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Article

Reactions of Cationic PNP-Supported Iridium Silylene Complexes with Polar Organic Substrates

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Reactions of PNP-supported silylene complexes [(PNP)(H)Ir=SiRR′][$B(C_6F_5)_4$] (R = R′ = Ph (**1**) and R = H, R′ = Mes (**2**)) with Lewis bases, carbonyl compounds, alcohols, and amines were investigated. Addition of DMAP (4-dimethylaminopyridine) to **1** and **2** produced base-stabilized silylene complexes [(PNP)(H)IrSiRR′(DMAP)][$B(C_6F_5)_4$] (R = R′ = Ph (**3**) and R = H, R′ = Mes (**4**)). Reactions of **2** with benzophenone and benzaldehyde afforded the products of stoichiometric hydrosilylation, heteroatom-substituted silylene complexes [(PNP)(H)Ir=SiMes(OCH(Ph)(R))][$B(C_6F_5)_4$] (R = Ph (**5**) and R = H (**6**)). Complex **1** reacted with DMF or benzophenone, and **2** reacted with DMF, to afford base-stabilized silylene complexes of the type [(PNP)(H)IrSiRR′(B)][$B(C_6F_5)_4$] (R = H, R′ = Mes, B = DMF (**7**); R = R′ = Ph, B = DMF (**8**) and O=CPh_2 (**9**)). In contrast, treatment of **1** with acetophenone afforded {(PNPH)IrH[$SiPh_2$(OC(=CH_2)Ph)]}[$B(C_6F_5)_4$] (**10**), from activation of a C−H bond at the α-carbon position of acetophenone. Reactions of alcohols and amines with **1** afforded [(PNPH)IrH($SiPh_2$OR)]-[$B(C_6F_5)_4$] (R = 3,5-^{t}Bu$_2C_6H_3$ (**11**), R = Ph (**12**), R = ^{i}Pr (**13**), and R = ^{t}Bu (**14**)) and [(PNPH)IrH-($SiPh_2$NHR)][$B(C_6F_5)_4$] (R = Ph (**15**), R = 3,5-$(CF_3)_2C_6H_3$ (**16**)). Exploration of the catalytic activity of iridium silylene complexes with these organic substrates demonstrated that **1** is an effective catalyst for silane alcoholysis and aminolysis and for the hydrosilylation of ketones.

Introduction

Investigations of transition-metal complexes featuring multiple bonds to main group elements are of interest with respect to the discovery of new reactivity and catalytic processes. Notable examples of important transformations promoted by these types of multiply bonded species include hydroamination by transition-metal imido complexes (M=NR)[1] and olefin metathesis by transition-metal carbene complexes (M=CR_2).[2] In this context, transition-metal complexes featuring multiple bonds to silicon have been targeted as promising compounds for the development of catalytic transformations of organosilanes. Research into the synthesis and reactivity of transition-metal silylene complexes (M=SiR_2), featuring a double bond between silicon and the metal center, has been motivated by their proposed intermediacy in catalytic cycles including silane redistribution,[3] the Direct Process for the synthesis of chlorosilanes,[4] silane dehydropolymerization,[5] and the hydrosilylation of alkenes.[6]

Investigations into the reactivity of silylene complexes with simple organic substrates have revealed a number of new stoichiometric transformations at silicon.[7] For example, reactions of chlorinated hydrocarbons with [Cp*$(PMe_3)_2$-Os=$SiMe_2$][$B(C_6F_5)_4$] and [Cp*(dmpe)$(H)_2$W=$SiMe_2$][B-$(C_6F_5)_4$] result in the formation of chlorinated silyl ligands or free chlorosilanes, in transformations that are significant as stoichiometric models for the Direct Process.[8] Other notable examples include the reaction of [Cp*$(PMe_3)_2$Ru=$SiMe_2$][$B(C_6F_5)_4$] with isocyanates, resulting in the only known example of a 1,2-dipolar cycloaddition to a transition-metal silylene complex.[9] Tobita et al. have described reactions of

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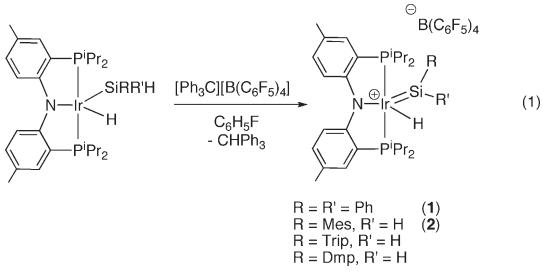
$Cp^*(CO)_2(H)W{=}SiH[C(SiMe_3)_3]$ with nitriles, epoxides, and α,β-unsaturated carbonyl compounds, illustrating a variety of reactivity modes for this silylene complex.[10] Similarly, recent reports by the same group have featured reactions of $Cp^*(CO)(H)Ru{=}SiH[C(SiMe_3)_3]$ with nitriles and carbonyl compounds.[11]

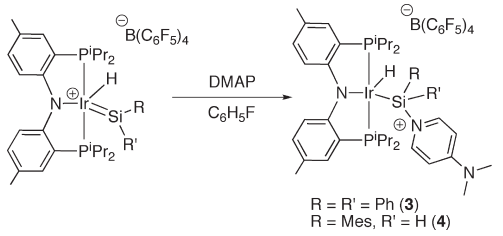
Recent investigations of alkene hydrosilylation by silylene complexes focused on the chemistry of PNP-supported iridium silylene species of the type $[(PNP)(H)Ir{=}SiR_2][B(C_6F_5)_4]$, synthesized via hydride abstraction from neutral iridium silyl hydride species (eq 1). Previous reports detailed structural and spectroscopic investigations of this family of cationic iridium silylene complexes and their reactions with alkenes in the context of hydrosilylation catalysis.[12] In this contribution, the reactivity of $[(PNP)(H)Ir{=}SiRR'][B(C_6F_5)]$ (R = R′ = Ph (**1**) and R = H, R′ = Mes (**2**)) toward a variety of organic molecules including Lewis bases, carbonyl compounds, alcohols, and amines is described. Furthermore, explorations of catalytic reactions mediated by PNP-supported iridium silylene complexes are presented.



(1)

Results and Discussion

Reactions of Iridium Silylene Complexes with Lewis Bases. The coordination of Lewis bases to a Lewis acidic silylene ligand is a common reaction pathway encountered for complexes of this type, reflecting considerable electrophilic character for the silicon center.[7] The behavior of **1** and **2** toward Lewis bases was investigated through reactions with 4-dimethylaminopyridine (DMAP). Addition of DMAP to **1** in C_6H_5F at ambient temperature produced a color change from bright purple to red-violet. The base-stabilized silylene complex $[(PNP)(H)IrSiPh_2(DMAP)][B(C_6F_5)_4]$ (**3**) was isolated in 82% yield as a red-violet solid in analytically pure form after washing with pentane (eq 2). Notably, the ^{29}Si NMR spectrum of **3** contained a single resonance at 8.7 ppm, over 250 ppm upfield from that of the parent silylene species **1** (265 ppm). This difference in chemical shift corresponds to quenching of the electronic unsaturation at silicon, as the chemical shift for **3** is in the range usually associated with a silyl ligand.[13] The ^1H NMR spectrum of **3** contained a resonance at −21.28 ppm, attributed to the hydride ligand at iridium.



(2)

Similarly, addition of 1 equiv of DMAP to hydrogen-substituted silylene complex **2** in C_6H_5F resulted in a dramatic color change from blue green to dark red. A red-violet solid identified as $[(PNP)(H)IrSiMes(H)(DMAP)][B(C_6F_5)_4]$ (**4**) was isolated following analogous procedures to those employed for **3**. The ^{29}Si NMR resonance for **4** appears at −12.1 ppm, representing a 258 ppm shift from that of the parent silylene species **2** (246 ppm). The ^1H NMR spectrum of **4** contains a resonance at 6.58 ppm (J_{SiH} 203 Hz), also shifted upfield from the resonance of the Si−H group for **2** at 10.7 ppm. Interestingly, the phosphorus donors for the ligand in **4** give rise to two distinct $^{31}P\{^1H\}$ NMR resonances. The J_{PP} coupling constant of 252 Hz is consistent with a *trans* arrangement of the phosphorus atoms. The inequivalence of phosphorus donors for **4** is attributed to the presence of three different substituents on the silicon center, which renders the P atoms diastereotopic.

The first example of a transition-metal silylene catalyst for the hydrosilylation of alkenes was the base-stabilized ruthenium silylene complex $[Cp^*(P^iPr_3)(H)_2Ru{=}SiH(Ph)(OEt_2)][B(C_6F_5)_4]$, which is a stable precatalyst due to weak binding between diethyl ether and the silicon center.[6] For comparison, Stradiotto and co-workers synthesized a base-stabilized ruthenium silylene species supported by the P,N ligand $2\text{-}NMe_2\text{-}2\text{-}P^iPr_2$-indene (the amine on the ligand acts as a Lewis base to the silicon), which is inactive for the hydrosilylation of alkenes.[14] Addition of 3 equiv of 1-hexene to DMAP-stabilized silylene complex **4** gave no alkene insertion after 2 days at 65 °C. In contrast, addition of 1-hexene to $[(PNP)(H)Ir{=}SiMes(H)][B(C_6F_5)_4]$ (**2**) in fluorobenzene at ambient temperature results in instantaneous conversion to $[(PNP)(H)Ir{=}SiMes(Hex)][B(C_6F_5)_4]$.[12a] Thus, the inertness of **4** toward reaction with 1-hexene supports the requirement for kinetic availability of a base-free silylene ligand for hydrosilylation to proceed.

Reactions of Iridium Silylene Complexes with Carbonyl Compounds. The observed Lewis acidity of the silylene ligand prompted investigations of the reactivity of **1** and **2** toward other polar organic substrates that might be activated via coordination to the silicon center. Initial efforts focused on the reaction of hydrogen-substituted silylene **2** with a variety of carbonyl compounds. To this end, addition of 1 equiv of benzophenone to a solution of **2** in C_6H_5F afforded $[(PNP)(H)Ir{=}SiMes(OC(H)Ph_2)][B(C_6F_5)_4]$ (**5**) as a dark purple solid isolated in 94% yield (eq 3). This reaction is analogous to that observed for **2** with alkene substrates to afford disubstituted silylene ligands.[12] Complex **5** exhibits greater thermal stability than **2**, as no decomposition was observed in bromobenzene-d_5 after 24 h at ambient temperature.

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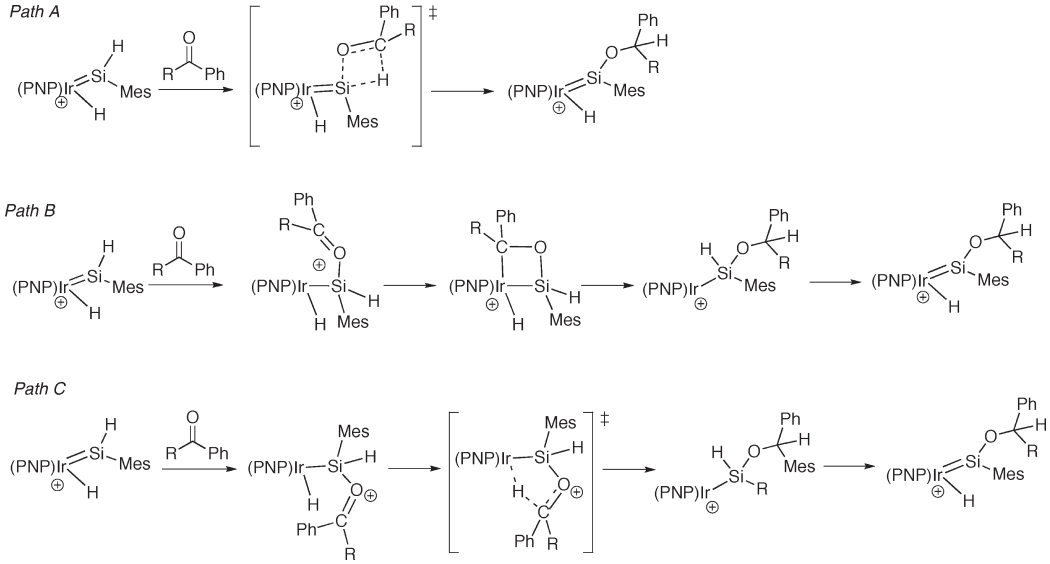
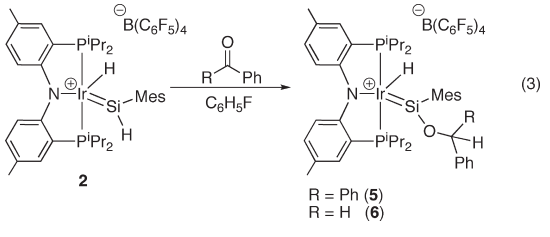
Scheme 1



The structure of **5** was confirmed through multinuclear and 2D NMR experiments. The ^{1}H NMR spectrum reveals a resonance at 5.79 ppm corresponding to the C*H*Ph$_2$ proton, corroborated by a correlation in the 2D ^{1}H,^{13}C{^{1}H} HMQC experiment with a signal at 84.8 ppm in the ^{13}C{^{1}H} NMR spectrum. Other significant NMR characteristics include the Ir−H resonance in the ^{1}H NMR at −20.24 ppm, appearing as a triplet due to couplings to phosphorus, and the silylene ligand resonance in the ^{29}Si NMR at 161.8 ppm. The upfield shift of the ^{29}Si NMR resonance of **5** in comparison to parent complex **2** is consistent with a heteroatom substituent in the silylene ligand, where π-donation of the oxygen lone pair to the empty p-orbital on silicon reduces the electronic unsaturation at the silylene center.[15]

Addition of benzophenone to **2** at −20 °C in fluorobenzene resulted in an intermediate color change to red-violet followed by a change to bright purple upon slight warming. The observation of an intermediate red-violet color is consistent with the formation a base-stabilized silylene complex. NMR studies *in situ* at −20 °C in bromobenzene-d_5 revealed an intermediate complex containing a resonance at −21.55 ppm for an Ir−H group. However, a signal for the Si−H group was not identified in the ^{1}H NMR spectrum, and signals were not observed at this temperature for the silylene ligand (in the 2D ^{1}H,^{29}Si HMBC spectrum) or the PNP ligand (in the ^{31}P NMR spectrum), precluding further elucidation of the identity of this intermediate.



(3)

Treatment of a solution of **2** in fluorobenzene with 1 equiv of benzaldehyde resulted in formation of [(PNP)(H)Ir=SiMes(OCH$_2$Ph)][B(C$_6$F$_5$)$_4$] (**6**), isolated in 89% yield as a purple solid (eq 3). Complex **6** exhibits NMR resonances that are analogous to those of [(PNP)(H)Ir=SiMes(OC(H)Ph$_2$)][B(C$_6$F$_5$)$_4$] (**5**), including a ^{1}H NMR resonance at 4.48 ppm, integrating to two protons, attributed to the benzylic group. Similarly, a ^{13}C{^{1}H} NMR resonance at 72.2 ppm is attributed to the benzylic carbon. The ^{29}Si NMR resonance at 159.3 ppm is consistent with the presence of a heteroatom-substituted silylene ligand. The ^{1}H NMR spectrum of **6** exhibits an upfield resonance at −20.24 ppm for the iridium hydride. Interestingly, this reaction requires strict control of the stoichiometry of the carbonyl substrate, as addition of 2 equiv of benzaldehyde resulted in a mixture of intractable products. In contrast, formation of complex **5** is independent of the stoichiometry, as addition of 2 equiv of benzophenone to **2** cleanly yielded only **5**. Additionally, reactions with enolizable carbonyl substrates such as acetone or acetophenone produced a mixture of organometallic products.

The reactivity of PNP-supported iridium silylene complex **2** parallels reactivity previously documented for hydrogen-substituted ruthenium and tungsten silylene species. The reaction of hydrogen-substituted silylene complexes with carbonyl substrates to afford heteroatom-substituted silylene products has been reported for the reaction of Cp*(CO)$_2$(H)W=SiH[C(SiMe$_3$)$_3$] with acetone[16] and for reactions of Cp*(CO)(H)Ru=SiH[C(SiMe$_3$)$_3$] with benzophenone, benzaldehyde, and propionaldehyde.[11a]

Several pathways are envisioned for reactions of carbonyl substrates with **2** to give **5** and **6**, and three of these possibilities are depicted in Scheme 1. One pathway involves direct addition of the carbonyl to the Si−H bond (path A). A similar process is postulated for the reaction of hydrogen-substituted silylene complex [Cp*(P^{i}Pr$_3$)(H)$_2$Ru=SiH(Ph)(OEt$_2$)][B(C$_6$F$_5$)$_4$] with alkenes, which is supported by experimental and theoretical investigations.[6,17] Note that the reaction of path A could involve prior coordination of the carbonyl group to silicon, before insertion into the Si−H bond. A second path involves a [2+2] cycloaddition to

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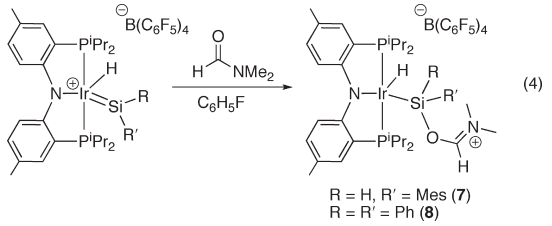
afford an intermediate metallacycle, which could reorganize via reductive elimination of a C−H bond followed by α-hydrogen migration (path B). The cycloaddition of a polar substrate (isocyanates) to a silylene complex has previously been documented, and experimental observations support a stepwise addition involving initial formation of a base-stabilized ruthenium silylene complex.[9] A third pathway involves formation of a base-stabilized silylene complex, which activates the carbonyl substrate to subsequent reaction with the hydride ligand at iridium, followed by α-hydrogen migration (path C). Tobita et al. have proposed pathways B and C for the reaction of Cp*(CO)(H)Ru=SiH-[C(SiMe$_3$)$_3$] with ketones and aldehydes and favor path B due to isolation of an intermediate featuring a Ru−C bond.[11a] Furthermore, theoretical investigations for the reaction of Cp*(CO)$_2$(H)W=SiH[C(SiMe$_3$)$_3$] with acetone support a mechanism similar to that presented in path C, involving initial formation of a base-stabilized silylene complex followed by nucleophilic attack of the transition-metal hydride.[18]

It was envisioned that obtaining the kinetic isotope effect for reactions of **2** with carbonyl compounds might aid in elucidating the mechanism of this transformation. The reaction of **2** with carbonyl compounds is fast (complete conversion within 1 min at room temperature), which makes direct measurements of the rates of reactions of **2** with carbonyl compounds difficult. Another method for determination of k_H/k_D involves a competition experiment, in which the carbonyl compound is allowed to react with an excess of an equimolar 1:1 mixture of [(PNP)(H)Ir=SiMes(H)][B(C$_6$F$_5$)$_4$] and [(PNP)(D)Ir=SiMes(D)][B(C$_6$F$_5$)$_4$]. Interestingly, combining [(PNP)(H)Ir=SiMes(H)][B(C$_6$F$_5$)$_4$] and [(PNP)(D)Ir=SiMes(D)][B(C$_6$F$_5$)$_4$] in bromobenzene-d_5 resulted in intermolecular scrambling to afford a mixture of isotopomers within 10 min at ambient temperature. A similar process for intermolecular redistribution of substituents between ruthenium silylene and silyl complexes has previously been reported, but the intermolecular scrambling of substituents between two silylene complexes appears to be unknown.[19] This rapid H/D scrambling process precludes determination of a kinetic isotope effect via a competition experiment.

A series of base-stabilized silylene complexes were isolated from reactions of **1** and **2** with other carbonyl compounds. For example, addition of DMF to **2** affords base-stabilized silylene complex [(PNP)(H)Ir=SiMes(H)(DMF)][B(C$_6$F$_5$)$_4$] (**7**), instead of the disubstituted silylene complex {(PNP)-(H)Ir=SiMes[OCH$_2$(NMe$_2$)]}[B(C$_6$F$_5$)$_4$] (eq 4). Complex **7** is red-violet, a characteristic color for the DMAP-stabilized silylene complexes **3** and **4**. Similarly, the NMR spectroscopy for **7** reveals features similar to those of [(PNP)(H)IrSiMes-(H)(DMAP)][B(C$_6$F$_5$)$_4$] (**4**). The ^{1}H NMR spectrum contains a resonance at 6.19 ppm attributed to the Si−H group, as indicated by observation of ^{29}Si satellites (J_{SiH} 207.5 Hz). Similar to **4**, the ^{31}P{^{1}H} NMR spectrum of **7** exhibits two distinct resonances appearing as doublets for an unsymmetrical PNP ligand, with a J_{PP} coupling constant of 267 Hz, consistent with a *trans* arrangement of the phosphorus donors about iridium. The ^{29}Si NMR resonance (13.8 ppm) is shifted to the silyl region. The ^{13}C{^{1}H} NMR spectrum reveals a signal for the carbonyl carbon of DMF at 165.2 ppm, confirming retention of the carbonyl moiety. Thus, the NMR data suggest a saturated and tetrahedral silicon center (sp^3 hybridized) featuring a single bond to iridium and a positive charge localized on the Lewis base.



(4)

Reactions of the diphenyl-substituted silylene complex **1** toward carbonyl substrates were also explored. Analogous to the reactivity of [(PNP)(H)Ir=SiMes(H)][B(C$_6$F$_5$)$_4$] (**2**), treatment of a solution of **1** with 1 equiv of DMF resulted in a color change to red-violet due to formation of [(PNP)(H)-IrSiPh$_2$(DMF)][B(C$_6$F$_5$)$_4$] (**8**) (eq 4). Salient NMR features for base-stabilized complex **8** include a ^{29}Si NMR resonance at 29.0 ppm attributed to the Lewis base adduct of the silylene ligand, a ^{1}H NMR resonance at 8.16 ppm for the aldehyde proton, a ^{1}H NMR resonance at −19.02 for the iridium hydride ligand, and a ^{13}C{^{1}H} NMR resonance at 164.9 for the carbonyl carbon. Similarly, addition of 1 equiv of benzophenone to a solution of **1** in fluorobenzene afforded [(PNP)(H)IrSiPh$_2$(OCPh$_2$)][B(C$_6$F$_5$)$_4$] (**9**), isolated in 93% yield after washing with pentane. The ^{29}Si NMR resonance for the silylene ligand appears relatively downfield at 46.8 ppm presumably due to the weaker Lewis basicity of benzophenone (vs DMAP and DMF). The ^{13}C{^{1}H} NMR spectrum exhibits a signal at 208.2 ppm for the carbonyl carbon, corroborating the presence of a carbonyl functionality.

In contrast, addition of 1 equiv of acetophenone to **1** in fluorobenzene at ambient temperature resulted in a color change to dark yellow, instead of the red-violet color observed for base-stabilized silylene complexes. A dark yellow solid identified as {(PNPH)IrH[SiPh$_2$(OC(=CH$_2$)Ph)]}-[B(C$_6$F$_5$)$_4$] (**10**) was isolated after precipitation from hexanes followed by drying under vacuum (eq 5). Complex **10** contains a protonated PNP ligand, an iridium hydride ligand, and a silyl group that is substituted by the enolate derived from acetophenone. These structural features were all determined by multinuclear and multidimensional NMR experiments. The ^{1}H NMR spectrum of **10** exhibits a broad signal at 7.93 ppm for the NH group on the PNPH ligand, a broad signal at 4.56 ppm for the alkene CH$_2$ group, and an upfield resonance at −17.69 for the hydride ligand. The ^{13}C{^{1}H} NMR spectrum of **10** reveals a signal at 94.6 ppm for the terminal alkene carbon correlating to the ^{1}H NMR signal at 4.56 ppm in a 2D ^{1}H,^{13}C{^{1}H} HMQC experiment. A ^{29}Si NMR resonance at −5.7 ppm was observed for the silyl ligand of **10**. In an attempt to determine the mechanism for the formation of **10**, a deuterium labeling experiment was undertaken involving addition of acetophenone to the deuterated silylene complex [(PNP)(D)Ir=SiPh$_2$][B(C$_6$F$_5$)$_4$] in bromobenzene-d_5 or fluorobenzene. These experiments resulted in significant deuterium incorporation into the NH, IrH, and alkene positions for **10** after 10 min at ambient

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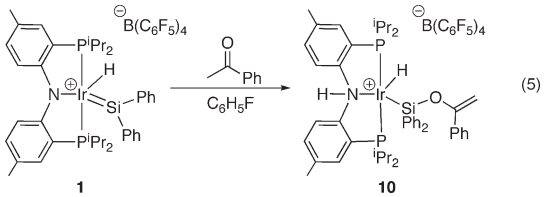
Table 1. Summary of NMR Data for Compounds 11−14

compound	δ^1H (Ir*H*)	δ^1H (PNP*H*)	δ^{29}Si (Ir*Si*)	δ^{31}P (PNP)
[(PNPH)IrH($SiPh_2OAr^{tBu}$)][$B(C_6F_5)_4$] (Ar^{tBu} = 3,5-^{t}Bu$_2$C$_6$H$_3$) (**11**)	−17.36	7.83	−3.6	48.5
[(PNPH)IrH($SiPh_2OPh$)][$B(C_6F_5)_4$] (**12**)	−17.45	7.82	−3.3	48.0
[(PNPH)IrH($SiPh_2O^iPr$)][$B(C_6F_5)_4$] (**13**)	−17.63	7.56	−2.3	47.9
[(PNPH)IrH($SiPh_2O^tBu$)][$B(C_6F_5)_4$] (**14**)	−17.60	7.16−7.08[a]	−14.8	45.5

[a] Signal obscured by aromatic proton resonances.

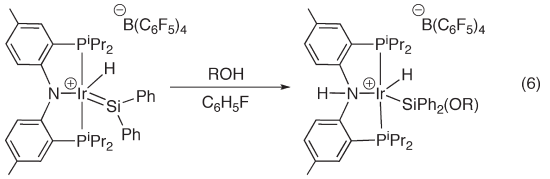
temperature. The deuteration of the alkene could result from reversible alkene insertion into the iridium hydride.



(5)

The formation of **10** by activation of an enolizable ketone has precedent in past studies of the reactivity of silylene ligands. The first example of this reactivity described the formation of silyl enol ethers from the reaction of acetophenone or acetone with [Cp*(PMe_3)$_2$Ru=$SiPh_2$(NCMe)][BPh_4], but in this case an intermediate adduct was not isolated.[20] Furthermore, Tobita et al. have recently published examples of similar reactions of transition-metal silylene complexes with enolizable carbonyl compounds.[10c,11a] For example, the reaction of Cp*(CO)(H)Ru=SiH[$C(SiMe_3)_3$] with acetophenone afforded Cp*(CO)(H)$_2$Ru{Si(H)[OC(=CH_2)Ph]$C(SiMe_3)_3$}, with NMR characteristics similar to those observed for **10** including a $^{13}C\{^1H\}$ NMR resonance at 93.1 ppm for the terminal alkene carbon. It is worth noting that the reaction of acetophenone with **1** results in formation of a N−H bond from participation of the PNP ligand, whereas in the ruthenium complex the deprotonation of acetophenone results in formation of a hydride ligand.

Reactions of Iridium Silylene Complexes with Alcohols and Phenol Derivatives. Addition of 1 equiv of EtOH, PhOH, or 3,5-di-*tert*-butylphenol to **2** at ambient temperature afforded mixtures of compounds. In contrast, **1** cleanly reacted with an array of ROH substrates. Treatment of a solution of **1** in fluorobenzene with 1 equiv of 3,5-di-*tert*-butylphenol produced a yellow compound, [(PNPH)IrH($SiPh_2OAr^{tBu}$)][$B(C_6F_5)_4$] (**11**, Ar^{tBu} = 3,5-^{t}Bu$_2$C$_6$H$_3$), isolated in 94% yield. Similarly, addition of PhOH, ^{i}PrOH, or ^{t}BuOH to a solution of **1** in fluorobenzene afforded [(PNPH)IrH($SiPh_2OPh$)][$B(C_6F_5)_4$] (**12**), [(PNPH)IrH($SiPh_2O^iPr$)][$B(C_6F_5)_4$] (**13**), and [(PNPH)IrH($SiPh_2O^tBu$)][$B(C_6F_5)_4$] (**14**), respectively, in good yields as yellow solids (eq 6).



(6)

The NMR data for complexes **11**−**14** are summarized in Table 1. The ^{1}H NMR spectra for these compounds contain signals between −17.36 and −17.63 ppm for the iridium hydride ligand and signals between 7.83 and 7.08 ppm for the amine proton on the pincer ligand. The ^{29}Si NMR resonance for the alkoxysilyl ligand appears in the region of −14.8 to −2.3 ppm. Interestingly, formation of the N−H bond could allow bond activations that might otherwise require access to high oxidation states, coordination numbers, and/or electron counts at the iridium center. The participation of this PNP ligand in the reactivity of iridium complexes has been previously observed in migratory insertions of silylene[12b] and carbonyl ligands to the amido group.[21]

Reactions of silylene complexes with alcohols have been documented previously.[7b] In some cases, such reactions directly afford silyl ether products, via loss of the silylene ligand from the metal center.[19,22] For example, addition of alcohols to [Cp*(PMe_3)RuSiPh_2(NCMe)][BPh_4] afforded the silyl ether product Ph_2SiH(OR).[19] In other instances, the controlled addition of an alcohol substrate to a silylene ligand resulted in OH addition across the M=Si bond to produce alkoxysilyl and hydride ligands.[7b] Similar reactivity has been documented for transition-metal germylene and stannylene complexes.[23]

Three possible mechanisms for the reaction of alcohols with **1** are depicted in Scheme 2. One pathway involves the concerted addition of the O−H bond across the Ir=Si double bond, followed by migration of the resulting iridium hydride to the amido group of the PNP ligand (path A). Alternatively, the O−H activation can occur via path B, in which the alcohol coordinates to the silicon center to form a base-stabilized silylene complex, followed by deprotonation by the amido nitrogen. Lastly, a third pathway involves a process initiated by proton transfer from the alcohol to the amido group, perhaps with significant, concurrent Si−O bond formation (path C). In an attempt to distinguish between these different pathways, deuterated 3,5-di-*tert*-butylphenol was employed in this stoichiometric reaction. NMR studies after 15 min at room temperature in bromobenzene-d_5 revealed deuterium incorporation into both the hydride and amine positions (approximately 45:55). Conducting this experiment at −10 °C revealed similar values for deuteration at the amine and hydride. This pattern is perhaps most consistent with path A, as migration to the amine could occur from either of the iridium hydride ligands, whereas paths B and C would result in deuteration only at the amine position. However, a separate, rapid scrambling process could also account for the observed deuterium labeling results. For example an intramolecular scrambling process,

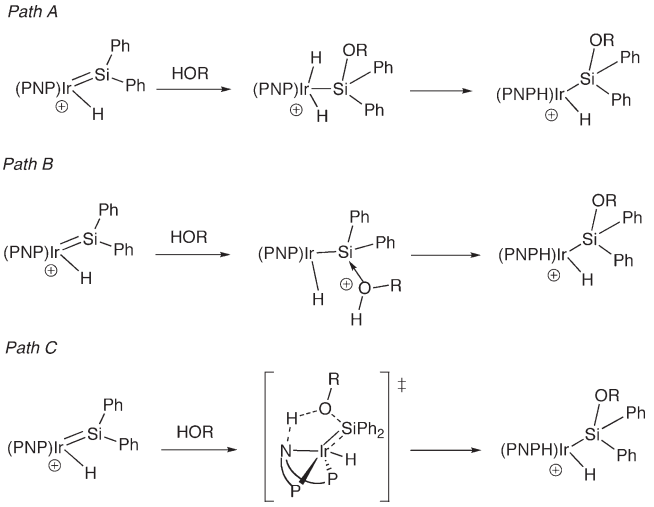
(20) Zhang, C.; Grumbine, S. D.; Tilley, T. D. *Polyhedron* **1991**, *10*, 1173–1176.

(21) Whited, M. T.; Grubbs, R. H. *Organometallics* **2008**, *27*, 5737–5740.

(22) Feldman, J. D.; Mitchell, G. P.; Nolte, J.-N.; Tilley, T. D. *J. Am. Chem. Soc.* **1998**, *120*, 11184–11185.

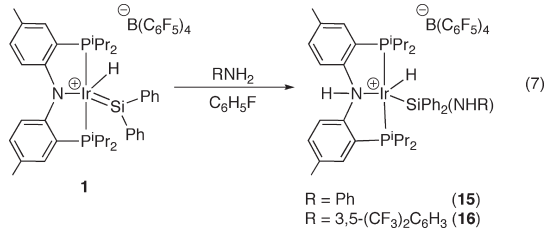
(23) (a) Schager, F.; Seevogel, K.; Pörschke, K.-R.; Kessler, M.; Krüger, C. *J. Am. Chem. Soc.* **1996**, *118*, 13075–13076. (b) Hayes, P. G.; Waterman, R.; Glaser, P. B.; Tilley, T. D. *Organometallics* **2009**, *28*, 5082–5089.

Scheme 2



perhaps mediated by the formation a transient dihydrogen complex of the type $[(PNP)Ir(\eta^2\text{-}H_2)(SiPh_2OR)][B(C_6F_5)_4]$, could lead to the observed ratio of N−D and Ir−D. Similar reversible N−H bond formation has been proposed for dihydrogen activation[24] and in the transfer hydrogenation of ketones with alcohols[25] by transition-metal complexes supported by similar PNP ligands.

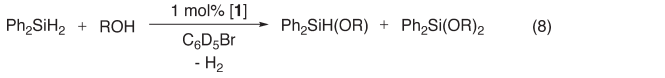
Reactions of Iridium Silylene Complexes with Anilines. The activation of O−H bonds by complex **1** prompted an investigation of similar transformations involving N−H bonds. Treatment of **1** with 1 equiv of aniline afforded the yellow compound $[(PNPH)IrH(SiPh_2NHPh)][B(C_6F_5)_4]$ (**15**), resulting from N−H activation (eq 7). The ^{1}H NMR spectrum of **15** contains a resonance at 7.78 ppm for the N−H group on the pincer ligand and a resonance at 4.19 ppm for the anilide proton of the silyl ligand. The iridium hydride resonance appears at −17.96 ppm, as a broad triplet from coupling to phosphorus. A diagnostic resonance at −21.9 ppm in the ^{29}Si NMR spectra is consistent with a silyl ligand (and a saturated silicon center).



(7)

Similarly, treatment of **1** with 1 equiv of 3,5-$(CF_3)_2C_6H_3$-NH_2 afforded $[(PNPH)IrH(SiPh_2(NHAr_F))][B(C_6F_5)_4]$ (**16**, Ar_F = 3,5-$(CF_3)_2C_6H_3$) isolated in 88% yield. Similar characteristic NMR resonances confirm the activation of an N−H bond of the aniline by **1**. The ^{1}H NMR spectrum for **16** reveals resonances at 7.79 and 4.58 ppm for the NH group of the pincer ligand and anilide group, respectively. The iridium hydride resonates at −17.99 ppm, with a small coupling to silicon of 3 Hz, indicating minimal interaction between the hydride and silylene ligand. Furthermore, the ^{29}Si NMR shift at −16.5 ppm corroborates the formation of a silyl ligand. Complex **1** was inert toward reaction with Ph_2NH in bromobenzene-d_5 after 1 h at ambient temperature, suggesting a steric limitation to reactions of **1** with amine substrates.

Catalytic Alcoholysis and Aminolysis of Silanes by $[(PNP)(H)Ir{=}SiPh_2][B(C_6F_5)_4]$ (1). Given the stoichiometric bond activations described above, it was of interest to explore related catalytic transformations that might be mediated by silylene complexes such as **1** and **2**. An investigation of catalytic alcoholysis of silanes by silylene complexes focused on complex **1**, as **2** did not afford clean products in stoichiometric reactions with alcohols. Catalytic runs were performed with 1−2 mol % loading of **1** in bromobenzene-d_5 at ambient temperature with a slight molar excess of the alcohol substrate (Table 2). Vigorous evolution of gas, identified as H_2 by ^{1}H NMR spectroscopy, was observed upon combining both substrates with the catalyst. Catalytic reactions involving Ph_2SiH_2 and a variety of alcohol substrates were complete after 4 h at ambient temperature (eq 8). The nature of the silane products depended on the alcohol substrate. Only one silane product, $Ph_2SiH(OR)$, was formed when 3,5-di-*tert*-butylphenol or *tert*-butanol was used as substrate (in 92% and 77% yields by NMR and GC-MS, respectively; entries a and b). With 2-propanol as a substrate, a trace amount of $Ph_2Si(O^iPr)_2$ was observed by GC-MS in addition to $Ph_2SiH(O^iPr)$ (82% yield, entry c). The catalytic coupling of Ph_2SiH_2 and methanol yielded a mixture of $Ph_2SiH(OMe)$ (70%) and $Ph_2Si(OMe)_2$ (22%) after 3.5 h (entry d). Hence, the secondary alcoholysis of $Ph_2SiH(OR)$ is sensitive to the steric demands of the alkoxy group.



(8)

The ability of tertiary silanes to undergo alcoholysis was investigated with triphenylsilane and triethylsilane substrates, in combination with 2-propanol. The reaction involving triphenylsilane was slower than that of the corresponding reaction with diphenylsilane. Incomplete conversion was observed after 21 h at ambient temperature, to afford a 45% yield of $Ph_3Si(O^iPr)$ (entry e). Under the same conditions, the triethylsilane substrate was completely consumed after 21 h at ambient temperature, to afford $Et_3Si(O^iPr)$ in a high 87% yield, as the only product observed by NMR spectroscopy (entry f). The ability of trisubstituted silanes to act as substrates suggests that a silylene ligand is not essential in this catalytic reaction. In fact, a 1 mol % loading of $(PNP)IrH(SiHPh_2)$ with 3,5-di-*tert*-butylphenol and diphenylsilane also resulted in formation of the alcoholysis product, $Ph_2SiH(OR)$, in 96% yield within 23 h at ambient temperature. However, $(PNP)IrH(SiHPh_2)$ is not as active as **1** and requires longer reaction times for complete conversion to product.

(24) (a) Fryzuk, M. D.; MacNeil, P. A. *Organometallics* **1983**, *2*, 682–684. (b) Fryzuk, M. D.; MacNeil, P. A.; Rettig, S. J. *Organometallics* **1985**, *4*, 1145–1147. (c) Fryzuk, M. D.; MacNeil, P. A.; Rettig, S. J. *J. Am. Chem. Soc.* **1987**, *109*, 2803–2812. (d) Fryzuk, M. D.; Montgomery, C. D.; Rettig, S. J. *Organometallics* **1991**, *10*, 467–473. (e) Ozerov, O. V.; Huffman, J. C.; Watson, L. A.; Caulton, K. G. *Organometallics* **2003**, 2539–2541. (f) Käss, M.; Friedrich, A.; Drees, M.; Schneider, S. *Angew. Chem., Int. Ed.* **2008**, *48*, 905–907.

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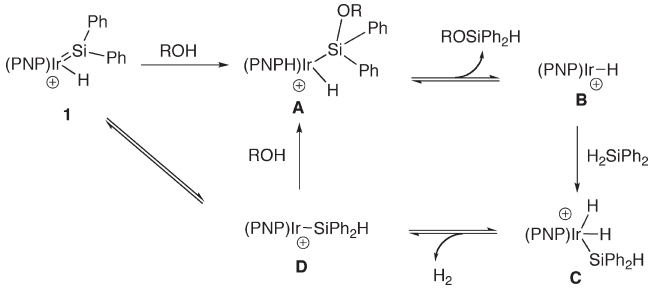
Table 2. Catalytic Results for the Alcoholysis of Silanes by 2

entry	silane	ROH	[1] mol %	time (h)	products (yield)
a	H_2SiPh_2	R = 3,5-$^tBu_2C_6H_3$	1	4	$Ph_2SiH(OR)$ (92%)
b	H_2SiPh_2	R = ^tBu	1	4	$Ph_2SiH(OR)$ (77%)
c	H_2SiPh_2	R = ^{i}Pr	1	4	$Ph_2SiH(OR)$ (84%) $Ph_2Si(OR)_2$ (trace)
d	H_2SiPh_2	R = Me	1	3.5	$Ph_2SiH(OR)$ (70%) $Ph_2Si(OR)_2$ (22%)
e	$HSiPh_3$	R = ^{i}Pr	2	21	$Ph_3Si(OR)$ (45%)
f	$HSiEt_3$	R = ^{i}Pr	2	21	$Et_3Si(OR)$ (87%)

Scheme 3



The catalytic reaction of silanes with anilines using **1** as a catalyst resulted in formation of silyl amine compounds, analogous to the formation of silyl ethers via catalytic alcoholysis. Catalytic runs involved a slight excess of amine and a 1 mol % loading of **1** in bromobenzene-d_5. Upon combining both substrates with the catalyst, evolution of H_2 gas was observed. Catalytic runs with H_2NPh were complete after 5 h and gave $Ph_2SiH(NHPh)$ in 85% yield (versus integration with an internal standard). Catalysis using H_2NAr_F (Ar_F = 3,5-$(CF_3)_2C_6H_3$) as a substrate resulted in slower conversion in comparison to H_2NPh. After 5 h at ambient temperature, a 48% yield of $Ph_2SiH(NHAr_F)$ was observed, yet high yields of the product (92%) were obtained after 21 h. This catalytic process is also promoted by (PNP)IrH($SiHPh_2$), although slow product formation was observed with H_2SiPh_2 and H_2NPh substrates (only 27% yield after 21 h under the same conditions). Thus, in both the dehydrogenative coupling of silanes with alcohols and amines, it appears that the silylene ligand is not required.

A simplified mechanism for the alcoholysis of diphenylsilane by **1** is depicted in Scheme 3. Addition of alcohol to silylene complex **1** would afford a complex of the type [(PNPH)IrH($SiPh_2OR$)][$B(C_6F_5)_4$] (**A**), as described above for the stoichiometric reaction of **1** with alcohols. The next step could involve reductive elimination of the silyl ether to afford hydride intermediate **B**. However, as complexes **11** to **14** are stable in solution at ambient temperature (> 2 weeks), this product-forming step may proceed through an associative mechanism via attack of a silane substrate. In support of this, reaction of 1 equiv of H_2SiPh_2 with [(PNPH)IrH($SiPh_2OAr^{tBu}$)][$B(C_6F_5)_4$] (Ar^{tBu} = 3,5-di-*tert*-butylphenyl, **11**) in bromobenzene-d_5 results in the release of a substoichiometric amount (52%) of $Ph_2SiH(OAr^{tBu})$ after 10 min at ambient temperature. The next step in the proposed catalytic cycle involves activation of the silane substrate via oxidative addition of an Si−H bond, to afford the Ir(V) silyl dihydride intermediate **C**. Alternatively, participation of the PNP ligand in bond activation could provide a lower energy pathway (compared to that involving the high oxidation state of intermediate **C**), to afford instead an Ir(III) complex of the type [(PNPH)IrH($SiPh_2H$)][$B(C_6F_5)_4$]. The next step involves the loss of dihydrogen to form silyl intermediate **D**, which could be in equilibrium with silylene complex **1** via a reversible α-migration. However, as tertiary silanes are suitable substrates in this process, the silylene intermediate is not necessary for the reaction with alcohols. Hence, it is proposed that species **D** could directly react with alcohols to produce species of type **A**. Previous mechanistic studies on silane alcoholysis by late transition-metal catalysts suggest that formation of the silyl ether product might proceed via nucleophilic attack of an alcohol onto an activated silane in the coordination sphere of the metal.[26] Usually the silicon center is activated toward attack via oxidative addition of the Si−H bond to the transition-metal center to afford a silyl hydride intermediate or by the formation of an η^2-silane complex on an electrophilic transition-metal center.[26] Thus, direct reaction of alcohol with species such as **D** may proceed via nucleophilic attack of the alcohol onto silicon, and this is consistent with the conversion of tertiary silanes to R_3SiOR products, and secondary silanes to $Ph_2Si(OR)_2$ products. A similar mechanism may be proposed for the dehydrogenative coupling of silanes with amines by **1**. Interestingly, the catalytic reaction of H_2NAr_F (Ar_F = 3,5-$(CF_3)_2C_6H_3$) with silanes was significantly slower than that of aniline, suggesting that the nucleophilicity of the amine is tied to the reaction rate of these catalytic processes.

A series of NMR experiments were undertaken to elucidate the nature of organometallic species under catalytic conditions in the coupling of diphenylsilane with 3,5-di-*tert*-butylphenol (using 1 to 5 mol % loading of **1**). After 1 h at room temperature in bromobenzene-d_5, $^{31}P\{^1H\}$ NMR spectra of the reaction mixture revealed the presence of an unidentified species with a resonance at 34.8 ppm. Attempts to isolate this intermediate by precipitation of the reaction mixture from hexanes resulted in isolation of a mixture of organometallic species, containing [(PNPH)IrH($SiPh_2OAr^{tBu}$)][$B(C_6F_5)_4$] (**11**, Ar^{tBu} = 3,5-$^tBu_2C_6H_3$) as the major species. Similarly, in a separate experiment, the $^{31}P\{^1H\}$ NMR spectrum of this catalytic reaction after 4 h revealed only one species, [(PNPH)IrH($SiPh_2OAr^{tBu}$)][$B(C_6F_5)_4$] (**11**, Ar^{tBu} = 3,5-$^tBu_2C_6H_3$) (after complete consumption of silane product). The $^{31}P\{^1H\}$ NMR spectra for reactions with diphenylsilane and other alcohol substrates exhibited similar resonances appearing between 33 and 37 ppm, for related organometallic intermediates. Hence, these reactions have separate intermediates, as indicated by the different chemical shifts depending on alcohol substrate. These intermediates might arise from the binding of alcohols to transient species (such as **B** and **D**) in the catalytic cycle presented in Scheme 3.

(26) (a) Luo, X.-L.; Crabtree, R. H. *J. Am. Chem. Soc.* **1989**, *111*, 2527–2535. (b) Doyle, M. P.; High, K. G.; Bagheri, V.; Pieters, R. J.; Lewis, P. J.; Pearson, M. M. *J. Org. Chem.* **1990**, 6082–6086. (c) Corbin, R. A.; Ison, E. A.; Abu-Omar, M. M. *Dalton Trans.* **2009**, 2850–2855.

Table 3. Catalytic Results for the Hydrosilylation of Ketones by 1 and 2[a]

entry	silane	ketone	catalyst	time (h)	products (yield)
a	H_2SiPh_2	benzophenone	**2**	5	$Ph_2SiH[OC(H)Ph_2]$ (90%)[b]
b	H_2SiPh_2	benzophenone	**2**	5	$Ph_2SiH[OC(H)Ph_2]$ (67%)[c]
c	H_2SiPh_2	benzophenone	**1**	4.5	$Ph_2SiH[OC(H)Ph_2]$ (88%)
d	H_2SiPh_2	acetophenone	**1**	5	$Ph_2SiH[OCH(Me)(Ph)]$ (48%) $Ph_2SiH[OC(=CH_2)Ph]$ (23%)

[a] Catalytic trials conducted with a 1 mol % loading of catalyst in bromobenzene-d_5 at room temperature; yields were determined by integration against an internal standard by ^{1}H NMR spectroscopy. [b] Order of addition: silane, catalyst, benzophenone, standard. [c] Order of addition: benzophenone, catalyst, silane, standard.

Catalytic Ketone Hydrosilylation by [(PNP)(H)Ir=SiPh$_2$][B(C$_6$F$_5$)$_4$] (1) and [(PNP)(H)Ir=SiMes(H)][B(C$_6$F$_5$)$_4$] (2). The reaction of **2** with benzophenone and benzaldehyde, to afford [(PNP)(H)Ir=SiMes(OC(H)Ph$_2$)][B(C$_6$F$_5$)$_4$] (**5**) and [(PNP)(H)Ir=SiMes(OCH$_2$Ph)][B(C$_6$F$_5$)$_4$] (**6**), motivated further studies of the ability of silylene complexes to catalyze the hydrosilylation of carbonyl compounds. Complex **2** was previously studied as a catalyst for the hydrosilylation of alkenes, and it was of interest to examine the generality of **2** in hydrosilylation catalysis with other substrates. Interestingly, complex **2** is not a viable catalyst for the hydrosilylation of benzaldehyde, as addition of more than stoichiometric amounts of benzaldehyde to **2** resulted in decomposition to multiple iridium-containing products and a color change to yellow-green. Attempts at catalysis using benzaldehyde as a substrate with equimolar amounts of H_3SiMes and a 1 mol % loading of **2** in bromobenzene-d_5 yielded a mixture of silane products, including some insoluble material. The mixture of silanes obtained could not be identified by NMR spectroscopy or GC-MS.

As stoichiometric studies of **2** with benzophenone demonstrated tolerance to excess benzophenone, it was of interest to evaluate the viability of **2** as a catalyst for the hydrosilylation of benzophenone (Table 3). Catalytic trials using benzophenone and $MesSiH_3$ at ambient temperature resulted in a mixture of silane products after 4.5 h at room temperature. GC-MS confirmed that one of the silane products is Mes_2SiH_2, from catalytic redistribution, which was previously documented for this system.[12] When employing H_2SiPh_2 as a substrate, the catalytic production of one major silane product, $HSiPh_2[OC(H)Ph_2]$, was observed in high yield after 5 h at ambient temperature (90%, entry a). Notably, the rate of reaction was observed to be dependent on the order of addition of the silane substrates. When a solution of benzophenone was first added to **2** followed by silane, only 67% of the silane product was produced after 5 h at room temperature, and the remaining H_2SiPh_2 substrate was observed in the ^{1}H NMR spectrum (entry b). In contrast, when a solution of H_2SiPh_2 was first added to **2** followed by benzophenone, complete conversion to product was observed after 5 h at ambient temperature (90% yield, entry a).

The coordination of benzophenone to **1** to form a base-stabilized silylene complex was also insensitive to addition of excess benzophenone. It was envisioned that the strong Lewis acidity of the silylene ligand could activate the carbonyl substrate upon coordination to the silicon center. To this end, complex **1** was studied as a catalyst for the hydrosilylation of ketones. The catalytic trials were conducted at ambient temperature using a 1 mol % loading of **1** in bromobenzene-d_5 with equimolar amounts of diphenylsilane and ketone substrates. The catalytic reaction with benzophenone as a substrate was complete within 4.5 h to afford $Ph_2SiH[OC(H)Ph_2]$ (determined by NMR and GC-MS, 88%, entry c). In contrast, addition of acetophenone gave a mixture of major silane products after 5 h, identified as $Ph_2SiH[OCH(Me)(Ph)]$ and $Ph_2SiH[OC(=CH_2)Ph]$ in 48% and 23% yield, respectively (entry d). Gas evolution was observed upon combining acetophenone with the silane and catalyst, presumably H_2 gas as a byproduct from formation of the $Ph_2SiH[OC(=CH_2)Ph]$ minor product (low concentrations precluded confirmation by ^{1}H NMR spectroscopy). The catalytic hydrosilylation of acetophenone with diphenylsilane to afford moderate yields of $Ph_2SiH[OCH(Me)(Ph)]$ was previously reported employing the silylene complex [Cp*(PMe$_3$)(H)Ir=SiPh$_2$][B(C$_6$F$_5$)$_4$] as a precatalyst.[27] For this ketone hydrosilylation, (PNP)IrH(SiHPh$_2$) (1 mol %, bromobenzene-d_5) is not a catalyst at room temperature or after heating to 60 °C for 15 h. However, formation of $Ph_2SiH[OC(H)Ph_2]$ (23%) and other unidentified minor products was observed after heating at 90 °C for 48 h.

Two possible mechanisms for the hydrosilylation of ketones by **1** are depicted in Scheme 4. In the first step in the mechanism of route A, α-migration from iridium silylene complex **1** generates a transient silyl complex (**A**). Subsequent steps involve the coordination of ketone to an empty coordination site on iridium (**B**), followed by insertion into the Ir−Si bond to generate an iridium alkyl complex (**C**). The release of product could then proceed via activation of silane substrate by Si−H oxidative addition, followed by reductive elimination of the product, to complete the catalytic cycle. Similar mechanisms involving insertion of a ketone into a silyl ligand have been proposed in other transition-metal-catalyzed hydrosilylation reactions and was first proposed by Ojima et al. for rhodium complexes supported by chiral phosphine ligands.[28]

A second possible mechanism, depicted in route B of Scheme 4, proceeds via a silylene complex and alludes to the postulated mechanisms for the stoichiometric hydrosilylation reactions of hydrogen-substituted silylene complex **1** with carbonyl compounds. As secondary silanes are viable substrates for this reaction, a mechanism involving the direct insertion of ketone into the Si−H bond of the silylene ligand is excluded from this discussion (see Scheme 1, path A). The first steps involve coordination of the ketone substrate to the iridium silylene complex to form a base-stabilized silylene ligand (**E**). Similar complexes were isolated from the stoichiometric reaction of **1** with DMF and benzophenone to afford base-stabilized silylene complexes **8** and **9**, respectively. Coordination of the ketone to the Lewis basic silylene ligand could activate the carbonyl substrate to further reactions by rendering the carbonyl carbon more electrophilic. As a next step in this mechanism, the iridium hydride is

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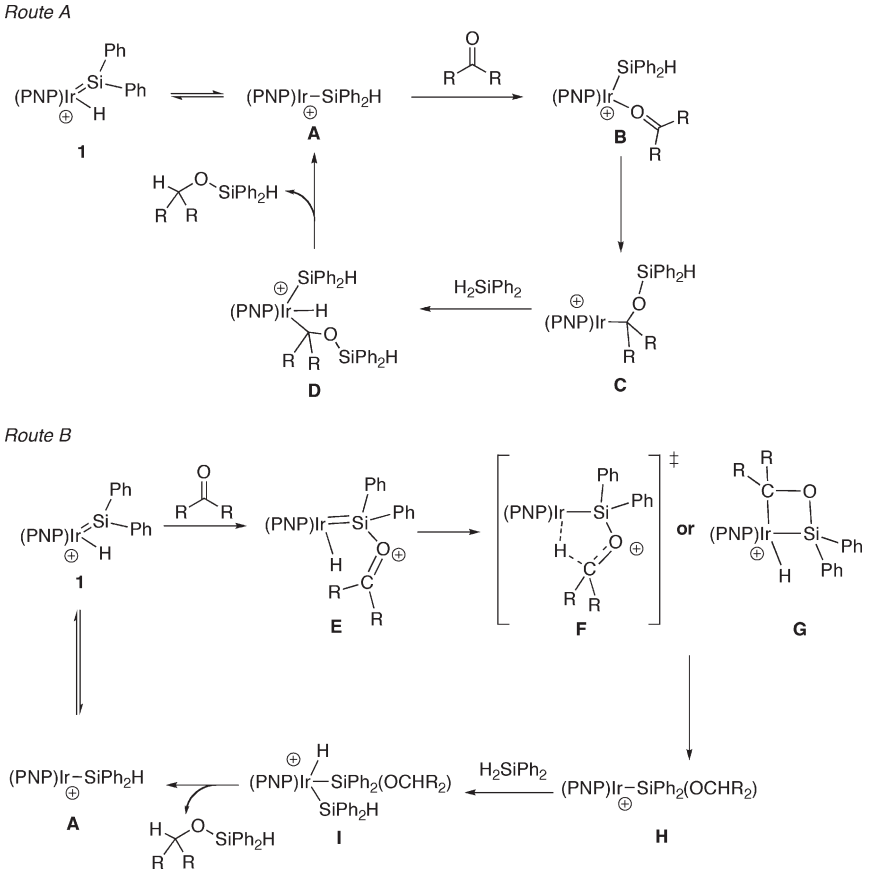
(28) Ojima, I.; Kogure, T.; Kumagai, M.; Horiuchi, S.; Sato, T. *J. Organomet. Chem.* **1976**, *122*, 83–97.

Scheme 4



transferred to the carbonyl group via a transition state containing a five-membered ring (**F**) to afford a silyl intermediate (**H**). Alternatively, a [2+2] cycloaddition of the carbonyl to produce intermediate **G** followed by C−H reductive elimination would afford a silyl intermediate (**H**). Subsequent steps include Si−H oxidative addition of diphenylsilane to form disilyl hydride complex **I**, followed by Si−H reductive elimination to release product. A final α-migration regenerates the silylene catalyst and completes the catalytic cycle. Notably, recent theoretical studies on ketone hydrosilylation catalyzed by oxazolinylcarbene-rhodium complexes implicate a mechanism analogous to route B, which proceeds via the formation of a transient rhodium silylene complex and hydride transfer through a transition state analogous to **F**.[29]

In order to differentiate between the two mechanisms proposed, a deuterium labeling experiment was designed involving $[(PNP)(D)Ir{=}SiPh_2][B(C_6F_5)_4]$. A solution of benzophenone (1 equiv) in bromobenzene-d_5 or fluorobenzene was added to $[(PNP)(D)Ir{=}SiPh_2][B(C_6F_5)_4]$ (1 equiv) at room temperature, and after 2 min the benzophenone was completely consumed to afford $[(PNP)(D)IrSiPh_2(OCPh_2)][B(C_6F_5)_4]$ (**9-d_1**). The resulting solution of **9-d_1** was then added to H_2SiPh_2 (1 equiv). The reaction mixture was monitored by ^{1}H NMR (for the bromobenzene-d_5 solution) and ^{2}H NMR spectroscopy (for the fluorobenzene solution) after 10 to 15 min at ambient temperature. It was envisioned that the product of this reaction would be $Ph_2SiD[OC(H)Ph_2]$ if route A was operative or $Ph_2SiH[OC(D)Ph_2]$ if route B was operative. Interestingly, the ^{2}H NMR spectra revealed resonances for both Si−H and C−H groups of the silyl ether product and the Si−H group of unreacted H_2SiPh_2 substrate. In addition, scrambling of deuterium into the aliphatic and aromatic regions of the ^{2}H NMR spectrum indicates participation of the PNP ligand in this chemistry. Thus, this labeling experiment does not provide insight into the mechanism of the hydrosilylation and suggests the occurrence of additional and/or competitive pathways in this reaction. Additionally, the organometallic species in solution under catalytic conditions were monitored by NMR spectroscopy using a 10 mol % loading of **1** with diphenylsilane and benzophenone substrates in bromobenzene-d_5. After 10 min at ambient temperature, the ^{1}H and ^{31}P{^{1}H} NMR spectra of the reaction mixture revealed the presence of base-stabilized complex **9** as the major species, along with an unidentified species containing a ^{31}P{^{1}H} NMR resonance at 34.4 ppm, and several other iridium-containing minor products. Note that the observed coordination of ketone to the silylene center does not exclude route A, as **E** could be in equilibrium with silyl intermediate **B** (Scheme 4).

Concluding Remarks

With the development of synthetic routes to transition-metal silylene complexes, research efforts are now targeting investigations of the stoichiometric and catalytic reactivity for these species. These studies have established potential modes of reactivity for these species, and it is clear that the

(29) Schneider, N.; Finger, M.; Haferkemper, C.; Bellemin-Laponnaz, S.; Hofmann, P.; Gade, L. H. *Angew. Chem., Int. Ed.* **2009**, *48*, 1609–1613.

steric and electronic properties of the metal-based fragment can play a large role in the observed chemistry of the silylene ligand. In this contribution, the stoichiometric reactivity of [(PNP)(H)Ir=$SiPh_2$][$B(C_6F_5)_4$] (**1**) and [(PNP)(H)Ir=SiMes(H)][$B(C_6F_5)_4$] (**2**) toward Lewis bases, alcohols, amines, and carbonyl compounds was described. The reaction of silylene complexes with Lewis bases has significant precedence, but there is still much to be learned concerning the activation of polar substrates by interactions with the Lewis acidic silicon center of a silylene ligand.

Examination of the catalytic properties of silylene complex **1** with alcohols, amines, and carbonyl compounds demonstrates potential applications for new transformations of organosilicon species. In related studies, hydrogen-substituted complex **2** has been shown to be effective for alkene hydrosilylations.[12b] As described here, complex **1** serves as a catalyst for the alcoholysis or aminolysis of silanes and for the hydrosilylation of ketones. Complexes **1** and **2** contain a Lewis acid functionality (the silylene ligand) and a Lewis base functionality (the amido nitrogen). Participation of the amido group of the PNP ligand appears to allow access to transformations that would otherwise require high oxidation states and coordination numbers at the iridium center. In addition, the amido group may serve as a Brønsted base to activate protic substrates and promote further reactivity at the silylene center, as proposed for reaction of alcohols and amines with **1**. In summary, a major theme evolving from these studies is the cooperative participation of silylene and amido ligands in the activation of substrates in stoichiometric and catalytic transformations. This theme can help motivate the design of related transition-metal catalysts that take advantage of the cooperation of Lewis acidic and Brønsted basic ligand centers within the coordination sphere of the metal.[30]

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 $MgSO_4$ and stored over activated 4 Å molecular sieves. Pentane and hexanes were dried by distilling from Na. Fluorobenzene was dried by vacuum distillation from CaH_2. C_6D_5Br was refluxed over CaH_2 for 20 h and then distilled under nitrogen. [(PNP)(H)Ir=SiMes(H)][$B(C_6F_5)_4$] (**2**)[12a] and [(PNP)-(H)Ir=$SiPh_2$][$B(C_6F_5)_4$] (**1**)[12b] were prepared according to literature methods. [(PNP)(D)Ir=$SiPh_2$][$B(C_6F_5)_4$] was prepared by addition of [CPh_3][$B(C_6F_5)_4$] to (PNP)IrD($SiPh_2$D) following analogous procedures detailed for **1**. (PNP)IrD($SiPh_2$D) was in turn synthesized from the reaction of D_2SiPh_2 with (PNP)Ir-(COE).[12b] DMAP, 3,5-di-*tert*-butylphenol, and benzophenone were purified by sublimation. Other alcohol, amine, and carbonyl reagents were degassed and dried over molecular sieves.

NMR spectra were recorded using Bruker DRX-500, AV-500, AVB-400, AVQ-400, and AV-600 spectrometers. ^1H NMR spectra were referenced internally to the residual solvent proton signal relative to tetramethylsilane. $^{13}C\{^1H\}$ NMR spectra were referenced internally relative to the ^{13}C signal of the NMR solvent relative to tetramethylsilane. $^{31}P\{^1H\}$ spectra were referenced relative to an 85% H_3PO_4 external standard. ^{29}Si NMR spectra were referenced relative to a tetramethylsilane external standard and obtained via 2D ^1H ^{29}Si HMBC unless specified otherwise. All spectra were recorded at room temperature unless otherwise noted. Complex multiplets are noted as "m" and broad resonances as "br". In $^{13}C\{^1H\}$ NMR spectra resonances obscured by the solvent signal are omitted. Elemental analyses were performed by the College of Chemistry Microanalytical Laboratory at the University of California, Berkeley.

[(PNP)(H)IrSiPh$_2$(DMAP)][B(C$_6$F$_5$)$_4$] (3). In the drybox, a solution of 4-dimethylaminopyridine (DMAP) (0.006 g, 0.047 mmol) in 0.5 mL of C_6H_5F was added to a solution of **1** (0.070 g, 0.047 mmol) in 0.5 mL of C_6H_5F. Upon addition of the DMAP, a color change from purple to red-violet was observed. After 2 min of mixing by taking the fluorobenzene solution into a pipet and redispensing it into the reaction vessel, the solution was added to pentane (15 mL) and placed in the −30 °C freezer for 1 h to allow a dark red-violet oil to settle out of the reaction mixture. A red-violet oil was collected by decanting the supernatant and dried under vacuum to give a burgundy solid. Yield: 0.062 mg (82%). ^1H NMR (C_6D_5Br, 500 MHz): δ 8.26 (2H, br, Ar*H*), 7.60 (4H, d, J = 6.6 Hz, Ar*H*), 7.56 (2H, d, J = 8.5 Hz, Ar*H*), 7.25 (6H, ov m, Ar*H*), 7.03 (2H, s, Ar*H*), 6.98 (2H, d, J = 8.5 Hz, Ar*H*), 6.04 (2H, d, J = 7.2 Hz), 2.35 (6H, s, NMe_2), 2.23 (6H, s, Ar*Me*), 2.19 (2 h, br m, C*H*Me_2), 1.21 (2H, br m, C*H*Me_2), 0.93 (18H, ov m, CHMe_2), 0.60 (6H, m, CHMe_2), −20.32 (1H, t, $^2J_{PH}$ = 8.4 Hz, $^2J_{SiH}$ = 3 Hz, Ir*H*). $^{13}C\{^1H\}$ NMR (C_6D_5Br, 125.8 MHz): δ 162.1 (t, J_{CP} = 9.7 Hz), 156.3 (s), 150.1 (br m), 148.0 (br m), 140.0 (br m), 137.9 (br m), 136.0 (br m) 135.7 (s), 132.8 (s), 132.7 (s), 129.3 (br m), 128.2 (s), 123.4 (t, J_{CP} = 22.5), 116.3 (br m), 106.3 (s) (Ar*C*), 39.2 (s, NMe_2), 27.9 (t, J_{CP} = 17.0 Hz), 22.5 (t, J_{CP} = 13.7 Hz), 20.9 (s, Ar*Me*), 20.7 (s, CHMe_2), 19.5 (s, CHMe_2), 18.8 (s, CHMe_2), 17.1 (s, CHMe_2). $^{31}P\{^1H\}$ NMR (C_6D_5Br, 202.5 MHz): δ 45.3 (s). ^{29}Si NMR (C_6D_5Br, 99.4 MHz): δ 8.7. Anal. Calcd for $C_{69}H_{61}N_3BF_{20}IrP_2Si$: C, 51.63; H, 3.83; N, 2.62. Found: C, 51.70; H, 3.82; N, 2.88.

[(PNP)(H)IrSiMes(H)(DMAP)][B(C$_6$F$_5$)$_4$] (4). In the drybox, a solution of 4-dimethylaminopyridine (DMAP) (0.008 g, 0.069 mmol) in 0.5 mL of C_6H_5F was added to a solution of **2** (0.100 g, 0.069 mmol) in 0.5 mL of C_6H_5F. Upon addition of the DMAP, a color change from blue-green to a violet-red color was observed. After 2 min of mixing by taking the fluorobenzene solution into a pipet and redispensing it into the reaction vessel, the solution was added to pentane (15 mL) and placed in the −30 °C freezer for 1 h to allow a violet-red oil to settle out of the reaction mixture. A violet-red oil was collected by decanting the supernatant and dried under vacuum to give a burgundy solid. Yield = 0.099 g (91%). ^1H NMR (C_6D_5Br, 500 MHz): δ 8.02 (2H, br s, DMAP), 7.53 (1H, d, J = 7.0 Hz, Ar*H*), 7.48 (1H, d, J = 7.1 Hz, Ar*H*), 7.01 (1H, d, J = 8.4 Hz, Ar*H*), 6.96 (3H, m, Ar*H*), 6.78 (2H, s, Ar*H*), 6.58 (1H, br s, $^1J_{SiH}$ = 203 Hz, Si*H*), 6.01 (2H, d, J = 6.4 Hz, DMAP), 2.38 (6H, s, NMe_2), 2.28 (6H, s, Ar*Me*), 2.24 (3H, s, Ar*Me*), 2.20 (6H, s, Ar*Me*), 2.38−2.20 (3H, under methyl resonances, C*H*Me_2), 2.10 (1H, br, C*H*Me_2), 1.14 (3H, br m, CHMe_2), 1.10−0.90 (9H, ov br m, CHMe_2), 0.85−0.81 (6H, ov br m, CHMe_2), 0.73−0.68 (6H, ov br m, CHMe_2), −21.18 (1H, br s, Ir*H*). $^{13}C\{^1H\}$ NMR (C_6D_5Br, 125.8 MHz): δ 161.8 (br m), 156.1 (s), 150.0 (br m), 148.1 (br m), 145.3 (br m), 143.8 (br m), 140.8 (s), 139.9 (br m), 137.9 (br m), 136.0 (br m), 133.3 (d, J_{CP} = 37.6 Hz), 132.4 (s), 132.0 (s), 128.2 (br m), 118.4 (br m), 113.7 (br m), 107.3 (s) (Ar*C*), 39.2 (s, NMe_2), 29.7 (br d, J_{CP} = 28.3 Hz, *C*HMe_2), 25.5 (br d, J_{CP} = 29.8 Hz, *C*HMe_2), 24.5 (br d, J_{CP} = 33.2 Hz, *C*HMe_2), 23.3 (br m, *C*HMe_2), 21.4 (s, Ar*Me*), 12.4 (br s, under methyl resonance, CHMe_2), 20.9 (s, Ar*Me*), 20.8 (s, Ar*Me*), 19.2 (br s, CHMe_2), 19.0 (s, CHMe_2), 18.0 (br s, CHMe_2), 17.1 (br s, CHMe_2), 17.0 (br s, CHMe_2), 16.9 (br s, CHMe_2). $^{31}P\{^1H\}$ NMR (C_6D_5Br, 202.5 MHz): δ 50.8, 49.5, 46.2, 44.8 (AB spin system, two d, $^2J_{PP}$ = 272 Hz). ^{29}Si NMR (C_6D_5Br, 99.4 MHz): δ −12.1. Anal. Calcd for $C_{66}H_{63}N_3BF_{20}IrP_2Si$: C, 50.45; H, 4.04; N, 2.67. Found: C, 50.76; H, 3.79; N, 2.84.

(30) For a review of amphoteric ligands containing both Lewis basic and Lewis acidic sites see: Fontaine, F.-G.; Boudreau, J.; Thibault, M.-H. *Eur. J. Inorg. Chem.* **2008**, 5439−5454, and references therein.

[(PNP)(H)Ir=SiMes(OCHPh$_2$)][B(C$_6$F$_5$)$_4$] (5). In the drybox, a solution of benzophenone (0.009 g, 0.052 mmol) in 0.5 mL of C_6H_5F was added to a solution of **2** (0.075 g, 0.052 mmol) in 0.5 mL of C_6H_5F. Upon addition of benzophenone at ambient temperature, a color change to bright purple was observed. After 2 min of mixing by taking the fluorobenzene solution into a pipet and redispensing it into the reaction vessel, the solution was added to pentane (10 mL) and placed in the −30 °C freezer for 1 h to allow a violet oil to separate. The pentane/fluorobenzene is decanted away, and the remaining oil was dried under vacuum for 1 h to afford **5** as a purple solid. Yield = 0.081 g (94%). ^{1}H NMR (C_6D_5Br, 500 MHz): δ 7.42 (2H, d, J = 8.5 Hz, Ar*H*), 7.22 (6H, ov m, Ar*H*), 7.17 (2H, t, J = 7.7 Hz, Ar*H*), 7.11 (4H, d, J = 6.8 Hz, Ar*H*), 7.02 (2H, s, Ar*H*), 6.91 (2H, J = 8.4 Hz, Ar*H*), 6.67 (2H, s, Ar*H*), 5.79 (1H, s, C*H*Ph$_2$), 2.29 (2H, m, C*H*Me$_2$), 2.24 (6H, s, Ar*Me*), 2.15 (3H, s, Ar*Me*), 2.14 (6H, brs, Ar*Me*), *2*.05 (2H, m, C*H*Me$_2$), 1.19 (6H, m, CH*Me*$_2$), 0.91 (6H, m, CH*Me*$_2$), 0.74 (6H, m, CH*Me*$_2$), 0.54 (6H, m, CH*Me*$_2$), −20.24 (1H, t, $^2J_{PH}$ = 7.8 Hz, Ir*H*). ^{13}C{^{1}H} NMR (C_6D_5Br, 125.8 MHz): δ 162.5 (t, J_{CP} = 10.1 Hz), 150.0 (br m), 148.1 (br m), 144.5 (s), 140.2 (s), 139.9 (br m), 137.9 (br m), 136.1 (br m), 133.4 (s), 133.3 (s), 132.8 (s), 131.1 (s), 129.4 (s), 129.4 (s), 128.3 (t, J_{CP} = 30.4 Hz), 127.2 (s), 121.1 (t, J_{CP} = 23.6 Hz), 117.2 (br s) (Ar*C*), 84.8 (s, *C*HPh$_2$), 27.1 (t, J_{CP} = 16.3 Hz, *C*HMe$_2$), 24.9 (t, J_{CP} = 15.5 Hz, *C*HMe$_2$), 24.0 (br, Ar*Me*), 21.7 (s, Ar*Me*), 21.0 (s, C*H*Me), 20.8 (s, Ar*Me*), 18.5 (s, CH*Me*$_2$), 18.2 (s, CH*Me*$_2$), 16.8 (s, CH*Me*$_2$). ^{31}P{^{1}H} NMR (C_6D_5Br, 162.0 MHz): δ 52.9 (s). ^{29}Si NMR (C_6D_5Br, 99.4 MHz): δ 161.8. Anal. Calcd for $C_{73}H_{67}NBF_{20}IrOP_2Si$: C, 53.22; H, 4.10; N, 0.85. Found: C, 53.31; H, 4.36; N, 0.89.

[(PNP)(H)Ir=SiMes(OCH$_2$Ph)][B(C$_6$F$_5$)$_4$] (6). In the drybox, a solution of benzaldehyde (0.006 g, 0.054 mmol) in 0.5 mL of C_6H_5F was added to a solution of **2** (0.080 g, 0.054 mmol) in 0.5 mL of C_6H_5F. Upon addition of benzophenone, a color change to bright purple was observed. After 2 min of mixing by taking the fluorobenzene solution into a pipet and redispensing it into the reaction vessel, the solution was added to hexanes (10 mL) and placed in the −30 °C freezer for 1 h to allow a violet oil to settle out of the reaction mixture. The hexanes/fluorobenzene was decanted away, and the remaining oil was dried under vacuum for 1 h to afford **6** as a purple foam. Yield = 0.075 g (89%). ^{1}H NMR (C_6D_5Br, 500 MHz): δ 7.40 (2H, br d, J = 8.6 Hz, Ar*H*), 7.23 (2H, m, Ar*H*), 7.18 (1H, m, Ar*H*), 7.03 (2H, br s, Ar*H*), 6.95 (2H, m, Ar*H*), 6.91 (2H, br d, J = 8.1 Hz, Ar*H*), 6.72 (2H, s, Ar*H*), 4.48 (2H, s, OC*H*$_2$), 2.32 (2H, ov m, C*H*Me$_2$), 2.27 (6H, br s, Ar*Me*), 2.24 (6H, s, Ar*Me*), 2.18 (3H, s, Ar*Me*), 2.11 (2H, m, C*H*Me$_2$), 1.11 (6H, m, CH*Me*$_2$), 0.95 (6H, m, CH*Me*$_2$), 0.75 (6H, m, CH*Me*$_2$), 0.63 (6H, m, CH*Me*$_2$), −20.42 (1H, t, $^2J_{PH}$ = 7.9 Hz, $^2J_{SiH}$ = 3 Hz, Ir*H*). ^{13}C{^{1}H} NMR (C_6D_5Br, 125.8 MHz): δ 162.4 (t, J_{CP} = 10.2 Hz), 150.1 (br m), 148.2 (br m), 144.4 (s), 139.9 (br m), 137.9 (br m), 136.3 (s), 136.1 (br m), 133.4 (s), 132.8 (s), 129.4 (s), 129.2 (s), 128.9 (s), 127.5 (s), 121.0 (t, J_{CP} = 22.9 Hz), 117.1 (br m) (Ar*C*), 72.2 (s, O*C*H$_2$), 26.9 (t, J_{CP} = 17.9 Hz, *C*HMe$_2$), 24.9 (t, J_{CP} = 14.6 Hz, *C*HMe$_2$), 23.7 (br, Ar*Me*), 21.7 (s, Ar*Me*), 20.8 (s, Ar*Me*), 20.6 (s, CH*Me*$_2$), 18.6 (s, CH*Me*$_2$), 18.2 (s, CH*Me*$_2$), 17.0 (s, CH*Me*$_2$). ^{31}P{^{1}H} NMR (C_6D_5Br, 202.5 MHz): δ 53.6 (s). ^{29}Si NMR (C_6D_5Br, 99.4 MHz): δ 159.3. Anal. Calcd for $C_{66}H_{59}NBF_{20}IrOP_2Si$: C, 50.97; H, 3.82; N, 0.90. Found: C, 51.34; H, 4.11; N, 0.87.

[(PNP)(H)IrSiMes(H)(DMF)][B(C$_6$F$_5$)$_4$] (7). A Schlenk flask was loaded with **2** (0.10 g, 0.07 mmol) and 3 mL of fluorobenzene. Using a 10 μL syringe, dimethylformamide (5.3 μL, 0.07 mmol) was added to the solution. Upon the addition, a color change to deep violet-red was observed. After 5 min, all volatile materials were removed under vacuum. The remaining foam was redissolved in 1 mL of fluorobenzene. The resulting solution was added to pentane (15 mL) and placed in the −30 °C freezer for 1 h to allow a red-violet oil to settle out of the reaction mixture. A dark red-violet oil was collected by decanting the supernatant, and this was dried under vacuum to give a burgundy solid. Yield = 0.10 g (93%). ^{1}H NMR (C_6D_5Br, 500 MHz): δ 7.87 (1H, s, *H*C=O), 7.46 (2H, m, Ar*H*), 7.05−6.99 (2H, m, Ar*H*), 6.93 (2H, br d, J = 8.4 Hz, Ar*H*), 6.73 (2H, s, Ar*H*), 6.19 (1H, t, J_{PH} = 5.6 Hz, $^1J_{SiH}$ = 207.5 Hz, Si*H*), 2.69 (3H, s, N*Me*), 2.38 (9H, br s, N*Me* + Ar*Me*), 2.27 (3H, s, Ar*Me*), 2.25 (3H, s, Ar*Me*), 2.08 (3H, s, Ar*Me*), 2.3−2.1 (4H, under methyl resonances, C*H*Me$_2$), 1.15 (6H, ov dd, CH*Me*$_2$), 1.05 (3H, dd, J_{HH} = 6.8 Hz, J_{PH} = 16.6 Hz, CH*Me*), 0.98−0.85 (9H, ov dd, CH*Me*$_2$), 0.77 (3H, dd, J_{HH} = 6.7 Hz, J_{PH} = 16.5 Hz, CH*Me*$_2$), 0.70 (3H, dd, J_{HH} = 6.7 Hz, J_{PH} = 15.9 Hz, CH*Me*$_2$), −20.85 (1H, t, $^2J_{PH}$ = 8.5 Hz, Ir*H*). ^{13}C{^{1}H} NMR (C_6D_5Br, 125.8 MHz): δ 165.2 (s, H*C*=O), 162.3 (m), 150.0 (br m), 148.1 (br m), 143.0 (s), 141.1 (s), 139.8 (br m), 138.0 (br m), 136.0 (br m), 133.2 (d, J_{CP} = 32.5 Hz), 132.4 (d, J_{CP} = 17.0 Hz), 128.7 (d, J_{CP} = 6.1 Hz), 123.5 (d, J_{CP} = 43.0 Hz), 122.0 (d, J_{CP} = 43.9 Hz), 118.1 (d, J_{CP} = 10.2 Hz), 114.4 (d, J_{CP} = 10.7 Hz) (Ar*C*), 40.2 (s, N*Me*), 35.5 (s, N*Me*), 29.0 (d, J_{CP} = 27.1 Hz, *C*HMe$_2$), 25.6 (d, J_{CP} = 23.9 Hz, *C*HMe$_2$), 24.7 (d, J_{CP} = 32.1 Hz, *C*HMe$_2$), 23.4 (br s, Ar*Me*), 22.0 (d, J_{CP} = 23.5 Hz, *C*HMe$_2$), 21.4 (s, Ar*Me*), 21.3 (d, CH*Me*$_2$), 20.8 (s, Ar*Me*), 19.1 (s, CH*Me*$_2$), 18.9 (s, CH*Me*$_2$), 18.8 (d, CH*Me*$_2$), 18.7 (d, CH*Me*$_2$), 17.8 (br s, CH*Me*$_2$), 17.1 (br s, CH*Me*$_2$), 16.7 (d, CH*Me*$_2$). ^{31}P{^{1}H} NMR (C_6D_5Br, 202.5 MHz): δ 50.5, 49.1, 47.6, 48.3 (AB spin system, two d, J_{PP} = 267 Hz). ^{29}Si NMR (C_6D_5Br, 99.4 MHz): δ 13.8. Anal. Calcd for $C_{62}H_{60}NBF_{20}IrOP_2Si$: C, 48.92; H, 3.97; N, 1.84. Found: C, 48.75; H, 3.95; N, 1.99.

[(PNP)(H)IrSiPh$_2$(DMF)][B(C$_6$F$_5$)$_4$] (8). A Schlenk flask was loaded with **1** (0.07 g, 0.05 mmol) and 3 mL of fluorobenzene. Using a 10 μL syringe, dimethylformamide (3.7 μL, 0.05 mmol) was added to the solution. Upon addition, a color change to red-violet was observed. After 5 min, all volatile materials were removed under vacuum. The remaining foam was redissolved in 1 mL of fluorobenzene. The solution was added to pentane (10 mL) and placed in the −30 °C freezer for 1 h to allow a red-violet oil to settle out of the reaction mixture. The red-violet oil was collected by decantation, and this oil was dried under vacuum to give a burgundy solid. Yield: 0.06 g (86%). ^{1}H NMR (C_6D_5Br, 500 MHz): δ 8.16 (1H, br s, *H*C=O), 7.57 (4H, m, Ar*H*), 7.51 (2H, d, J = 8.4 Hz, Ar*H*), 7.22 (6H, ov m, Ar*H*), 7.00 (2H, br s, Ar*H*), 6.95 (2H, 8.9 Hz, Ar*H*), 2.76 (3H, s, N*Me*), 2.44 (3H, s, N*Me*), 2.24 (2H, m, C*H*Me$_2$), 2.23 (6H, s, Ar*Me*), 1.46 (2H, m, C*H*Me$_2$), 1.13 (6H, m, CH*Me*$_2$), 0.92 (12H, ov m, CH*Me*$_2$), 0.52 (6H, m, CH*Me*$_2$), −19.02 (1H, br t, Ir*H*). ^{13}C{^{1}H} NMR (C_6D_5Br, 125.8 MHz): δ 164.9 (s, *C*=O), 161.9 (t, J_{CP} = 10.0 Hz), 150.0 (br m), 148.1 (br m), 140.0 (br m), 139.2 (br s), 138.8 (br m), 136.1 (br m), 134.9 (s), 133.0 (s), 132.8 (s), 130.8 (s), 129.5 (s), 116.2 (br m) (Ar*C*), 49.4 (s, N*Me*), 35.8 (s, N*Me*), 27.9 (br m, *C*HMe$_2$), 23.3 (br m, *C*HMe$_2$), 21.1 (s, CH*Me*$_2$), 20.8 (s, Ar*Me*), 19.3 (s, CH*Me*$_2$), 18.0 (s, CH*Me*$_2$), 17.2 (s, CH*Me*$_2$). ^{31}P{^{1}H} NMR (C_6D_5Br, 202.5 MHz): δ 47.6 (s). ^{29}Si NMR (C_6D_5Br, 99.4 MHz): δ 29.0. Anal. Calcd for $C_{65}H_{58}N_2BF_{20}IrOP_2Si$: C, 50.17; H, 3.76; N, 1.80. Found: C, 50.25; H, 3.73; N, 1.75.

[(PNP)(H)IrSiPh$_2$(OCPh$_2$)][B(C$_6$F$_5$)$_4$] (9). In the drybox, a solution of benzophenone (0.012 g, 0.067 mmol) in 0.5 mL of C_6H_5F was added to a solution of **1** (0.10 g, 0.067 mmol) in 0.5 mL of C_6H_5F. Upon addition of benzophenone, a color change to red-violet was observed. After 2 min of mixing by taking the fluorobenzene solution into a pipet and redispensing it into the reaction vessel, the solution was added to pentane (10 mL), and this mixture was placed in the −30 °C freezer for 1 h to allow a red-violet oil to settle out of the reaction mixture. A red-violet oil was collected by decanting the supernatant, and the oil was dried under vacuum to give a burgundy solid. Yield = 0.11 g (94%). ^{1}H NMR (C_6D_5Br, 500 MHz): δ 7.64 (4H, d, J = 7.1 Hz, Ar*H*), 7.58 (2H, d, J = 7.9 Hz, Ar*H*), 7.45 (6H, ov m, Ar*H*), 7.15−7.07 (10H, ov m, Ar*H*), 7.01 (4H, ov m, Ar*H*), 2.24 (6H, s, Ar*Me*), 2.24 (2H, br m, C*H*Me$_2$), 1.66 (2H, br m, C*H*Me$_2$), 1.13 (6H, m, CH*Me*$_2$), 0.98 (6H, m, CH*Me*$_2$), 0.81 (6H, m, CH*Me*$_2$), 0.60 (6H, m, CH*Me*$_2$), −19.95 (1H, t, $^2J_{PH}$ = 8.6 Hz, Ir*H*). ^{13}C{^{1}H} NMR (C_6D_5Br, 125.8 MHz): δ 208.19

(s, C=O), 162.2 (t, J_{CP} = 10.2 Hz), 150.0 (br m), 148.2 (br m), 139.8 (br m), 138.5 (br m), 137.9 (br m), 136.9 (s), 136.0 (br m), 134.5 (s), 133.8 (s), 133.0 (s), 132.6 (s), 129.4 (s), 128.2 (s), 116.2 (br m) (Ar*C*), 27.8 (br m, *C*HMe$_2$), 23.8 (br m, *C*HMe$_2$), 20.9 (s, Ar*Me*), 20.8 (s, CH*Me*$_2$), 19.4 (s, CH*Me*$_2$), 18.17 (s, CH*Me*$_2$), 17.2 (s, CH*Me*$_2$). ^{31}P{^{1}H} NMR (C_6D_5Br, 202.5 MHz): δ 49.5 (s). ^{29}Si NMR (C_6D_5Br, 99.4 MHz): δ 46.8 (s). Anal. Calcd for $C_{75}H_{60}NBF_{20}IrOP_2Si$: C, 54.13; H, 3.63; N, 0.84. Found: C, 53.75; H, 3.53; N, 0.83.

{(PNPH)IrH[SiPh$_2$(OC(=CH$_2$)Ph)]}[B(C$_6$F$_5$)$_4$] (10). A solution of acetophenone (0.006 g, 0.05 mmol) in 0.5 mL of fluorobenzene was added to a solution of **1** (0.080 g, 0.05 mmol) in 1 mL of C_6H_5F. An immediate color change to yellow-brown was observed. After 2 min, the reaction mixture was added to hexanes (15 mL), and the resulting mixture was placed in the −20 °C freezer for 1 h. A brown oil was collected by decantation, and the oil was dried under vacuum to give a light yellow solid. Yield: 0.077 g (89%). ^{1}H NMR (C_6D_5Br, 500 MHz): δ 7.93 (1H, br s, N*H*), 7.67 (4H, d, J = 6.9 Hz, Ar*H*), 7.46 (2H, d, J = 3.6 Hz, Ar*H*), 7.21−7.16 (13H, ov m, Ar*H*), 7.04 (2H, br m, Ar*H*), 4.56 (2H, br s, OC=C*H*$_2$), 2.31 (2H, br m, C*H*Me$_2$), 2.24 (6H, s, Ar*Me*), 2.04 (2H, br m, C*H*Me$_2$), 0.97 (6H, m, CH*Me*$_2$), 0.85 (6H, m, CH*Me*$_2$), 0.69 (6H, m, CH*Me*$_2$), 0.58 (6H, m, CH*Me*$_2$), −17.69 (t, $^2J_{PH}$ = 10.1 Hz, Ir*H*). ^{13}C{^{1}H} NMR (C_6D_5Br, 150.9 MHz): δ 156.9 (s), 149.9 (br m), 148.3 (br m), 145.3 (t, J_{CP} = 5.9 Hz), 140.9 (s), 139.6 (br t, J_{CP} = 12.5 Hz), 138.3 (s), 138.0 (s, SiO*C*), 137.9 (br m), 136.2 (br m), 136.1 (s), 134.4 (s), 134.3 (s), 130.4 (s), 129.1 (s), 128.8 (s), 128.7 (s) 128.2 (s) (Ar*C*), 94.6 (br s, =*C*H$_2$), 26.3 (t, J_{CP} = 14.2 Hz, *C*HMe$_2$), 25.4 (t, J_{CP} = 15.3 Hz, *C*HMe$_2$), 21.1 (s, Ar*Me*), 21.0 (s, CH*Me*$_2$), 19.1 (s, CH*Me*$_2$), 18.1 (s, CH*Me*$_2$), 16.9 (s, CH*Me*$_2$). ^{31}P{^{1}H} NMR (C_6D_5Br, 202.5 MHz): δ 47.2 (s). ^{29}Si NMR (C_6D_5Br, 99.4 MHz): δ −5.7. Anal. Calcd for $C_{70}H_{59}NBF_{20}IrOP_2Si$: C, 52.44; H, 3.71; N, 0.87. Found: C, 52.77; H, 3.95; N, 1.26.

[(PNPH)IrH(SiPh$_2$OAr^{tBu})][B(C$_6$F$_5$)$_4$] (Ar^{tBu} = 3,5-^{t}Bu$_2$C$_6$H$_3$) (11). A solution of 3,5-di-*tert*-butylphenol (0.011 g, 0.05 mmol) in 0.5 mL of fluorobenzene was added to a solution of **1** (0.080 g, 0.05 mmol) in 1 mL of C_6H_5F. Upon addition of the alcohol, a color change to bright blue was observed initially, followed by a gradual color change to light yellow-green within 2 min. After 10 min, the reaction mixture was added to hexanes (10 mL), and the resulting mixture was placed in the −20 °C freezer for 1 h. A yellow-green oil was collected by decantation, and then the oil was dried under vacuum to give a light green solid. Yield: 0.079 g (94%). ^{1}H NMR (C_6D_5Br, 500 MHz): δ 7.83 (1H, s, N*H*), 7.53 (4H, d, J = 7.2 Hz, Ar*H*), 7.18 (6H, ov m, Ar*H*), 7.11−7.05 (7H, ov m, Ar*H*), 6.64 (2H, d, J = 0.8 Hz, Ar*H*), 2.36 (4H, m, C*H*Me$_2$), 2.27 (6H, s, Ar*Me*), 1.14 (18 H, s, C*Me*$_3$), 1.03 (6H, m, CH*Me*$_2$), 0.87 (6H, m, CH*Me*$_2$), 0.76 (6H, m, CH*Me*$_2$), 0.51 (6H, m, CH*Me*$_2$), −17.36 (1H, t, $^2J_{PH}$ = 10.5 Hz, Ir*H*). ^{13}C{^{1}H} NMR (C_6D_5Br, 150.9 MHz): δ 155.9 (s), 152.3 (s), 149.9 (br m), 148.3 (br m), 145.6 (t, J_{CP} = 7.3 Hz), 140.8 (s), 139.7 (br m), 138.9 (s), 137.9 (br m), 136.2 (br m), 135.5 (s), 134.6 (s), 134.3 (s), 130.5 (s), 128.3 (s), 125.9 (br), 115.8 (s), 115.1 (s) (Ar*C*), 35.1 (s, *C*Me$_3$) 31.8 (s, C*Me*$_3$), 26.5 (br t, J_{CP} = 16.0 Hz, *C*HMe$_2$), 25.5 (br t, J_{CP} = 13.6 Hz, *C*HMe$_2$), 21.1 (s, Ar*Me*), 20.7 (s, *C*HMe$_2$), 19.7 (br s, *C*HMe$_2$), 17.6 (s, *C*HMe$_2$), 17.2 (s, *C*HMe$_2$). ^{31}P{^{1}H} NMR (C_6D_5Br, 202.5 MHz): δ 48.5 (s). ^{29}Si NMR (C_6D_5Br, 99.4 MHz): δ −3.6. Anal. Calcd for $C_{76}H_{73}NBF_{20}IrOP_2Si$: C, 54.03; H, 4.36; N, 0.83. Found: C, 54.40; H, 4.35; N, 0.98.

[(PNPH)IrH(SiPh$_2$OPh)][B(C$_6$F$_5$)$_4$] (12). A solution of phenol (0.006 g, 0.064 mmol) in 0.5 mL of fluorobenzene was added to a solution of **1** (0.080 g, 0.053 mmol) in 1 mL of C_6H_5F. Within 2 min after alcohol addition, a color change to light yellow-green was observed. After 10 min, the reaction mixture was dried under vacuum. The resulting oil was redissolved in fluorobenzene, this solution was added to hexanes (10 mL), and the resulting mixture was placed in the −20 °C freezer for 1 h. A yellow oil was collected by decantation, and then the oil was dried under vacuum to give a light yellow solid. Yield: 0.067 g (81%). ^{1}H NMR (C_6D_5Br, 500 MHz): δ 7.82 (1H, br s, N*H*), 7.53 (4H, d, J = 7.0 Hz, Ar*H*), 7.18−7.02 (14H, ov m, Ar*H*), 6.9 (1H, t, J = 8.5 Hz, Ar*H*), 6.78 (2H, d, J = 7.6 Hz, Ar*H*), 2.32 (4H, br m, C*H*Me$_2$), 2.26 (6H, s, Ar*Me*), 1.02 (6H, m, CH*Me*$_2$), 0.86 (6H, m, CH*Me*$_2$), 0.73 (6H, m, CH*Me*$_2$), 0.47 (6H, m, CH*Me*$_2$), −17.45 (1H, $^2J_{PH}$ = 10.2 Hz, Ir*H*). ^{13}C{^{1}H} NMR (C_6D_5Br, 125.8 MHz): δ 156.1 (s), 150.1 (br m), 148.1 (br m), 145.5 (t, J_{CP} = 6.7 Hz), 140.9 (s), 139.9 (br m), 138.6 (s), 137.9 (br m), 136.0 (br m), 135.4 (s), 134.5 (s), 134.4 (s), 130.6 (s), 128.3 (s), 125.9 (br m), 122.3 (s), 120.6 (s) (Ar*C*), 26.4 (t, J_{CP} = 16.5 Hz, *C*HMe$_2$), 25.5 (t, J_{CP} = 15.8 Hz, *C*HMe$_2$), 21.1 (s, Ar*Me*), 20.8 (s, CH*Me*$_2$), 19.6 (s, CH*Me*$_2$), 17.7 (s, CH*Me*$_2$), 17.2 (s, CH*Me*$_2$). ^{31}P{^{1}H} NMR (C_6D_5Br, 202.5 MHz): δ 48.0 (s). ^{29}Si NMR (C_6D_5Br, 99.4 MHz): δ −3.3. Anal. Calcd for $C_{68}H_{57}NBF_{20}IrOP_2Si$: C, 51.78; H, 3.64; N, 0.89. Found: C, 52.09; H, 3.30; N, 1.03.

[(PNPH)IrH(SiPh$_2$O^{i}Pr)][B(C$_6$F$_5$)$_4$] (13). An excess of 2-propanol (approximately 0.2 mL) was added via cannula to a solution of **1** (0.080 g, 0.05 mmol) in 1.5 mL of C_6H_5F. Upon addition of the alcohol, a color change to light yellow-green was observed. After 10 min, the reaction mixture was dried under vacuum. The resulting oil was redissolved in fluorobenzene (1 mL), and this solution was added to hexanes (10 mL). The resulting mixture was placed in the −20 °C freezer for 1 h. A yellow oil was collected by decantation, and then the oil was dried under vacuum to give a light yellow solid. Yield: 0.067 g (81%). ^{1}H NMR (C_6D_5Br, 500 MHz): δ 7.56 (1H, br s, N*H*), 7.48 (4H, d, J = 6.9 Hz, Ar*H*), 7.24 (2H, m, Ar*H*), 7.18−7.14 (8H, ov m, Ar*H*), 6.99 (2H, d, J = 8.3 Hz, Ar*H*), 3.85 (1H, spt, J = 6 Hz, OC*H*Me$_2$), 2.36 (4H, br m, C*H*Me$_2$), 2.25 (6H, s, Ar*Me*), 1.06 (6H, m, CH*Me*$_2$), 1.02 (6H, d, J = 6 Hz, OCH*Me*$_2$), 0.87 (6H, m, CH*Me*$_2$), 0.74 (6H, m, CH*Me*$_2$), 0.43 (6H, m, CH*Me*$_2$), −17.63 (1H, t, $^2J_{PH}$ = 10.5 Hz, Ir*H*). ^{13}C{^{1}H} NMR (C_6D_5Br, 150.9 MHz): δ 149.9 (br m), 148.3 (br m), 145.8 (t, J_{CP} = 7.2 Hz), 140.6 (s), 139.7 (br m), 139.5 (s), 137.9 (br m), 136.2 (br m), 135.2 (s), 134.5 (s), 134.1 (s), 130.2 (s), 128.2 (s), 125.8 (s) (Ar*C*), 68.7 (s, O*C*HMe$_2$), 26.6 (t, J_{CP} = 15.4 Hz, *C*HMe$_2$), 25.9 (s, OCH*Me*$_2$), 25.5 (t, J_{CP} = 14.7 Hz, *C*HMe$_2$), 21.1 (s, Ar*Me*), 20.8 (s, CH*Me*$_2$), 20.1 (s, CH*Me*$_2$), 17.6 (s, CH*Me*$_2$), 17.2 (s, CH*Me*$_2$). ^{31}P{^{1}H} NMR (C_6D_5Br, 202.5 MHz): δ 47.9 (s). ^{29}Si NMR (C_6D_5Br, 99.4 MHz): δ −2.3. Anal. Calcd for $C_{65}H_{59}NBF_{20}IrOP_2Si$: C, 50.59; H, 3.85; N, 0.91. Found: C, 50.66; H, 3.65; N, 0.99.

[(PNPH)IrH(SiPh$_2$O^{t}Bu)][B(C$_6$F$_5$)$_4$] (14). An excess of *tert*-butanol (ca. 0.2 mL) was added via cannula to a solution of **1** (0.080 g, 0.05 mmol) in 1.5 mL of C_6H_5F. Upon addition of the alcohol, a color change to light yellow-green was observed. After 10 min, the reaction mixture was dried under vacuum. The resulting oil was redissolved in fluorobenzene (1 mL), and the solution was added to hexanes (10 mL). The resulting mixture was placed in the −20 °C freezer for 1 h. A yellow oil was collected by decantation, and then the oil was dried under vacuum to give a light yellow solid. Yield: 0.078 g (93%). ^{1}H NMR (C_6D_5Br, 500 MHz): δ 7.53 (4H, d, J = 7.1 Hz, Ar*H*), 7.24 (2H, t, J = 7.4 Hz, Ar*H*), 7.16−7.08 (9H, ov m, Ar*H* + N*H*), 6.84 (2H, d, J = 8.3 Hz, Ar*H*), 2.34 (4H, ov m, C*H*Me$_2$), 2.24 (6H, s, Ar*Me*), 1.13 (9H, ^{t}*Bu*O), 1.12 (6H, m, CH*Me*$_2$), 0.88 (6H, m, CH*Me*$_2$), 0.69 (6H, m, CH*Me*$_2$), 0.38 (6H, m, CH*Me*$_2$), −17.60 (1H, t, $^2J_{PH}$ = 10.6 Hz, Ir*H*). ^{13}C{^{1}H} NMR (C_6D_5Br, 150.9 MHz): δ 149.9 (br m), 148.3 (br m), 146.1 (t, J_{CP} = 7.1 Hz), 140.8 (s), 140.3 (s), 139.8 (br m), 136.2 (br m), 135.3 (s), 134.2 (s), 133.8 (s), 128.2 (s), 125.4 (br m), 76.5 (s, O*C*Me$_3$), 32.2 (s, OC*Me*$_3$), 26.8 (t, J_{CP} = 12.3 Hz, *C*HMe$_2$), 25.2 (t, J_{CP} = 14.2 Hz, *C*HMe$_2$), 21.1 (s, Ar*Me*), 21.1 (s, CH*Me*$_2$), 20.1 (s, CH*Me*$_2$), 18.3 (s, CH*Me*$_2$), 17.3 (s, CH*Me*$_2$). ^{31}P{^{1}H} NMR (C_6D_5Br, 202.5 MHz): δ 45.5 (s). ^{29}Si NMR (C_6D_5Br, 99.4 MHz): δ −14.8. Anal. Calcd for $C_{66}H_{61}NBF_{20}IrOP_2Si$: C, 50.91; H, 3.95; N, 0.90. Found: C, 51.05; H, 3.97; N, 0.89.

[(PNPH)IrH(SiPh$_2$NHPh)][B(C$_6$F$_5$)$_4$] (15). Aniline (4.9 μL, 0.05 mmol) was added via syringe to a solution of **1** (0.08 g, 0.05 mmol) in 1 mL of C_6H_5F. An immediate color change to dark

yellow was observed. After 15 min, the reaction mixture was added to hexanes (15 mL), and the resulting mixture was placed in the −20 °C freezer for 18 h. A yellow oil was collected by decantation, and then the oil was dried under vacuum to give a light yellow solid. Yield: 0.07 g (86%). ^{1}H NMR (C_6D_5Br, 500 MHz): δ 7.78 (1H, br s, N*H*), 7.64 (4H, d, J = 7.2 Hz, Ar*H*), 7.20−7.10 (10 H, ov m, Ar*H*), 6.99 (2H, under solvent signal, Ar*H*), 6.97 (2H, d, J = 7.9 Hz, Ar*H*), 6.66 (1H, t, J = 7.1 Hz, Ar*H*), 6.60 (2H, d, J = 7.9 Hz, Ar*H*), 4.19 (1H, s, N*H*), 2.31 (2H, m, C*H*Me$_2$), 2.24 (6H, s, Ar*Me*), 1.86 (2H, m, C*H*Me$_2$), 0.98 (6H, m, CH*Me*$_2$), 0.88 (6H, m, CH*Me*$_2$), 0.67 (6H, m, CH*Me*$_2$), 0.53 (6H, m, CH*Me*$_2$), −17.96 (1H, br t, J_{PH} = 9.3 Hz, Ir*H*). ^{13}C{^{1}H} NMR (C_6D_5Br, 150.9 MHz): δ 149.9 (br m), 148.3 (brm m), 140.9 (br), 139.7 (br m), 137.9 (br m), 136.2 (br m), 135.5 (s), 134.3 (s), 128.5 (s), 126.4 (br), 119.3 (br), 117.8 (br) (Ar*C*), 26.5 (t, J_{CP} = 17 Hz, *C*HMe$_2$), 25.5 (t, J_{CP} = 12 Hz, *C*HMe$_2$), 21.1 (s, Ar*Me*), 21.1 (s, CH*Me*$_2$), 19.5 (s, CH*Me*$_2$), 18.6 (s, CH*Me*$_2$), 17.2 (s, CH*Me*$_2$). ^{31}P{^{1}H} NMR (C_6D_5Br, 202.5 MHz): δ 45.4 (s). ^{29}Si NMR (C_6D_5Br, 99.4 MHz): δ −21.9. Anal. Calcd for $C_{68}H_{58}N_2BF_{20}IrP_2Si$: C, 51.82; H, 3.71; N, 1.78. Found: C, 52.01; H, 3.50; N, 2.11.

[(PNPH)IrH(SiPh$_2$NHAr$_F$)][B(C$_6$F$_5$)$_4$] (Ar$_F$ = 3,5-(CF$_3$)$_2$C$_6$H$_3$) (16). H_2NAr_F (4.9 μL, 0.05 mmol) was added via syringe to a solution of **1** (0.08 g, 0.05 mmol) in 1 mL of C_6H_5F. An immediate color change to dark yellow was observed. After 15 min, the reaction mixture was added to hexanes (15 mL), and the resulting mixture was placed in the −20 °C freezer for 6 h. A yellow oil was collected by decantation, and then the oil was dried under vacuum to give a light yellow solid. Yield: 0.08 g (88%). ^{1}H NMR (C_6D_5Br, 500 MHz): δ 7.79 (1H, br s, N*H*), 7.55 (4H, d, J = 6.9 Hz, Ar*H*), 7.20−7.10 (11H, ov m, Ar*H*), 7.00−6.97 (4H, ov d + s, Ar*H*), 4.58 (1H, s, N*H*), 2.35 (2H, m, C*H*Me$_2$), 2.24 (6H, s, Ar*Me*), 1.87 (2H, m, C*H*Me$_2$), 1.00 (6H, m, CH*Me*$_2$), 0.88 (6H, m, CH*Me*$_2$), 0.68 (6H, m, CH*Me*$_2$), 0.49 (6H, m, CH*Me*$_2$), −17.99 (1H, t, J_{PH} = 10.4 Hz, $^2J_{SiH}$ = 3 Hz, Ir*H*). ^{13}C{^{1}H} NMR (C_6D_5Br, 150.9 MHz): δ 149.9 (br m), 148.6 (s), 148.2 (br m), 145.3 (t, J_{CP} = 7.4 Hz), 141.2 (br m), 139.7 (br m), 137.6 (br m), 137.8 (s), 136.2 (br m), 135.2 (s), 134.7 (s), 134.4 (s), 132.4 (s), 132.2 (s), 131.0 (s), 128.8 (s), 125.9 (s), 124.8 (s), 117.2 (br), 111.8 (br) (Ar*C*), 26.5 (t, J_{CP} = 17.2 Hz, *C*HMe$_2$), 25.7 (t, J_{CP} = 13.5 Hz, *C*HMe$_2$), 21.1 (s, Ar*Me*), 21.0 (s, CH*Me*$_2$), 19.4 (s, CH*Me*$_2$), 18.4 (s, CH*Me*$_2$), 17.1 (s, CH*Me*$_2$). ^{31}P{^{1}H} NMR (C_6D_5Br, 202.5 MHz): δ 46.1 (s). ^{29}Si NMR (C_6D_5Br, 99.4 MHz): δ −16.5. ^{19}F{^{1}H} NMR (C_6D_5Br, 376.5 MHz): δ −61.9 (s, CF_3), −130.8 (br s, B(C$_6$F$_5$)$_4$), −161.3 (t, J = 20.7 Hz, B(C$_6$F$_5$)$_4$), −165.1 (br t, J = 19.3 Hz, B(C$_6$F$_5$)$_4$). Anal. Calcd for $C_{70}H_{56}N_2BF_{26}IrP_2Si$: C, 49.10; H, 3.30; N, 1.64. Found: C, 49.32; H, 3.04; N, 1.46.

Representative Procedure for Catalytic Alcoholysis Reactions. In a representative catalytic run, **1** (0.005 g, 0.003 mmol, 1 mol %) was dissolved in 0.5 mL of bromobenzene-d_5, and the resulting solution was added to bis(*p*-fluorophenyl)methane (0.0068 g, 0.034 mmol) (as a standard) followed by the silane (0.034 mmol). The NMR tube was then capped with a rubber septum and taken out of the drybox, where the alcohol was added by syringe (0.040 mmol) through the septum. The NMR tube was vented by piercing the septa with a syringe after 1 h and again after 3 h to release the buildup of H_2 gas. 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.

Representative Procedure for Catalytic Aminolysis and Hydrosilylation Reactions. In a representative catalytic run, **1** (0.005 g, 0.003 mmol, 1 mol %) was dissolved in 0.5 mL of bromobenzene-d_5, and the resulting solution was added to bis(*p*-fluorophenyl)methane (0.0068 g, 0.034 mmol) (as a standard), silane (0.034 mmol), and then the aniline or ketone (0.040 mmol). This solution was then transferred to a Teflon-capped J. Young NMR tube. The reaction was monitored via ^{1}H NMR spectroscopy, and yields were obtained by integration against the internal 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.

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