Ir{=}SiMes(R)][B(C_6F_5)_4]}$ ($\mathrm{R = C_8H_{15}, (CH_2)_5CH_3, CH_2CH_2Ph}$), with anti-Markovnikov regiochemistry.[17] Furthermore, complex **1** serves as a catalyst for the hydrosilation of alkenes with primary silane substrates, to afford disubstituted silane products ($\mathrm{RR'SiH_2}$) with anti-Markovnikov selectivity. The disubstituted silane products are inactive toward further hydrosilation.

In addition to hydrosilation, complex **1** was found to promote redistribution of both silane substrates and hydrosilation products. For example, heating a bromobenzene-d_5 solution of $\mathrm{MesSiH_3}$ with 2 mol % of **1** to 60 °C for 18 h resulted in formation of $\mathrm{Mes_2SiH_2}$ (6%), as determined by ^{1}H NMR spectroscopy. Under the same conditions, $\mathrm{Hex_2SiH_2}$ was formed in 20% yield from the redistribution of $\mathrm{HexSiH_3}$. Furthermore, addition of $\mathrm{PhSiH_3}$ to a solution of **1** (2 mol %) in bromobenzene-d_5 afforded $\mathrm{Ph_2SiH_2}$ (17%) after 18 h at ambient temperature. Due to this competitive redistribution, a mixture of silanes

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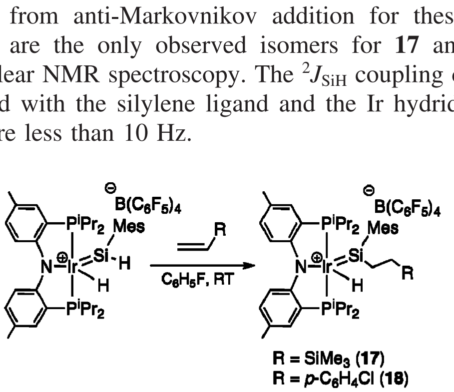
is generally obtained from catalytic hydrosilation reactions by **1**, and for this reason reduced yields of the hydrosilation products were sometimes observed.

Previous mechanistic investigations for hydrosilation by $[Cp^*(P^iPr_3)(H)_2Ru{=}SiH(Ph)][B(C_6F_5)_4]$ suggested that the reaction with alkenes proceeds via direct insertion of the alkene into the Si−H bond, analogous to the insertion of alkenes into a B−H bond in hydroboration. The regioselectivity for hydroboration with simple boranes is dependent on the alkene substrate. For example, hydroboration of styrene by diborane produces a 81:19 ratio of anti-Markovnikov to Markovnikov hydroboration products.[34] In contrast, hydrogen-substituted silylene complex **1** reacts with styrene in fluorobenzene at ambient temperature to give $[(PNP)(H)Ir{=}SiMes(CH_2CH_2Ph)][B(C_6F_5)_4]$, isolated in quantitative yield as the only regioisomer (by NMR spectroscopy). In addition, catalytic hydrosilation of styrene with primary silanes ($RSiH_3$, 5 mol % **1**, bromobenzene-d_5, 16−46 h at 60 °C) afforded $H_2SiR(CH_2CH_2Ph)$ (34−77%) as the only regioisomer.[17] Similarly, $[Cp^*(P^iPr_3)(H)_2Ru{=}SiH(Ph)][B(C_6F_5)_4]$ catalyzes the hydrosilation of styrene with $PhSiH_3$ to produce $H_2SiPh(CH_2CH_2Ph)$ in >99% yield by NMR spectroscopy.[13]

To further probe electronic factors that might influence the regioselectivity of this hydrosilation, alkene substrates that have been observed to afford a higher percentage of Markovnikov borane additions were examined.[35] For example, the hydroboration of trimethylvinylsilane with trimethylamineborane in diethylene glycol at 80 °C is reported to give a 66:34 ratio of β-trimethylsilylethanol to α-trimethylsilylethanol after oxidation of the boranes to alcohols.[36] Similarly, the hydroboration of *p*-chlorostyrene by diborane afforded a 73:25 ratio of β- to α-alcohol after oxidation.[34] Addition of a slight excess of vinyltrimethylsilane to **1** in C_6H_5F at room temperature afforded the disubstituted silylene complex $[(PNP)(H)Ir{=}Si(Mes)(CH_2CH_2SiMe_3)][B(C_6F_5)_4]$ (**17**), isolated in 85% yield (eq 5). The ^1H NMR spectrum of **17** exhibits a hydride resonance at −18.63 ppm, and the $^{31}P\{^1H\}$ NMR spectrum contains a broad singlet at 60.7 ppm. Two ^{29}Si NMR resonances are observed for **17**, at −3.1 and 301.1 ppm, corresponding to the *Si*Me$_3$ and the silylene ligand, respectively. Similarly, addition of *p*-chlorostyrene to **1** in C_6H_5F at ambient temperature afforded $[(PNP)(H)Ir{=}Si(Mes)(CH_2CH_2Ph_{Cl})][B(C_6F_5)_4]$ (**18**) (Ph_{Cl} = *p*-C_6H_4Cl), isolated in 82% yield (eq 5). Complex **18** exhibits NMR resonances similar to those of **17**, including a ^1H NMR resonance at −19.05 ppm for the hydride ligand, a broad $^{31}P\{^1H\}$ NMR resonance at 60.9 ppm, and a ^{29}Si NMR resonance at 293.3 ppm for the silylene ligand. The products resulting from anti-Markovnikov addition for these alkene subtrates are the only observed isomers for **17** and **18** by multinuclear NMR spectroscopy. The $^2J_{SiH}$ coupling constants associated with the silylene ligand and the Ir hydride for **17** and **18** are less than 10 Hz.



(5)

The very high anti-Markovnikov regioselectivity for catalysis by **1** may result from the steric crowding provided by the PNP ligand at the iridium center. A similar dependence of the regioselectivity of hydroboration on the steric properties of the borane has been reported, with increasing steric crowding at the boron center resulting in higher anti-Markovnikov selectivity.[35,37] For example, the regioselectivity for hydroboration of styrene by dicyclohexylborane is 99% for the anti-Markovnikov product, compared to 89% selectivity with diborane as the reagent.[37b]

This regioselectivity for stoichiometric Si−H addition to alkenes is also observed in hydrosilation catalysis with the same alkene substrates. Hydrosilations employing vinyltrimethylsilane or *p*-chlorostyrene substrates were conducted using a 5 mol % loading of **1** in bromobenzene-d_5 at 50 or 60 °C (Table 3, entries a and b). Exclusive formation of anti-Markovnikov products was observed in these catalytic reactions, as with styrene as the substrate. High yields were observed for these reactions involving H_3SiMes as the substrate, as the concurrent redistribution of this silane is relatively slow.

The catalytic hydrosilation reactions previously reported involved a 5 mol % loading of catalyst **1**. A lower catalyst loading (1 mol %) was investigated for the hydrosilation of $MesSiH_3$ with 1-hexene in bromobenzene-d_5 (Table 3, entry c). This hydrosilation catalysis is slower but is complete after 18 h, and the hydrosilation products are obtained in comparable yield. In order to test for the activity of the catalyst after one catalytic run, another 100 equiv of $MesSiH_3$ and 1-hexene were added to the reaction mixture, and this resulted in further formation of product in 84% yield after 20 h at 60 °C (Table 3, entry d). It should be noted, however, that the stability of the catalyst is dependent on the nature of the silane substrate. For example, it was found that use of $PhSiH_3$ as a substrate with a 1 mol % catalyst loading limited the recyclability of the catalyst, which lost activity after one catalytic run, presumably due to decomposition of the active catalyst under these conditions (Table 3, entries e and f).

The disubstituted silylene complex **14** was investigated as a catalyst for olefin hydrosilation, since it is easier than **1** to prepare and store, given its greater thermal stability. Hydrosilation runs were conducted using a 5 mol % loading of **14** with equimolar amounts of silane and alkene in bromobenzene-d_5 (Table 3, entries g and h). As shown in Table 3, complexes **14** and **1** catalyze alkene hydrosilation with comparable yields and selectivities.

Mechanistic Investigations of Alkene Hydrosilation by Iridium Silylene Complexes. The first step of alkene hydrosilation catalysis by **1** is thought to involve formation of a disubstituted silylene complex (such as **17** and **18**) via reaction of an H-substituted iridium silylene complex with an alkene. Two possible mechanisms for the formation of the disubstituted iridium silylene complexes from the reaction of alkenes might be envisioned (Scheme 2): one involves direct insertion of the alkene into the Si−H bond (path A), and a second possibility involves insertion of the alkene into the Ir−H bond, followed by migration of the resulting alkyl group to the unsaturated silylene ligand and then α-hydrogen migration to regenerate a silylene ligand (path B). The former mechanism is favored, as it would explain the observed high selectivity for primary silane substrates in hydrosilation catalysis by **1**.

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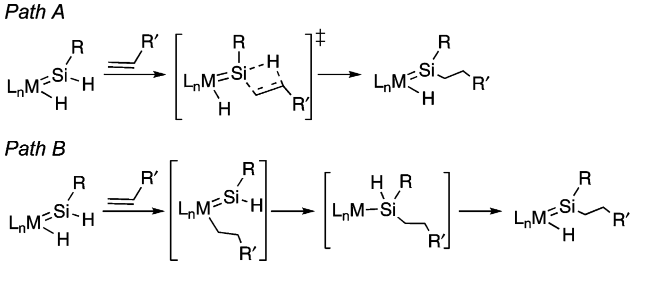
Table 3. Results of Catalytic Trials for Alkene Hydrosilation

entry	silane	alkene	catalyst (mol %)	time (h)	product	yield (%)
a	H_3SiMes	*p*-chlorostyrene	**1** (5)	20	$H_2SiMes(CH_2CH_2Ph_{Cl})$	73
b	H_3SiMes	vinyltrimethylsilane	**1** (5)	24[a]	$H_2SiMes(CH_2CH_2SiMe_3)$	66
c	H_3SiMes	1-hexene	**1** (1)	20	$H_2SiMes(Hex)$	78
d	H_3SiMes	1-hexene	**1** (1)[b]	19	$H_2SiMes(Hex)$	84
e	H_3SiPh	styrene	**1** (1)	20	$H_2SiPh(CH_2CH_2Ph)$	30
f	H_3SiPh	styrene	**1** (1)[b]	38	$H_2SiPh(CH_2CH_2Ph)$	11
g	H_3SiMes	1-hexene	**14** (5)	16	$H_2SiMes(Hex)$	74
h	H_3SiHex	1-hexene	**14** (5)	3.5	$H_2Si(Hex)_2$	52
i	H_3SiMes	1-hexene	**20** (5)	3	$H_2SiMes(Hex)$	81

[a] Catalysis conducted at 50 °C. [b] After addition of second substrate.

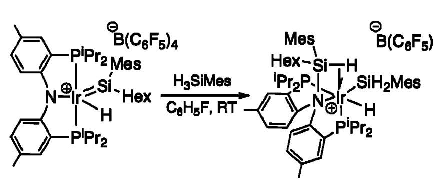
Scheme 2



In subsequent steps of the catalytic cycle, product release and regeneration of an H-substituted silylene ligand would involve reactions with the incoming silane substrate. Computational studies on the hydrosilation of alkenes by $[Cp^*(P^iPr_3)(H)_2Ru{=}SiH(Ph)][B(C_6F_5)_4]$ suggest that, after addition of the alkene $CH_2{=}CHR$ to form $[Cp^*(P^iPr_3)(H)_2Ru{=}Si(CH_2CH_2R)(Ph)][B(C_6F_5)_4]$, the catalytic cycle proceeds via migration of a hydride ligand to silicon, followed by binding of the silane substrate to the ruthenium center.[14] These studies also suggest that product release and regeneration of the silylene ligand occur by low-barrier rearrangements involving several intermediates that contain silyl and hydride groups and exhibit nonclassical Si···H interactions. Experimentally, the reaction of a silylene complex with a hydrosilane has been characterized for the reaction of $PhSiH_3$ with $Cp^*(dmpe)(H)Mo{=}SiH(Ph)$, to afford the disilyl complex $Cp^*(dmpe)Mo(H)(SiH_2Ph)_2$ via initial α-hydrogen migration to the silylene ligand followed by Si−H activation of the free silane.[5d]

To gain insight into the nature of silane activation by a PNP−iridium silylene complex, a slight excess of H_3SiMes was added to a bromobenzene-d_5 solution of $[(PNP)(H)Ir{=}Si(Mes)Hex][B(C_6F_5)_4]$ (obtained from the reaction of 1-hexene with **1**), and the resulting reaction was monitored by multinuclear NMR spectroscopy at ambient temperature. Upon addition of the silane, a color change from intense to pale blue was observed. ^1H and $^{31}P\{^1H\}$ NMR spectroscopy revealed formation of one major organometallic product (**19**, 33−43%), $H_2SiMes(Hex)$ (39%), and several unidentified organometallic species. In a related experiment, 1-hexene and H_3SiMes were added to a 5 mol % loading of **1** in bromobenzene-d_5 at room temperature, and the resulting solution was monitored over 3 days by NMR spectroscopy. After 4 h, the formation of $H_2SiMes(Hex)$ (19%) was observed, and the $^{31}P\{^1H\}$ spectrum revealed the presence of **19** in solution as the major iridium-containing species. Over the course of 72 h, all of the silane substrate was consumed, and the major Ir-based species remaining was **19** (by $^{31}P\{^1H\}$ NMR spectroscopy). Notably, complex **1** was not observed during the catalytic reaction, and **19** appears to be the resting state in the catalytic mixture.

Addition of 1 equiv of H_3SiMes to $[(PNP)(H)Ir{=}Si(Mes)Hex][B(C_6F_5)_4]$ in fluorobenzene at ambient temperature produced a color change to light blue. The reaction mixture was then added to pentane at −30 °C, and a light blue oil settled out after 1 h at −30 °C. The solvent was decanted to remove the organic components, and the remaining oil was dried under vacuum to give a light blue solid. Multinuclear NMR spectroscopy of this mixture led to the proposed structure for the major organometallic species (**19**) depicted in eq 6. The ^1H NMR spectrum of **19** exhibits two resonances at 4.78 and 4.68 ppm assigned to diasterotopic Si−*H* hydrogens of an $Ir{-}SiH_2Mes$ group, as indicated by a large one-bond J_{SiH} coupling constant of ca. 180 Hz. The ^1H NMR spectrum of **19** also exhibits two upfield resonances at −5.81 and −11.94 ppm. The resonance at −5.81 ppm is assigned to a β-agostic Si−H group on the basis of observable silicon satellites (J_{SiH} = 102 Hz) in conjunction with the unusual, relative downfield shift for a hydride resonance in this system.[38] The resonance at −11.94 ppm is identified as an iridium hydride ligand with a small $^2J_{SiH}$ coupling constant of 8 Hz, indicating little to no interaction between this hydride and silicon atom. A 2D $^1H,^{29}Si$ HMBC experiment revealed a resonance at −78.1 ppm attributed to the $Ir{-}\mathit{Si}H_2Mes$ group, via correlation with the diasterotopic Si−*H* signals, and a resonance at 0.83 ppm attributed to the nitrogen-bound silyl group, via a correlation with the β-agostic Si−H signal. In addition, the $^{31}P\{^1H\}$ NMR spectrum of **19** displays two doublets at 39.8 and 9.9 ppm for inequivalent phosphorus atoms. The J_{PP} coupling constant of 244.6 Hz is slightly decreased from that observed for **11**, implying a small deviation from a *trans* arrangement of the phosphorus atoms. Some of the unidentified organometallic species are likely isomers of complex **19**, as these give rise to similar features in the hydride region of the ^1H NMR spectrum. Thus, **19** appears to result from migration of a silylene group to the nitrogen atom of the PNP ligand. A similar migratory insertion, of a carbene into the Ir−N bond of an iridium PNP complex, was previously documented by Grubbs and co-workers as resulting from reaction of carbon monoxide with $(PNP)Ir{=}CH(O^tBu)$.[39]

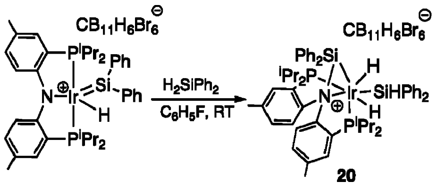


19

(6)

Attempts to crystallize **19** gave oils instead of crystalline material, even when employing $CB_{11}H_6Br_6$ as the anion. For this reason, an analogue to **19** was synthesized by reaction of an excess of H_2SiPh_2 with **16** in C_6H_5F to afford $[(PNP)(SiPh_2)Ir(SiPh_2H)(H)_2][CB_{11}H_6Br_6]$ (**20**) in 86% yield as off-white crystals from vapor diffusion of hexanes into an o-$C_6H_4Cl_2$ solution. The ^1H NMR spectrum for **20** at ambient temperature contains broadened signals for the PNP, silyl, and hydride ligands, suggesting a dynamic process. The ^1H NMR spectrum at low temperature (−70 °C) contains sharp signals for the Si−H hydrogen and for the iridium hydrides, although there are several broad resonances in the aromatic region. The Si−H resonance at −70 °C appears at 5.56 ppm as a doublet of doublets due to couplings to phosphorus (J_{PH} = 21.6 Hz) and one of the hydride ligands (J_{HH} = 2.9 Hz). The inequivalent iridium hydride ligands give rise to resonances at −11.31 ppm ($^1J_{PH}$ = 111.7 Hz, indicating a *trans* arrangement with a phosphorus atom) and −11.95 ppm (as a broad singlet). In contrast to **19**, both Ir−H resonances of **20** appear upfield of −10 ppm and exhibit small J_{SiH} values (≤10 Hz), suggesting full Si−H oxidative addition to the iridium center. The ^{29}Si NMR spectrum for **20** exhibits resonances at 6.1 and −37.3 ppm, for the nitrogen-bound silylene group (N−*Si*Ph_2) and the silyl ligand ($SiPh_2H$), respectively. Thus, the NMR data for **20** indicate that this compound is better described as an Ir(V) disilyl dihydride complex. The $^{31}P\{^1H\}$ NMR spectrum for **20** contains two doublets with a small J_{PP} coupling constant of 17.1 Hz, indicating a *cis* relationship between the phosphorus atoms, in contrast to complex **19**, where a *trans* geometry is indicated. A small impurity (~10%) gives rise to a second set of Si*H* (1H) and Ir*H* (2H) signals, suggesting the presence of a second regioisomer (**20b**), and this is consistent with an occupational disorder observed in the crystal structure (*vide infra*).

The structure of **20** was confirmed by single-crystal X-ray crystallography; however, the hydride ligands were not located from the difference Fourier map (Figure 4). The X-ray structure confirms N−Si bond formation, consistent with the NMR assignments for complexes **19** and **20**. The Ir1−Si1 distance of 2.318(2) Å and the Ir1−Si2A distance of 2.365(2) Å are within the expected range for iridium silyl Ir−Si bond lengths.[22] The Ir1−N1 distance at 2.294(4) Å is elongated with respect to that observed for **16** but still within bonding distance of the iridium center. The PNP ligand is bound in a facial manner to the iridium center, with the phosphorus donors in a *cis* arrangement. The silyl group on iridium is disordered such that it occupies two positions in an 85:15 ratio. This disorder is likely due to the cocrystallization of both regioisomers of **20**.



(7)

The catalytic competence of **20** in alkene hydrosilation was examined by subjecting it to the same catalytic conditions employed for **1**. Thus, H_3SiMes and 1-hexene were combined with a 5 mol % loading of **20** in bromobenzene-d_5 (Table 3, entry i). After 3 h at 60 °C, complete conversion of the substrates to $H_2SiMes(Hex)$ was observed, with high yields similar to those observed with **1** and **14** as catalysts. Therefore, complex **20** is an efficient precatalyst for alkene hydrosilation. Furthermore, addition of 2 equiv of (p-tolyl)$_2SiH_2$ to **20** in bromobenzene-d_5 followed by heating at 60 °C for 19 h gave a mixture of silane products including H_2SiPh_2 and H_2SiPh(p-tolyl) (26 and 30% yield vs **20**, respectively) as determined by ^1H NMR spectroscopy and GC/MS, revealing the ability of **20** to promote silane redistribution.

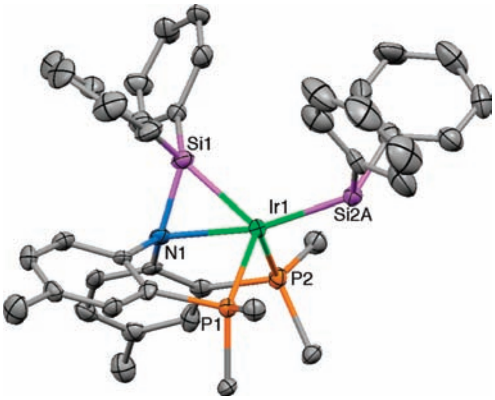
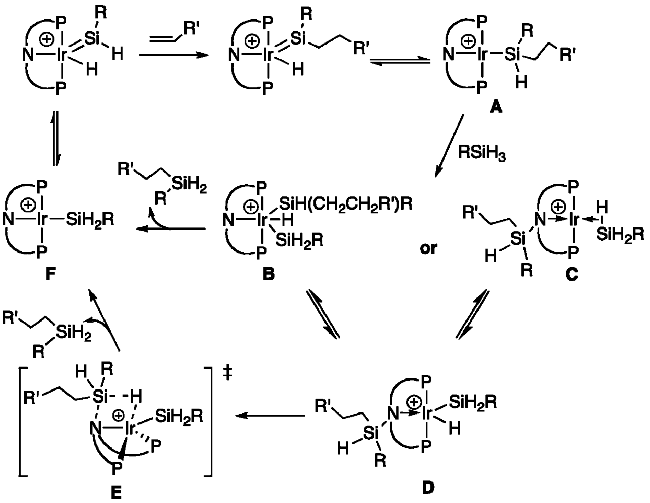


Figure 4. Molecular structure of the cation in **20**, displaying thermal ellipsoids at the 50% probability level. H-atoms, the carborane anion, and Si2B have been omitted for clarity. Selected bond lengths (Å): Ir1−Si1 = 2.318(2), Ir1−Si2A = 2.365(2), Ir1−N1 = 2.294(4), N1−Si1 = 1.795(5). Selected angles (deg): P1−Ir1−P2 = 102.39(5), Si1−Ir1−Si2A = 121.01(6), N1−Ir1−Si1 = 45.8(1).

Scheme 3



The results presented above suggest that the N donor atom of PNP complexes may play an important role in substrate activation. In particular, the migration of hydride or silyl ligands to the N atom may provide lower energy pathways for bond activations, which avoid high coordination numbers and high valence states for iridium. A possible mechanism that illustrates the potential role of the PNP amido group in alkene hydrosilation is shown in Scheme 3. The involvement of the amido group of a PNP ligand in bond activations by transition metal complexes has been proposed for dihydrogen activation,[40] intramolecular CH activation,[41] hydrogenation of ketones,[42] and migratory insertions of carbonyl,[43] vinylidene,[44] and carbene ligands.[39]

As a first step in the proposed mechanism of Scheme 3, reaction of an alkene with the hydrogen-substituted silylene complex generates the disubstituted silylene complex. This step has been observed in stoichiometric reactions for this system and in related reactions of $[Cp^*(P^iPr_3)(H)_2Ru{=}SiH(Ph)][B(C_6F_5)_4]$,[13] $[Cp^*(P^iPr_3)(H)_2Os{=}SiH(Trip)][B(C_6F_5)_4]$,[13] and $[PhB(CH_2PPh_2)_3](H)_2Ir{=}SiH(Mes)$.[5b] The disubstituted silylene could be in equilibrium with a cationic silyl intermediate **A** via an α-migration step.[3] This equilibrium would strongly favor the silylene isomer, as **A** was not observed in solution by NMR spectroscopy. For the next step, involving activation of the silane substrate, two possibilities are illustrated. One involves oxidative addition of the silane to produce an Ir(V) disilyl hydride species **B**. A second pathway involves binding of the silane substrate, accompanied by migration of the silyl ligand to the amido nitrogen to create an open coordination site. This could produce a σ-complex such as **C**, which would proceed to oxidative addition product **D**. Structure **D** might be stabilized by a secondary interaction of the Si−H bond of the silyl amido ligand with the iridium center, as observed in complexes **19** and **20** (depicted in Scheme 3 in a simplified form without this interaction). Elimination of the silane product may proceed directly from **D** via a concerted transition state (**E**) or from the disilyl hydride complex **B** by reductive elimination. Eliminations of the type shown for **E** have been proposed for early transition metal complexes.[45] Regeneration of the H-substituted silylene could proceed by a second α-migration from coordinatively unsaturated silyl intermediate **F**. Note that a competitive reaction of the hydrogen-substituted silylene complex with more silane, prior to reaction with the alkene, could also be operative and could result in catalyst inhibition and/or unproductive side reactions.

Concluding Remarks

Suitable silyl hydride precursors for the synthesis of iridium silylene complexes are readily accessed via Si−H activations by (PNP)IrH_2 or (PNP)IrCOE. There is a limitation in the availability of silyl hydride precursors to silylene complexes with this system, as small monosubstituted silanes give disilyl species from the reaction of 2 equiv of silanes with (PNP)Ir starting materials. Hydride abstractions from the silyl hydride precursors afford cationic iridium silylene complexes, and the substitution pattern at the silylene ligand is important in determining the thermal stability of the complex.

Iridium silylene complexes **1** and **14** catalyze the regioselective hydrosilation of alkenes, thus providing a second example of silylene complexes acting as catalysts for this reaction. Similar to catalysis with $[Cp^*(P^iPr_3)(H)_2Ru{=}SiH(Ph)][B(C_6F_5)_4]$, the only other known silylene catalyst for this reaction, hydrosilations mediated by **1** and **14** feature selectivity for primary silane substrates and exclusive anti-Markovnikov selectivity. Previous studies of hydrosilation mediated by $[Cp^*(P^iPr_3)(H)_2Ru{=}SiH(Ph)][B(C_6F_5)_4]$ suggest a mechanism in which the alkene inserts into the Si−H bond in a manner analogous to that in hydroboration. This is consistent with the presence of a cationic silylene complex that possesses significant silylenium character and an empty orbital at silicon that allows interaction with an alkene as an incoming nucleophile. Similarly, investigations on the regioselectivity of hydrosilations catalyzed by **1** demonstrate strict anti-Markovnikov selectivity, even with vinyltrimethylsilane and *p*-chlorostyrene. The observed regioselectivity is similar to that of hydroboration with sterically hindered borane reagents, suggesting that the sterics at the transition metal fragment might contribute to the observed regioselectivity.

Investigations of stoichiometric reactions between silane substrates and iridium silylene complexes indicate that the catalytic reaction involves interesting silyl complexes of iridium that possess Si−N bonds. These complexes are catalytically competent and appear to represent the resting state for the catalyst. Thus, it is of interest to design related catalysts based on pincer ligands that do not contain a donor amido group. Especially since structural variations in pincer ligands of this type should influence the behavior of related hydrosilation catalysts, research along such directions is ongoing.

Experimental Section

General Considerations. All experiments were carried out under a nitrogen atmosphere using standard Schlenk techniques or an inert atmosphere (N_2) glovebox. Olefin impurities were removed from pentane by treatment with concentrated H_2SO_4, 0.5 N $KMnO_4$ in 3 M H_2SO_4, and $NaHCO_3$. Pentane was then dried over $MgSO_4$, stored over activated 4 Å molecular sieves, and dried over alumina. Thiophene impurities were removed from benzene and toluene by treatment with H_2SO_4 and saturated $NaHCO_3$. Benzene and toluene were then dried over $CaCl_2$ and further dried over alumina. Tetrahydrofuran, diethyl ether, dichloromethane, and hexanes were dried over alumina. Fluorobenzene was dried over P_2O_5, degassed, and distilled under N_2. Benzene-d_6 was dried by vacuum distillation from Na/K alloy. C_6D_5Br was refluxed over CaH_2 for 20 h and then distilled under nitrogen. Methylene chloride-d_2 was dried by vacuum distillation from CaH_2. (PNP)IrH_2,[21] H_3SiMes,[46] $H_3SiTrip$,[47] H_3SiDmp,[48] $[Ph_3C][B(C_6F_5)_4]$,[49] and $[Ph_3C][CB_{11}H_6Br_6]$[50] were prepared according to literature methods. Hydrosilanes were prepared via lithium aluminum hydride reduction of the corresponding chlorosilane. All other chemicals were purchased from commercial sources and used without further purification.

NMR spectra were recorded using Bruker DRX-500, AV-500, AVB-400, and AVQ-400 spectrometers. ^{1}H NMR spectra were referenced internally by the residual solvent proton signal relative to tetramethylsilane. ^{13}C{^{1}H} NMR spectra were referenced internally relative to the ^{13}C signal of the NMR solvent relative to

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tetramethylsilane. ^{19}F{^{1}H} spectra were referenced relative to a C_6F_6 external standard. ^{31}P{^{1}H} spectra were referenced relative to an 85% H_3PO_4 external standard. ^{29}Si NMR spectra were referenced relative to a tetramethylsilane standard and obtained via 2D ^{1}H ^{29}Si HMBC unless specified otherwise. All spectra were recorded at room temperature unless otherwise noted. Virtual quartets are denoted as "vq", complex multiplets as "m", and broad resonances as "br". In ^{13}C{^{1}H} NMR spectra, resonances obscured by the solvent signal are omitted. Elemental analyses were performed at the College of Chemistry Microanalytical Laboratory, University of California, Berkeley.

(PNP)IrH(SiH$_2$Cy) (3). A solution of $CySiH_3$ (0.018 g, 0.16 mmol) in 1 mL of hexanes was added dropwise to (PNP)IrH$_2$ (0.100 g, 0.16 mol) in 4 mL of hexanes. Upon addition of the silane, rapid evolution of dihydrogen gas was observed. After 30 min at ambient temperature, the reaction mixture was filtered, evaporated to dryness, and lyophilized in 2 mL of benzene to give a dark orange powder. Yield: 0.094 g (85%). ^{1}H NMR (C_6D_6, 500 MHz): δ 7.76 (2H, d, $J = 8.5$ Hz, Ar*H*), 7.01 (2H, br s, Ar*H*), 6.86 (2H, d, $J = 8.4$ Hz, Ar*H*), 4.07 (2H, br m, $^1J_{SiH} = 168.4$ Hz, Si*H*), 2.71 (2H, m, C*H*Me$_2$), 2.35 (2H, br d, $J = 12.8$ Hz, C*H$_2$*), 2.20 (6H, s, Ar*Me*), 2.20 (2H, ov m, C*H*Me$_2$), 1.94 (2H, br d, $J = 11.1$ Hz, C*H$_2$*), 1.82 (1H, br m, C*H$_2$*), 1.54−1.43 (5H, ov m, C*H$_2$*), 1.25 (6H, vq, CH*Me$_2$*), 1.19 (6H, vq, CH*Me$_2$*), 1.11 (6H, vq, CH*Me$_2$*), 1.05 (1H, m, C*H*), 0.95 (6H, vq, CH*Me$_2$*), −20.76 (t, $^2J_{PH} = 9.2$ Hz, Ir*H*). ^{13}C{^{1}H} NMR (C_6D_6, 125.8 MHz): δ 163.8 (t, $J_{CP} = 10.8$ Hz), 132.8, 131.9, 126.7 (t, $J_{CP} = 3.4$ Hz), 124.2 (t, $J_{CP} = 21.0$ Hz), 115.6 (t, $J_{CP} = 5.1$ Hz) (Ar*C*), 32.3 (s, *C*H$_2$), 29.6 (s, *C*H), 29.3 (*C*H$_2$), 27.6 (*C*H$_2$), 25.6 (t, $J_{CP} = 15.7$ Hz, *C*HMe$_2$), 23.6 (t, $J_{CP} = 14.6$ Hz, *C*HMe$_2$), 20.4 (s, Ar*Me*), 19.7 (s, CH*Me$_2$*), 19.0 (s, CH*Me$_2$*), 18.4 (s, CH*Me$_2$*), 16.8 (s, CH*Me$_2$*). ^{31}P{^{1}H} NMR (C_6D_6, 202.5 MHz): δ 49.0 (s). ^{29}Si NMR (C_6D_6, 99.4 MHz): δ −27.3. Anal. Calcd for $C_{32}H_{54}NIrP_2Si$: C, 52.29; H, 7.40; N, 1.91. Found: C, 53.71; H, 7.68; N, 1.76. Despite recrystallizations, compound **3** did not provide consistent and reliable combustion data. However, the compound is pure by NMR spectroscopy.

(PNP)IrH(SiH$_2$C$_6$F$_5$) (4). A solution of $(C_6F_5)SiH_3$ (0.032 g, 0.16 mmol) in 1 mL of hexanes was added dropwise to (PNP)IrH$_2$ (0.100 g, 0.16 mol) in 4 mL of hexanes. Upon addition of the silane, rapid evolution of dihydrogen gas and a color change to red were observed. After standing at ambient temperature for 45 min, the solution was filtered, concentrated to ca. 1 mL, and cooled at −30 °C until red crystals formed. The dark red crystals were collected and dried under vacuum. Yield: 0.100 g (76%). ^{1}H NMR (C_6D_6, 500 MHz): δ 7.71 (2H, $J = 8.5$ Hz, Ar*H*), 6.95 (2H, br, Ar*H*), 6.83 (2H, d, $J = 8.0$ Hz, Ar*H*), 4.60 (2H, br t, $J = 5.0$ Hz, $^1J_{SiH} = 189.0$ Hz, Si*H*), 2.59 (2H, m, C*H*Me$_2$), 2.17 (6H, s, Ar*Me*), 2.10 (2H, m, C*H*Me$_2$), 1.14 (6H, vq, CH*Me$_2$*), 1.02 (12H, ov m, CH*Me$_2$*), 0.84 (6H, vq, CH*Me$_2$*), −21.67 (t, $J_{PH} = 9.1$ Hz, Ir*H*). ^{13}C{^{1}H} NMR (C_6D_6, 125.8 MHz): δ163.8 (t, $J_{CP} = 10.5$ Hz), 132.8, 132.1, 123.7 (t, $J_{CP} = 21.3$ Hz), 115.8 (t, $J_{CP} = 5.5$ Hz) (Ar*C*), 25.7 (t, $J_{CP} = 16.5$ Hz, *C*HMe$_2$), 23.4 (t, $J_{CP} = 14.7$ Hz, *C*HMe$_2$), 20.3 (s, Ar*Me*), 18.7 (s, CH*Me$_2$*), 18.7 (s, CH*Me$_2$*), 18.1 (s, CH*Me$_2$*), 16.7 (s, CH*Me$_2$*). ^{19}F{^{1}H} NMR (C_6D_6, 376.5 MHz): δ −125.3 (m), −154.2 (t, $J = 20.3$ Hz), −161.7 (m). ^{31}P{^{1}H} NMR (C_6D_6, 202.5 MHz): δ 48.8 (s). ^{29}Si NMR (C_6D_6, 99.4 MHz): δ −79.0. Anal. Calcd for $C_{32}H_{43}NF_5IrP_2Si$: C, 46.93; H, 5.29; N, 1.71. Found: C, 47.20; H, 5.50; N, 1.67.

(PNP)IrH(SiH$_2$Trip) (5). A solution of $TripSiH_3$ (0.041 g, 0.18 mmol) in 1 mL of hexanes was added dropwise to (PNP)IrH$_2$ (0.109 g, 0.18 mmol) in 4 mL of hexanes. Upon addition of the silane, rapid evolution of dihydrogen gas and a color change to bright orange were observed. After standing for 1 h, the solution was filtered, evaporated to dryness, and lyophilized in ca. 2 mL of benzene to afford **5** as an orange powder. Yield: 0.110 g (73%). ^{1}H NMR (C_6D_6, 500 MHz): δ 7.73 (2H, d, $J = 8.5$ Hz, Ar*H*), 7.16 (under solvent signal, Trip*H*), 6.99 (2H, br s, Ar*H*), 6.85 (2H, d, $J = 8.0$ Hz, Ar*H*), 5.02 (2H, br, $^1J_{SiH} = 173.1$ Hz, Si*H*), 4.19 (2H, sept, $J = 6.6$ Hz, Trip C*H*Me$_2$), 2.89 (1H, sept, $J = 6.9$ Hz, Trip C*H*Me$_2$), 2.62 (2H, br m, C*H*Me$_2$), 2.19 (6H, s, Ar*Me*), 2.18 (2H, br, C*H*Me$_2$), 1.45 (12H, d, $J = 6.6$ Hz, Trip CH*Me$_2$*), 1.30 (6H, d, $J = 6.9$ Hz, Trip CH*Me$_2$*), 1.20 (6H, vq, CH*Me$_2$*), 1.10 (6H, vq, CH*Me$_2$*), 0.97 (12H, br m, CH*Me$_2$*), −21.24 (1H, t, $^2J_{PH} = 9.2$ Hz, Ir*H*). ^{13}C{^{1}H} NMR (C_6D_6, 125.8 MHz): δ 163.6 (t, $J_{CP} = 10.5$ Hz), 155.2, 149.2, 135.7, 132.5, 131.8, 128.8, 126.9 (t, $J_{CP} = 3.4$ Hz), 124.4 (t, $J_{CP} = 20.8$ Hz), 120.4, 115.6 (t, $J_{CP} = 4.8$ Hz), 34.9 (s, Trip *C*HMe$_2$), 33.3 (s, Trip *C*HMe$_2$), 25.8 (br m, *C*HMe$_2$), 24.9 (s, Trip CH*Me$_2$*), 24.4 (s, Trip CH*Me$_2$*), 23.5 (br m, *C*HMe$_2$), 20.4 (s, Ar*Me*), 19.0 (br, CH*Me$_2$*), 18.4 (br, CH*Me$_2$*), 18.2 (br, CH*Me$_2$*), 16.9 (br, CH*Me$_2$*). ^{31}P{^{1}H} NMR (C_6D_6, 202.5 MHz): δ 47.2 (s). ^{29}Si NMR (C_6D_6, 99.4 MHz): δ −74.1. Anal. Calcd for $C_{41}H_{66}NIrP_2Si$: C, 57.58; H, 7.78; N, 1.64. Found: C, 57.79; H, 7.63; N, 1.82.

(PNP)IrH(SiH$_2$Dmp) (6). A solution of $(Dmp)SiH_3$ (0.143 g, 0.42 mmol) in 3 mL of hexanes was added to a solution of (PNP)IrH$_2$ (0.259 g, 0.42 mmol) in 10 mL of hexanes. Upon addition of the silane, rapid evolution of dihydrogen gas was observed. After standing at ambient temperature for 30 min, the solution was concentrated (ca. 3 mL) until initial crystal formation was observed and then placed in a −30 °C freezer over 18 h to afford bright orange crystals. Yield: 0.320 g (80%). ^{1}H NMR (C_6D_6, 500 MHz): δ 7.60 (2H, d, $J = 8.4$ Hz, Ar*H*), 7.20 (1H, t, $J = 7.6$ Hz, Ar*H*), 6.99 (4H, overlapping signals, Ar*H*), 6.88 (4H, s, Ar*H*), 6.78 (2H, d, $J = 8.3$ Hz), 4.39 (2H, t, $^3J_{PH} = 4.4$ Hz, $^1J_{SiH} = 185.6$ Hz, Si*H*), 2.36 (12H, s, Ar*Me*), 2.22 (6H, s, Ar*Me*), 2.20 (6H, s, Ar*Me*), 2.15 (2H, m, C*H*Me$_2$), 2.01 (2H, m, C*H*Me), 1.12 (6H, vq, CH*Me$_2$*), 1.02−0.9 (18H, overlapping signals, CH*Me$_2$*), −20.21 (1H, t, $^2J_{PH} = 8.7$ Hz, Ir−*H*). ^{13}C{^{1}H} NMR (C_6D_6, 125.8 MHz): δ 163.6 (t, $J_{CP} = 10.2$ Hz, Ar*C*), 149.0 (s, Ar*C*), 142.0 (s, Ar*C*), 141.7 (s, Ar*C*), 136.7 (s, Ar*C*), 135.7 (s, Ar*C*), 133.0 (s, Ar*C*), 131.6 (s, Ar*C*), 129.6 (s, Ar*C*), 128.5 (s, Ar*C*), 126.4 (t, $J_{CP} = 3.3$ Hz, Ar*C*), 124.3 (t, $J_{CP} = 21.2$ Hz, *C*HMe$_2$), 22.2 (s, Ar*Me*), 21.1 (s, Ar*Me*), 20.6 (s, CH*Me$_2$*), 20.4 (s, Ar*Me*), 19.3 (s, CH*Me$_2$*), 18.6 (s, CH*Me$_2$*), 17.5 (s, CH*Me$_2$*). ^{31}P{^{1}H} NMR (C_6D_6, 163.0 MHz): δ 47.3 (s). ^{29}Si (C_6D_6, 99.4 MHz) NMR: δ −50.9. Anal. Calcd for $C_{50}H_{68}NIrP_2Si$: C, 62.21; H, 7.10; N, 1.45. Found: C, 62.37; H, 7.27; N, 1.83.

(PNP)IrH(SiHPh$_2$) (7). A solution of Ph_2SiH_2 (0.039 g, 0.21 mmol) in 2 mL of hexanes was added to a solution of (PNP)IrH$_2$ (0.130 g, 0.21 mmol) in 10 mL of hexanes. Upon addition of the silane, rapid evolution of dihydrogen gas was observed. After standing at ambient temperature for 30 min, some initial crystal nucleation occurred and the reaction mixture was placed in a −30 °C freezer for 18 h to afford red-orange crystals. The resulting solid can be recrystallized via a toluene/hexanes layer diffusion at −30 °C. Yield: 0.115 g (68%). ^{1}H NMR (C_6D_6, 500 MHz): δ 7.94 (4H, d, $J = 6.8$ Hz, Ar*H*), 7.73 (2H, d, $J = 8.5$ Hz, Ar*H*), 7.16 (4H, s, Ar*H*), 7.10 (2H, t, $J = 7.3$ Hz, Ar*H*), 6.95 (2H, s, Ar*H*), 6.87(2H, d, $J = 8.5$ Hz, Ar*H*), 6.28 (1H, td, $^3J_{PH} = 8.6$ Hz, $J_H = 4.6$ Hz, $^1J_{SiH} = 179.6$ Hz, Si*H*), 2.16 (6H, s, ArC*H$_3$*), 2.15 (2H, m, C*H*Me$_2$), 2.09 (2H, m, C*H*Me$_2$), 1.27 (6H, vq, CH*Me$_2$*), 1.01 (6H, vq, CH*Me$_2$*), 0.88 (6H, vq, CH*Me$_2$*), 0.78 (6H, vq, CH*Me$_2$*), −19.83 (1H, td, $^2J_{PH} = 9.5$ Hz, $J_H = 4.6$ Hz). ^{13}C{^{1}H} NMR (C_6D_6, 125.8 MHz): δ 163.1 (t, $J_{CP} = 10.1$ Hz, Ar*C*), 142.0 (s, Ar*C*), 136.9 (s, Ar*C*), 132.6 (s, Ar*C*), 132.0 (s, Ar*C*), 127.2 (s, Ar*C*), 126.8 (t, $J_{CP} = 3.3$ Hz, Ar*C*), 125.0 (t, $J_{CP} = 20.9$ Hz, Ar*C*), 115.5 (t, $J_{CP} = 4.7$ Hz, Ar*C*), 27.1 (t, $J_{CP} = 16.0$ Hz, *C*HMe$_2$), 22.4 (t, $J_{CP} = 14.5$ Hz, *C*HMe$_2$), 20.4 (s, Ar*Me*), 20.4 (s, CH*Me$_2$*), 19.06 (s, CH*Me$_2$*), 17.68 (s, CH*Me$_2$*), 17.25 (s, CH*Me$_2$*). ^{31}P{^{1}H} NMR (C_6D_6, 202.5 MHz): δ 46.8. ^{29}Si NMR (C_6D_6, 99.4 MHz): δ −21.0. Anal. Calcd for $C_{38}H_{52}NIrP_2Si$: C, 56.69; H, 6.51; N, 1.74. Found: C, 57.00; H, 6.76; N, 2.03.

(PNP)IrH(SiClPh$_2$) (8). A solution of Ph_2SiHCl (0.035 g, 0.16 mmol) in 2 mL of hexanes was added to a solution of (PNP)IrH$_2$ (0.100 g, 0.16 mmol) in 5 mL of hexanes. Upon addition of the chlorosilane, rapid evolution of dihydrogen gas was observed. After standing at ambient temperature for 45 min, the solution was placed in a −30 °C freezer for 18 h to afford red crystals. Yield: 0.104 g

(77%). ^{1}H NMR (C_6D_6, 500 MHz): δ 8.11 (4H, d, J = 7.1 Hz, Ar*H*), 7.69 (2H, d, J = 8.5 Hz, Ar*H*), 7.12 (4H, t, J = 7.3 Hz, Ar*H*), 7.06 (2H, t, J = 7.3 Hz, Ar*H*), 7.01 (2H, brs, Ar*H*), 6.85 (2H, d, J = 8.4 Hz, Ar*H*), 2.16 (4H, C*H*Me$_2$ under methyl signal), 2.14 (6H, s, ArC*H*$_3$), 1.37 (6H, vq, CH*Me*$_2$), 1.02 (6H, vq, CH*Me*$_2$), 0.92 (6H, vq, CH*Me*$_2$), 0.78 (6H, vq, CH*Me*$_2$), −19.59 (1H, t, $^2J_{PH}$ = 9.2 Hz, $^2J_{SiH}$ = 2.7 Hz, Ir-*H*). ^{13}C{^{1}H} NMR (benzene-d_6, 125.8 MHz): δ 163.1 (t, J_{CP} = 10.1 Hz, Ar*C*), 143.5 (s, Ar*C*), 136.2 (s, Ar*C*), 132.6 (s, Ar*C*), 131.9 (s, Ar*C*), 128.8 (s, Ar*C*), 127.5 (s, Ar*C*), 127.1 (s, Ar*C*), 125.0 (t, J_{CP} = 21.4 Hz, Ar*C*), 115.9 (s, Ar*C*), 28.0 (t, J_{CP} = 15.1 Hz, *C*HMe$_2$), 23.2 (t, J_{CP} = 13.8 Hz, *C*HMe$_2$), 21.3 (s, CH*Me*$_2$), 20.4 (s, Ar*Me*), 19.4 (s, CH*Me*$_2$), 18.48 (s, CH*Me*$_2$), 17.4 (s, CH*Me*$_2$). ^{31}P{^{1}H} NMR (C_6D_6, 163.0 MHz): δ 45.9 (s). ^{29}Si NMR (C_6D_6, 99.4 MHz): δ 10.8. Anal. Calcd for $C_{38}H_{51}NClIrP_2Si$: C, 54.37; H, 6.12; N, 1.67. Found: C, 54.70; H, 6.37; N, 1.96.

(PNP)Ir(SiH$_2$Ph)$_2$ (9). A solution of PhSiH$_3$ (0.018 g, 0.16 mmol) in 1 mL of pentane was added to a solution of (PNP)IrH$_2$ (0.050 g, 0.08 mmol) in 5 mL of pentane. Upon addition of the silane, rapid evolution of dihydrogen gas and a color change to dark red were observed. After 15 min, the solution was decanted to leave a burgundy microcrystalline solid. Yield: 0.053 g (79%). ^{1}H NMR (C_6D_6, 500 MHz): δ 7.93 (4H, d, J = 6.6 Hz, Ar*H*), 7.69 (2H, d, J = 8.5 Hz, Ar*H*), 7.12−7.02 (6H, ov m, Ar*H*), 6.84 (2H, d, J = 8.5 Hz, Ar*H*), 6.72 (2H, brs, Ar*H*), 5.21 (4H, t, J_{PH} = 5.8 Hz, $^1J_{SiH}$ = 177.6 Hz, Si*H*$_2$Ph), 2.49 (4H, m, C*H*Me$_2$), 2.14 (6H, s, Ar*Me*), 1.09 (12H, vq, CH*Me*$_2$), 0.84 (12H, vq, CH*Me*$_2$). ^{13}C{^{1}H} NMR (C_6D_6, 125.8 MHz): δ 162.6 (t, J_{CP} = 9.4 Hz, Ar*C*), 140.1 (s, Ar*C*), 137.2 (s, Ar*C*), 132.6 (s, Ar*C*), 132.4 (s, Ar*C*), 128.9 (s, Ar*C*), 127.9 (t, J_{CP} = 3.5 Hz, Ar*C*), 127.8 (s, Ar*C*), 123.4 (t, J_{CP} = 21.6 Hz, Ar*C*), 116.1 (t, J_{CP} = 5.2 Hz, Ar*C*), 26.0 (t, J_{CP} = 15.4 Hz, *C*HMe$_2$), 20.8 (s, Ar*Me*), 18.4 (s, CH*Me*$_2$), 17.9 (s, CH*Me*$_2$). ^{31}P{^{1}H} NMR (C_6D_6, 202.5 MHz): δ 35.2 (s). ^{29}Si NMR (C_6D_6, 99.4 MHz): δ −37.5. Anal. Calcd for $C_{38}H_{54}NIrP_2Si_2$: C, 54.65; H, 6.52; N, 1.68. Found: C, 54.53; H, 6.60; N, 1.78.

(PNP)Ir(SiH$_2$(*m*-Xylyl))$_2$ (10). A solution of XylSiH$_3$ (0.022 g, 0.16 mmol) in 1 mL of hexanes was added to a solution of (PNP)IrH$_2$ (0.050 g, 0.08 mmol) in 5 mL of hexanes. Upon addition of the silane, rapid evolution of dihydrogen gas and a color change to dark red were observed. After 15 min, the solution was concentrated (ca. 2 mL) and cooled to −30 °C to afford dark red microcrystals. Yield: 0.040 g (56%). ^{1}H NMR (C_6D_6, 500 MHz): δ 7.72 (2H, d, J = 8.4 Hz, Ar*H*), 2.63 (4H, s, Ar*H*), 6.90 (2H, d, J = 8.2 Hz, Ar*H*), 6.77 (4H, two overlapping s, Ar*H*), 5.23 (t, $^3J_{PH}$ = 5.9 Hz, $^1J_{SiH}$ = 177 Hz, Si*H*), 2.56 (4H, m, C*H*Me$_2$), 2.14 (6H, s, Ar*Me*), 2.12 (12H, s, Ar*Me*), 1.18 (12H, vq, CH*Me*$_2$), 0.85 (12H, vq, CH*Me*$_2$). ^{13}C{^{1}H} NMR (C_6D_6, 125.7 MHz): δ 162.4 (t, J_{CP} = 9.7 Hz, Ar*C*), 139.7 (s, Ar*C*), 136.4 (s, Ar*C*), 135.3 (s, Ar*C*), 132.5 (s, Ar*C*), 132.3 (s, Ar*C*), 130.3 (s, Ar*C*), 127.6 (t, J_{CP} = 3.4 Hz, Ar*C*), 123.8 (t, J_{CP} = 21.2 Hz, Ar*C*), 116.1 (t, J_{CP} = 4.8 Hz, Ar*C*), 25.9 (t, J_{CP} = 15.3 Hz, *C*HMe$_2$), 21.8 (s, Ar*Me*), 20.8 (s, Ar*Me*), 18.5 (s, CH*Me*$_2$), 18.1 (s, CH*Me*$_2$). ^{31}P{^{1}H} NMR (C_6D_6, 202.5 MHz): δ 35.2 (s). ^{29}Si NMR (C_6D_6, 99.4 MHz): δ −38.2. Anal. Calcd for $C_{42}H_{62}NIrP_2Si_2$: C, 56.60; H, 7.01; N, 1.57. Found: C, 56.39; H, 7.03; N, 1.78.

(PNP)Ir(C$_8$H$_{14}$) (11). A solution of (PNP)Li (0.26 g, 0.59 mmol) in toluene (5 mL) was added dropwise to a solution of [(COE)$_2$IrCl]$_2$ (0.26 g, 0.29 mmol) in toluene (5 mL). Upon addition, the solution turned dark orange-red and a fine precipitate formed. After standing for 30 min at ambient temperature, the solution was evacuated to dryness, extracted into pentane (10 mL), and filtered through Celite to remove the LiCl precipitate. The clear red solution was concentrated to approximately 1 mL of pentane and cooled to −30 °C to afford bright orange crystals. Yield (combined first and second crops): 0.28 g (64%). ^{1}H NMR (C_6D_6, 500 MHz, ambient temperature): δ 7.69 (2H, d, J = 7.9 Hz, Ar*H*), 7.00 (1H, d, J_{PH} = 6.1 Hz, Ar*H*), 6.90 (1H, d, J_{PH} = 6.2 Hz, Ar*H*), 6.81 (2H, vt, Ar*H*), 3.04 (2H, br, C*H* = C*H*), 2.38 (6H, ov, C*H*$_2$ and C*H*Me$_2$), 2.25 (3H, s, Ar*Me*), 2.21 (3H, s, Ar*Me*), 1.86 (2H, m, C*H*$_2$), 1.76 (2H, m, C*H*$_2$), 1.61 (2H, m, C*H*$_2$), 1.51 (4H, br m, C*H*$_2$), 1.37 (6H, br m, CH*Me*$_2$), 1.19 (6H, br m, CH*Me*$_2$), 1.04 (12H, ov m, CH*Me*$_2$). ^{1}H NMR (toluene-d_8, 500 MHz, 90 °C): δ 7.50 (2H, d, J = 7.9 Hz, Ar*H*), 6.92 (2H, s, Ar*H*), 6.75 (2H, d, J = 7.7 Hz, Ar*H*), 3.01 (2H, br s, C*H* = C*H*), 2.41 (4H, br s, C*H*Me), 2.30 (2H, d, J = 11.2 Hz, C*H*$_2$), 2.20 (6H, s, Ar*Me*), 1.78 (2H, m, C*H*$_2$), 1.70 (2H, m, C*H*$_2$), 1.51−1.47 (6H, ov m, C*H*$_2$), 1.33 (12H, br s, CH*Me*$_2$), 1.06 (12H, br m, CH*Me*$_2$). ^{13}C{^{1}H} NMR (C_6D_6, 125.8 MHz): δ 165.3 (m), 164.5 (m), 132.2 (d, J_{CP} = 22.2 Hz), 131.8 (d, J_{CP} = 20.9 Hz), 128.9 (s), 125.9 (br m), 125.1 (d, J_{CP} = 40.2 Hz), 123.1 (d, J_{CP} = 45.7 Hz), 116.2 (m), 116.1 (m) (Ar*C*), 41.1 (s, *C*H=*C*H), 36.2 (br, *C*HMe$_2$), 33.4 (s, *C*H$_2$), 27.7 (s, *C*H$_2$), 21.1 (s, Ar*Me*), 20.9 (s, Ar*Me*), 17.6 (s, CH*Me*$_2$), 17.3 (s, CH*Me*$_2$). ^{31}P{^{1}H} NMR (C_6D_6, 202.5 MHz): δ 29.4, 27.7, 26.2, 24.5 (AB quartet, $^2J_{PP}$ = 351 Hz). Anal. Calcd for $C_{34}H_{54}NIrP_2$: C, 55.87; H, 7.45; N, 1.92. Found: C, 55.56; H, 7.26; N, 2.16.

[(PNP)(H)Ir=SiH(Trip)][B(C$_6$F$_5$)$_4$] (12). A solution of [Ph$_3$C]-[B(C$_6$F$_5$)$_4$] (0.011 g, 0.01 mmol) in 0.5 mL of C$_6$D$_5$Br was added to **5** (0.010 g, 0.01 mmol). The solution turned bright green. The resulting solution was immediately analyzed by NMR spectroscopy. Complex **12** decomposed after 45 min at ambient temperature. ^{1}H NMR (C$_6$D$_5$Br, 500 MHz): δ 10.76 (1H, vq, $^1J_{SiH}$ = 206.2 Hz, Si*H*), −18.37 (1H, vq, Ir*H*). ^{29}Si NMR (C$_6$D$_5$Br, 99.4 MHz): δ 233.9.

[(PNP)(H)Ir=SiH(Dmp)][B(C$_6$F$_5$)$_4$] (13). A solution of [Ph$_3$C]-[B(C$_6$F$_5$)$_4$] (0.066 g, 0.07 mmol) in 0.5 mL of C$_6$H$_5$F was added to a solution of **6** (0.070 g, 0.07 mmol) in 1 mL of C$_6$H$_5$F. Upon addition, a color change from orange to an intense blue occurred. The resulting C$_6$H$_5$F solution was added to 15 mL of cold pentane and placed in the −30 °C freezer. After 2 h, a blue oil settled out. The solution was carefully decanted (the washing procedure can be repeated to remove any persistent triphenylmethane impurities). The resulting blue oil was dried under vacuum for 1 h. Yield: 0.119 g (65% yield of **13** by integration of Ir−*H* and Si−*H* groups). The resulting solid can be stored at −30 °C for approximately 2 weeks before significant decomposition. The ^{1}H NMR indicates the presence of two diasteromers of **13** in a 2:1 ratio. Due the complexity of the resulting spectra, only the Si−H and Ir−H data are given. The ^{29}Si NMR resonance was obtained via a 2D ^{1}H,^{29}Si{^{1}H} HMBC experiment as a crosspeak with the downfield Si*H* resonance. No other ^{29}Si resonances were found via this experiment. ^{1}H NMR (C$_6$D$_5$Br, 500 MHz): for **13a**, δ 9.75 (t, Si*H*, $^1J_{SiH}$ = 206 Hz), −20.49 (t, Ir*H*); for **13b**, δ 9.73 (t, Si*H*) −20.43 (t, Ir*H*). ^{31}P{^{1}H} NMR (C$_6$D$_5$Br, 202.5 MHz): for **13a**, δ 54.6 (br s); **13b**, δ 54.4 (br s). ^{29}Si NMR (C$_6$D$_5$Br, 99.4 MHz): δ 226.6. ^{19}F{^{1}H} NMR (C$_6$D$_5$Br, 376.5 MHz): δ −130.8 (br s), −161.3 (t, J = 20.7 Hz), −165.1 (br t, J = 19.3 Hz). Anal. Calcd for $C_{74}H_{67}NBF_{20}IrP_2Si$: C, 54.08; H, 4.11; N, 0.85. Found: C, 53.77; H, 4.01; N, 1.20.

[(PNP)(H)Ir=SiPh$_2$][B(C$_6$F$_5$)$_4$] (14). A solution of [Ph$_3$C]-[B(C$_6$F$_5$)$_4$] (0.192 g, 0.21 mmol) in 0.5 mL of C$_6$H$_5$F was added to a solution of **7** (0.168 g, 0.21 mmol) in 1 mL of C$_6$H$_5$F. Upon addition, a color change from red-orange to a purple occurred. The resulting C$_6$H$_5$F solution was added to 15 mL of cold pentane and placed in the −30 °C freezer. After 2 h, a purple oil settled to the bottom of the vial. The solution was carefully decanted (the washing procedure can be repeated to remove any persistent triphenylmethane impurities). The resulting violet oil was dried under vacuum for 1 h to afford **14** as a purple foam. Yield: 0.300 g (97%). ^{1}H NMR (C$_6$D$_5$Br, 500 MHz): δ 7.76 (4H, br, Ar*H*), 7.50 (2H, d, J = 8.2 Hz, Ar*H*), 7.43 (2H, br, Ar*H*), 7.30 (4H, br, under solvent signal, Ar*H*), 7.01 (2H, d, J = 8.3 Hz, Ar*H*), 6.90 (2H, s, Ar*H*), 2.25 (6H, s, Ar*Me*), 2.24 (2H, br, C*H*Me$_2$, under methyl signal), 2.01 (2H, br, C*H*Me$_2$), 0.96 (6H, vq, CH*Me*$_2$), 0.84 (6H, vq, CH*Me*$_2$), 0.61 (12H, overlapping m, CH*Me*$_2$), −20.6 (1H, t, $^2J_{PH}$ = 8.9 Hz, $^2J_{SiH}$ = 10 Hz, Ir−*H*). ^{13}C{^{1}H} NMR (C$_6$D$_5$Br, 125.8 MHz): δ 162.2 (t, J_{CP} = 10.0 Hz, Ar*C*), 150.1 (br m, Ar*C*), 148.1 (br m, Ar*C*), 139.9 (br m, Ar*C*), 138.0 (br m, Ar*C*), 137.3 (s, Ar*C*), 136.0 (br m, Ar*C*), 135.2 (br s, Ar*C*), 134.1 (s, Ar*C*), 132.7 (s, Ar*C*), 128.3 (t, $J_{\mathrm{CP}} = 23.3$ Hz, Ar*C*), 120.3 (t, $J_{\mathrm{CP}} = 23.9$ Hz, Ar*C*), 116.3 (t, $J_{\mathrm{CP}} = 4.9$ Hz, Ar*C*), 27.0 (t, $J_{\mathrm{CP}} = 16.5$ Hz, *C*HMe$_2$), 25.2 (t, $J_{\mathrm{CP}} = 16.3$ Hz, *C*HMe$_2$), 20.8 (s, Ar*Me*), 19.9 (s, CH*Me*$_2$), 18.7 (s, CH*Me*$_2$), 18.5 (s, CH*Me*$_2$), 18.2 (s, CH*Me*$_2$). ^{31}P{^{1}H} NMR (C_6D_5Br, 163.0 MHz): δ 66.0. ^{19}F{^{1}H} NMR (C_6D_5Br, 376.5 MHz): δ −130.8 (br s), −161.3 (t, $J = 20.7$ Hz), −165.1 (br t, $J = 19.3$ Hz). ^{29}Si NMR (C_6D_5Br, 99.4 MHz): δ 264.8. Anal. Calcd for $C_{62}H_{50}NBF_{20}IrP_2Si$: C, 50.24; H, 3.40; N, 0.95. Found: C, 49.90; H, 3.28; N, 1.02.

[(PNP)(H)Ir=SiH(Mes)][$CB_{11}H_6Br_6$] (15). A solution of [Ph_3C][$CB_{11}H_6Br_6$] (0.044 g, 0.05 mmol) in 1 mL of C_6H_5F was added to a solution of **2** (0.040 g, 0.05 mmol) in 1 mL of C_6H_5F. The reaction solution was stirred for 10 min giving an intense blue solution. The resulting C_6H_5F solution was added to 10 mL of cold hexanes and placed in the −30 °C freezer. After 1 h, the blue solid was collected via filtration. The solid was redissolved in C_6H_5F, and the washing procedure was repeated to ensure removal of the triphenylmethane byproduct. The collected solid was washed with hexanes and dried. Yield: 0.068 g (94%). ^{1}H NMR (C_6D_5Br, 400 MHz): δ 10.69 (1H, br, $^{1}J_{\mathrm{SiH}} = 208$ Hz, Si*H*), 7.43 (2H, d, $J = 8.4$ Hz, Ar*H*), 6.65 7.02 (2H, s, Ar*H*), 6.88 (2H, d, $J = 8.3$ Hz, Ar*H*), (2H, s, Ar*H*), 3.5−2.5 (6H, br, carborane), 2.4−2.2 (8H, overlapping br m, C*H*Me$_2$ + Ar*Me*), 2.28 (6H, s, Ar*Me*), 2.12 (3H, s, Ar*Me*), 2.11 (2H, under methyl resonance, br m, C*H*Me$_2$,), 1.07 (6H, vq, CH*Me*$_2$), 0.95−079 (18H, ov m, CH*Me*$_2$), −18.83 (1H, br H, Ir*H*). ^{31}P{^{1}H} NMR (C_6D_5Br, 202.5 MHz): δ 58.3 (s). ^{29}Si NMR (C_6D_5Br, 99.4 MHz): δ 244.7. Anal. Calcd for $C_{36}H_{59}NB_{11}Br_6IrP_2Si_2$: C, 31.19; H, 4.29; N, 1.01. Found: C, 31.06; H, 4.16; N, 1.08.

[(PNP)(H)Ir=$SiPh_2$)][$CB_{11}H_6Br_6$] (16). A solution of [Ph_3C][$CB_{11}H_6Br_6$] (0.106 g, 12.4 mmol) in 1 mL of C_6H_5F was added to a solution of **7** (0.100 g, 12.4 mmol) in 1 mL of C_6H_5F. The reaction solution was stirred for 10 min to give an intense violet solution. The resulting C_6H_5F solution was added to 10 mL of cold hexanes and placed in the −30 °C freezer. After 1 h, the purple solid was collected via filtration. The solid was redissolved in C_6H_5F, and the washing procedure was repeated to ensure removal of the triphenylmethane byproduct. The collected solid was washed with hexanes and dried. Yield: 0.145 g (82%). ^{1}H NMR (C_6D_5Br, 500 MHz): δ 7.79 (4H, br, Ar*H*), 7.50 (2H, d, $J = 8.5$ Hz, Ar*H*), 7.43 (4H, br, Ar*H*), 7.01 (2H, d, $J = 8.6$ Hz, Ar*H*), 6.90 (2H, br, Ar*H*), 3.5−2.5 (6H, br, carborane), 2.33 (2H, m, C*H*Me$_2$), 2.29 (6H, s, Ar*Me*), 2.08 (2H, m, C*H*Me$_2$), 0.99 (6H, vq, CH*Me*$_2$), 0.88 (6H, vq, CH*Me*$_2$), 0.61 (12H, ov m, CH*Me*$_2$), −20.42 (1H, t, $^{2}J_{\mathrm{PH}} = 9.2$ Hz). ^{13}C{^{1}H} NMR (C_6D_5Br, 125.8 MHz): δ 162.3 (t, $J_{\mathrm{CP}} = 8.7$ Hz), 137.4 (br s), 135.3 (br s), 134.0 (s), 132.9 (s), 128.6 (t, $J_{\mathrm{CP}} = 22.2$ Hz), 120.6 (t, $J_{\mathrm{CP}} = 23.8$ Hz), 116.3 (t, $J_{\mathrm{CP}} = 5.1$ Hz) (Ar*C*), 41.5 (br, carborane), 27.1 (t, $J_{\mathrm{CP}} = 16.5$ Hz, *C*HMe$_2$), 25.2 (t, $J_{\mathrm{CP}} = 17.6$ Hz, *C*HMe$_2$), 21.0 (s, Ar*Me*), 20.3 (s, CH*Me*$_2$), 19.0 (s, CH*Me*$_2$), 18.8 (s, CH*Me*$_2$), 18.5 (s, CH*Me*$_2$). ^{31}P{^{1}H} NMR (C_6D_5Br, 162.0 MHz): δ 67.5 (s). ^{29}Si{^{1}H} NMR (CD_2Cl_2, 99.4 MHz): δ 265.6 (br m). ^{11}B{^{1}H} NMR (C_6D_5Br, 128.4 MHz): δ −1.0 (s), −9.4 (s), −20.3 (s). Anal. Calcd for $C_{39}H_{58}NB_{11}Br_6IrP_2Si$: C, 32.95; H, 4.11; N, 0.99. Found: C, 34.48; H, 4.25; N, 0.95. Partial cocrystallization of fluorobenzene accounts for the discrepancy. Anal. Calcd for $C_{39}H_{58}NB_{11}Br_6IrP_2Si \cdot 0.6(C_6H_5F)$: C, 34.59; H, 4.16; N, 0.95.

[(PNP)(H)Ir=SiMes($CH_2CH_2SiMe_3$)][$B(C_6F_5)_4$] (17). An excess of vinyltrimethylsilane (0.006 g, 0.06 mmol) was added to a solution of **1** (0.070 g, 0.05 mmol) in 3 mL of C_6H_5F to give a dark blue solution. After 10 min, the reaction mixture was added to cold pentane and placed in the −30 °C freezer for 1 h. A dark blue oil was collected by decanting the supernatant and dried under vacuum to give a dark blue solid. Yield: 0.063 g (85%). ^{1}H NMR (C_6D_5Br, 500 MHz): δ 7.33 (2H, under solvent signal, Ar*H*), 6.95 (4H, ov m, Ar*H*), 6.63 (s, Ar*H*), 2.32 (2H, br m, C*H*Me$_2$), 2.23 (6H, s, Ar*Me*), 2.18 (6H, s, Ar*Me*), 2.10 (3H, s, Ar*Me*), 2.08 (2H, br m, C*H*Me$_2$), 1.36 (2H, br m, C*H*$_2$), 1.05 (6H, vq, CH*Me*$_2$), 0.98 (6H, vq, CH*Me*$_2$), 0.80 (12H, ov m, CH*Me*$_2$), 0.02 (9H, s, Si*Me*$_3$), −18.63 (1H, t, $^{2}J_{\mathrm{PH}} = 9.0$ Hz, $^{2}J_{\mathrm{SiH}} = 10$ Hz, Ir*H*). ^{13}C{^{1}H} NMR (C_6D_5Br, 125.8 MHz): δ 161.4 (t, $J_{\mathrm{CP}} = 9.3$ Hz), 150.1 (br m), 148.2 (br m), 143.8 (s), 140.0 (br m), 138.0 (br m), 136.1 (br m), 134.0 (s), 132.3 (s), 120.2 (t, $J_{\mathrm{CP}} = 24.5$ Hz), 116.5 (br m) (Ar*C*), 34.4 (*C*H$_2$), 25.9 (br m, *C*HMe$_2$), 24.8 (s, Ar*Me*), 24.6 (br m, *C*HMe$_2$), 21.6 (s, Ar*Me*), 20.8 (s, Ar*Me*), 20.6 (s, CH*Me*$_2$), 18.5 (s, CH*Me*$_2$), 17.9 (s, CH*Me*$_2$), 17.5 (s, CH*Me*$_2$), −2.0 (s, Si*Me*$_3$). ^{31}P{^{1}H} NMR (C_6D_5Br, 202.5 MHz): δ 60.7 (br s). ^{29}Si NMR (C_6D_5Br, 99.4 MHz): δ 3.1 (*Si*Me$_3$), 301.1 (Ir=*Si*). ^{19}F{^{1}H} NMR (C_6D_5Br, 376.5 MHz): δ −130.8 (br s), −161.3 (t, $J = 20.7$ Hz), −165.1 (br t, $J = 19.3$ Hz). Anal. Calcd for $C_{64}H_{65}NBF_{20}IrP_2Si_2$: C, 49.61; H, 4.23; N, 0.90. Found: C, 49.47; H, 4.34; N, 1.08.

[(PNP)(H)Ir=SiMes($CH_2CH_2(C_6H_4Cl)$][$B(C_6F_5)_4$] (18). An excess of *p*-chlorostyrene (0.008 g, 0.06 mmol) was added to a solution of **1** (0.080 g, 0.06 mmol) in 3 mL of C_6H_5F to give a dark blue solution. After 10 min, the reaction mixture was added to cold pentane (5 mL) and placed in the −30 °C freezer for 1 h. The resulting dark blue oil was collected by decantation of the supernatant and dried under vacuum to give a dark blue solid. Yield: 0.072 g (82%). ^{1}H NMR (C_6D_5Br, 500 MHz): δ 7.30 (2H, under solvent signal, Ar*H*), 7.15 (2H, d, $J = 8.3$ Hz, Ar*H*), 6.95 (4H, ov m, Ar*H*), 6.74 (2H, d, $J = 8.3$ Hz), 6.65 (2H, s, Ar*H*), 2.65 (2H, t, $J = 7.7$ Hz, C*H*$_2$), 2.32 (2H, m, C*H*Me$_2$), 2.23 (6H, s, Ar*Me*), 2.14 (3H, s, Ar*Me*), 2.13 (6H, s, Ar*Me*), 2.04 (2H, m, C*H*Me$_2$), 1.58 (2H, br t, C*H*$_2$), 1.07 (6H, vq, CH*Me*$_2$), 0.89 (6H, vq, CH*Me*$_2$), 0.80 (6H, vq, CH*Me*$_2$), 0.71 (6H, vq, CH*Me*$_2$), −19.05 (1H, t, $^{2}J_{\mathrm{PH}} = 9.0$ Hz, $^{2}J_{\mathrm{SiH}} = 10$ Hz, Ir*H*). ^{13}C{^{1}H} NMR (C_6D_5Br, 125.8 MHz): δ 161.4 (t, $J_{\mathrm{CP}} = 8.2$ Hz), 150.0 (br m), 148.1 (br m), 144.2 (s), 139.9 (br m), 139.7 (s), 138.0 (s), 136.0 (br m), 135.4 (s), 134.0 (s), 133.2 (s), 132.8 (s), 129.5 (s), 120.2 (t, $J_{\mathrm{CP}} = 23.1$ Hz), 116.6 (br m) (Ar*C*), 43.7 (s, *C*H$_2$), 31.0 (s, *C*H$_2$), 26.5 (br m, *C*HMe$_2$), 25.1 (br m, *C*HMe$_2$), 24.6 (s, Ar*Me*), 21.7 (s, Ar*Me*), 20.8 (s, Ar*Me*), 20.6 (s, CH*Me*$_2$), 18.6 (s, CH*Me*$_2$), 17.7 (s, CH*Me*$_2$), 17.4 (s, CH*Me*$_2$). ^{31}P{^{1}H} NMR (C_6D_5Br, 202.5 MHz): δ 60.9 (br s). ^{29}Si NMR (C_6D_5Br, 99.4 MHz): δ 293.3. ^{19}F{^{1}H} NMR (C_6D_5Br, 376.5 MHz): δ −130.8 (br s), −161.3 (t, $J = 20.7$ Hz), −165.1 (br t, $J = 19.3$ Hz). Anal. Calcd for $C_{67}H_{60}NBClF_{20}IrP_2Si$: C, 50.69; H, 3.81; N, 0.88. Found: C, 50.91; H, 4.02; N, 0.90.

[(PNP)(SiH(Mes)(Hex))IrH(SiH_2Mes)][$B(C_6F_5)_4$] (19). Determination of a yield by NMR spectroscopy: A solution of H_3SiMes (0.0016 g, 0.01 mmol) and bis(*p*-fluorophenyl)methane (0.0021 g, 0.01 mmol) in bromobenzene-*d*$_5$ (0.5 mL) was added to [(PNP)(H)Ir=SiMes(Hex)][$B(C_6F_5)_4$] (0.016 g, 0.01 mmol), and the reaction mixture was analyzed by NMR spectroscopy. Yield: 33−43% for **19**, 39% for H_2SiMes(Hex). The mixture of iridium-containing products can be separated from organic impurities by washing with pentane and drying under vacuum to afford a light blue foam. ^{1}H NMR (C_6D_5Br, 500 MHz): δ 4.75 (1H, br m, $^{1}J_{\mathrm{SiH}} = 183.2$ Hz, Si*H*$_2$Mes), 4.67 (1H, br m, $^{1}J_{\mathrm{SiH}} = 179.8$ Hz, Si*H*$_2$Mes), −5.81 (1H, br s, $^{1}J_{\mathrm{SiH}} = 101.9$ Hz, η^2Si*H*), −11.94 (1H, t, $^{2}J_{\mathrm{PH}} = 18.3$ Hz, $^{2}J_{\mathrm{SiH}} = 8.5$ Hz, Ir*H*). ^{31}P{^{1}H} NMR (C_6D_5Br, 162.0 MHz): δ 39.8 (d), 9.9 (d, $J_{\mathrm{PP}} = 244.6$ Hz). ^{29}Si NMR (C_6D_5Br, 99.4 MHz): δ 0.83 (N*Si*Mes(Hex)(H)), −78.1 (Ir*Si*H$_2$Mes).

[(PNP)($SiPh_2$)Ir($SiPh_2H$)(H)$_2$][$CB_{11}H_6Br_6$] (20). An excess of H_2SiPh_2 (0.030 g, 0.16 mmol) was added to a solution of **16** (0.078 g, 0.05 mmol) in 7 mL of C_6H_5F. The reaction mixture was stirred for 18 h at ambient temperature to give a colorless solution. The reaction mixture was dried under vacuum, giving a light blue foam. Off-white crystals of **20** were obtained by the vapor diffusion of hexanes into a *o*-$C_6H_4Cl_2$ solution of the complex. Yield: 0.076 g (86%). ^{1}H NMR (CD_2Cl_2, 500 MHz, 203 K): δ 8.41 (1H, br, Ar*H*), 7.98 (d, $J = 7.2$ Hz, Ar*H*), 7.60 (1H, br, Ar*H*), 7.52 (1H, br, Ar*H*), 7.39 (5H, m, Ar*H*), 7.23 (3H, m, Ar*H*), 7.25−7.07 (9H, ov m, Ar*H*), 6.99−6.89 (7H, ov m, ArH), 6.79 (2H, ov m, Ar*H*), 6.12 (1H, br d, $J = 7.2$ Hz, Ar*H*), 5.56 (1H, dd, $J_{\mathrm{PH}} = 21.6$ Hz, $J_{\mathrm{HH}} = 2.9$ Hz, $^{1}J_{\mathrm{SiH}} = 170.2$ Hz, $^{3}J_{\mathrm{SiH}} = 5.9$ Hz, Si*H*), 2.73 (1H, m, C*H*Me$_2$), 2.68 (1H, br s, carborane), 2.6−1.8 (5H, br, carborane), 2.30 (3H, s, Ar*Me*), 2.24 (3H, s, Ar*Me*), 2.30−2.22 (2H, under methyl resonance, C*H*Me$_2$), 1.69 (1H, m, C*H*Me$_2$), 1.51−1.39 (9H, ov m, CH*Me*$_2$), 1.26 (3H, vq, CH*Me*$_2$), 0.29 (3H, dd, $J_{\mathrm{PH}} = 23.8$ Hz, J_{HH}

= 6.0 Hz, CH*Me*$_2$), 0.18 (6H, ov m, CH*Me*$_2$), −0.10 (3H, dd, J_{PH} = 17.5 Hz, J_{HH} = 6.3 Hz, CH*Me*$_2$), −11.31 (1H, ddd, J_{PH} = 111.7 Hz, J_{PH} = 18.0 Hz, J_{HH} = 4.5 Hz, Ir*H*), −11.95 (1H, br s, $^2J_{SiH}$ = 10.3 Hz); for **20b** (13%), δ 5.72 (1H, t, J_{PH} = 7.3 Hz, $^1J_{SiH}$ = 184.6 Hz, Si*H*), −10.23 (2H, dd, J_{PH} = 80.8 Hz, J_{PH} = 17.1 Hz, Ir*H*). ^{13}C{^{1}H} NMR (CD_2Cl_2, 125.8 MHz, 203 K): δ 153.7 (d, J_{PC} = 16.8 Hz), 152.2 (d, J_{PC} = 15.2 Hz), 141.2 (d, J_{PC} = 4.2 Hz), 139.6 (d, J_{PC} = 6.2 Hz), 139.4 (br m), 138.9 (s), 136.4 (ov m), 135.9 (s), 135.3 (ov m), 134.9 (s), 133.7 (s), 132.6 (s), 132.2 (s), 132.2 (s), 132.1 (s), 131.9 (s), 131.8 (s), 131.1 (s), 130.8 (d, J_{CP} = 7.8 Hz), 130.5 (s), 130.3 (s), 129.7 (s), 128.3 (s), 128.0 (s), 127.1 (s), 126.3 (s), 125.1 (br m), 122.9 (d, J_{CP} = 9.0 Hz, Ar*C*), 41.4 (s, carborane), 34.1 (d, J_{CP} = 28.0 Hz, *C*HMe$_2$), 30.8 (d, J_{CP} = 21.7 Hz, *C*HMe$_2$), 26.2 (d, J_{CP} = 13.5 Hz, *C*HMe$_2$), 25.1 (d, J_{CP} = 8.4 Hz, CH*Me*$_2$), 23.0 (d, J_{CP} = 34.1 Hz, *C*HMe$_2$), 21.9 (br m, CH*Me*$_2$), 20.7 (s, Ar*Me*), 20.4 (s, Ar*Me*), 18.6 (ov s, CH*Me*$_2$), 18.2 (ov s, CH*Me*$_2$), 17.0 (s, CH*Me*$_2$), 16.5 (s, CH*Me*$_2$). ^{31}P{^{1}H} NMR (CD_2Cl_2, 99.4 MHz, 203 K): δ 38.8 (d), 19.9 (d, J_{PP} = 17.1 Hz). ^{29}Si NMR (CD_2Cl_2, 99.4 MHz, 203 K): δ 6.1 (N*Si*Ph$_2$), −37.3 (Ir*Si*Ph$_2$H). Anal. Calcd for $C_{51}H_{69}NB_{11}Br_6IrP_2Si_2$: C, 38.17; H, 4.33; N, 0.87. Found: C, 38.55; H, 4.31; N, 1.17.

Detailed Procedure for Small-Scale Catalytic Redistribution Reactions. Catalytic runs for silane redistribution were performed in Teflon-capped J. Young NMR tubes. In a representative catalytic run, **1** (0.007 g, 0.005 mmol, 2 mol %) was dissolved in 0.6 mL of bromobenzene-d_5, and the resulting solution was added to bis(*p*-fluorophenyl)methane (0.0099 g, 0.05 mmol) (as a standard) followed by the silane (0.24 mmol). The solution was transferred to a Teflon-capped J. Young NMR tube. For $PhSiH_3$ substrate, the solution was left at ambient temperature for 18 h. For the remaining silane substrates, the reaction mixture was heated to 60 °C in an oil bath with a temperature-controlled hot plate for 18 h (see Table 3). The progress of the reaction was then monitored via ^{1}H NMR spectroscopy, and yields were obtained by integration against a standard. The reaction solution was then opened to air, diluted with 2 mL of hexanes, filtered through silica gel to remove any metal species, and analyzed by GC/MS.

Detailed Procedure for Small-Scale Catalytic Hydrosilation Reactions. Hydrosilation catalytic runs were performed in Teflon-capped J. Young NMR tubes. In a representative catalytic run, **1** (0.010 g, 0.007 mmol, 5 mol %) was dissolved in 0.6 mL of bromobenzene-d_5, and the resulting solution was added to bis(*p*-fluorophenyl)methane (0.0143 mg, 0.14 mmol) (as a standard), followed by the alkene (0.14 mmol) and the silane (0.14 mmol). The solution was transferred to a Teflon-capped J. Young NMR tube and heated to 60 °C in an oil bath with a temperature-controlled hot plate for 3−46 h (see Table 3). The progress of the reaction was monitored by ^{1}H NMR spectroscopy, and yields were obtained by integration against a standard. The reaction solution was then opened to air, diluted with 2 mL of hexanes, filtered through silica gel to remove any metal species, and analyzed by GC/MS.

X-ray Crystallography. General Considerations. The single-crystal X-ray analyses of compounds **6**, **11**, **16**, and **20** were carried out at the UC Berkeley CHEXRAY crystallographic facility. All measurements were made on a Bruker SMART or APEX CCD area detector with graphite-monochromated Mo Kα radiation (λ = 0.71069 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 or Patterson methods using the SHELX program package. For **6**, the checkcif report featured alert level "A" associated with disordered hexanes in the unit cell, but this does not affect the crystallographic data associated with **6**. For **20**, PLATON SQUEEZE[51] was used to treat disordered hexanes (see Supporting Information). Crystallographic data are summarized in the Supporting Information, and CIF files for all structures are also included.

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Supporting Information Available: Tables of atomic coordinates, thermal displacement parameters, selected bond lengths and angles, and crystallographic information files for **6**, **11**, **16**, and **20**; GC/MS and NMR spectroscopy for hydrosilation products. This material is available free of charge via the Internet at http://pubs.acs.org.

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