Stoichiometric and Catalytic Behavior of Cationic Silyl and Silylene Complexes

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Reactions of Ir(III) silyl and silylene complexes with a variety of unsaturated substrates were investigated. The reactivity of these complexes toward small molecules was also examined, and this led to the discovery of a nitrile carbon−carbon bond cleavage under mild conditions. Both silyl and silylene complexes of Ir(III) are precatalysts for catalytic hydrosilylation of ketones, and the mechanism of this reaction is discussed. In the course of studying the catalytic reaction mechanism, analogous new ruthenium silylene complexes of the form $[Cp^*(PMe_3)_2Ru(SiR_2)][B(C_6F_5)_4]$ ($Cp^* = \eta^5$-C_5Me_5, R = ^{i}Pr, SPh) were prepared. A comparison of $[Cp^*(PMe_3)Ir(SiPh_2)(H)][B(C_6F_5)_4]$ and the known Lewis acid hydrosilylation catalyst $B(C_6F_5)_3$ is also made.

Introduction

A major focus of organometallic chemistry has been the enhancement of both the stoichiometric and catalytic reactivity of metal complexes through the generation of open coordination sites.[1,2] Two pathways available in pursuit of such a goal are neutral (eq 1) and anionic (eq 2) ligand dissociation. Although there is some evidence

$$L_nM \xrightarrow{\text{dative ligand dissociation}} L_{n-1}M + L \quad (1)$$

$$L_nMX \xrightarrow{\text{anionic ligand dissociation}} L_nM^+ X^- \quad (2)$$

to suggest that neutral ligand dissociation can be enhanced by the presence of added Lewis acids,[3,4] increasing anionic ligand dissociation of metal complexes through anion metathesis with salts of weakly coordinating anions has generally proven to be more straightforward.[5−7] Both early and late transition metal polymerization chemistry has benefited from this approach, and evidence exists that stoichiometric reactivity can be similarly affected.[8−10]

We have been interested in the reaction chemistry associated with cationic Ir(III) alkyl complexes since the discovery of mild C−H activation behavior by the Ir(III) complex $Cp^*(PMe_3)Ir(Me)OTf$ (OTf = OSO_2CF_3, **1**).[11] The novel stoichiometric reactivity associated with the related compounds $Cp^*(PMe_3)Ir(Me)(CH_2Cl_2)][X]$ (**2**, X = $B(3,5\text{-}(CF_3)_2C_6H_3)_4$ = BAr_f, $MeB(C_6F_5)_3$) and $[Tp^*\text{-}(PMe_3)Ir(Me)(N_2)][BAr_f]$ (**3**) has been reported recently.[12,13] When comparing the rates of C−H activation by **1** and **2**, the observed increase in reaction rate that can be achieved through anion metathesis is clearly evident.

Attempts to generate and study silyl analogues of **1** led to the observation of facile 1,2-group migration from silicon to iridium to give $Cp^*(PMe_3)Ir(SiR_2OTf)(R)$ as the products (eq 3). These products can be viewed as

$$Cp^*(PMe_3)Ir(Me)(OTf) \xrightarrow[-\ CH_4]{HSiR_3} Cp^*(PMe_3)Ir(SiR_2OTf)(R) \quad (3)$$

1

metal silylene complexes that are stabilized by the coordination of triflate to silicon. Silylene complexes are postulated intermediates in a number of transition metal-catalyzed reactions involving organosilanes, including the Direct Process.[14] Iridium silylene complexes have been invoked as intermediates in a number of reactions, including the reaction of $(TFB)Ir(OCOCH_3)\text{-}(PR_3)$ to give $(TFB)Ir(H)_2(PR_3)SiPh_2(OCOCH_3)$ (TFB = tetrafluorobenzobarrelene; R = Ph, Cy, ^{i}Pr), the reaction of $(\eta^2\text{-}MesHSi(CH_2)_2PPh_2)Ir(PMe_3)_2(Me)(H)$ with MeOH to afford $(\eta^2\text{-}Mes(MeO)Si(CH_2)_2PPh_2)Ir(PMe_3)_2(H)_2$, and rearrangements involving $(Me_3P)_3IrSi(SiMe_3)_3$.[15−17]

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Establishing the reactivity patterns of metal silylenes has been hampered by the small number of methods that provide access to them. The first base-free metal silylene complexes to be isolated were $[Cp^*(PMe_3)_2Ru(Si(SR)_2)][BPh_4]$ (R = *p*-tol, Et), which were reported in 1990.[18] The list of isolable base-free metal silylene complexes now includes complexes of platinum,[19] iridium,[20,21] osmium,[22] tungsten,[23,24] and molybdenum.[25]

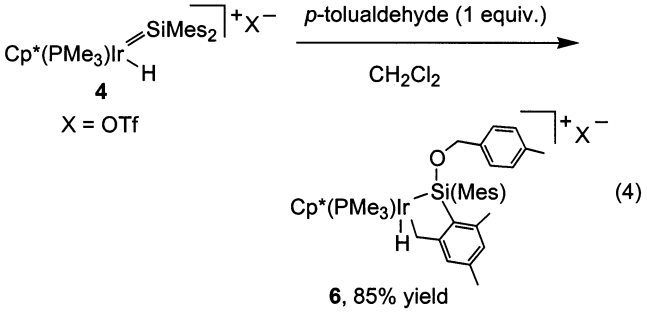
Reactions of silylene complexes with unsaturated substrates to afford isolable products are rare. Cycloaddition of base-free ruthenium silylene complexes with isocyanates is known,[26] and the complex $[Cp^*(PMe_3)_2RuSiPh_2(NCMe)][BPh_4]$ reacts with enolizable ketones to generate the corresponding silyl enol ether and $[Cp^*(PMe_3)_2Ru(NCMe)][BPh_4]$.[27] Other known reactions of silylene complexes include coordination to Lewis bases[28] and a halogen atom abstraction by an osmium silylene complex, in which the silylene ligand facilitates a redox reaction at the metal center.[22]

There are a number of reasons to study the insertion behavior of silyliridium(III) complexes, especially if catalytic processes involving them are to be developed. The traditional Chalk−Harrod mechanism for hydrosilylation cannot account for the formation of dehydrogenative silylated products,[14] and Brookhart and coworkers have provided evidence for an alternative pathway that proceeds by insertion into a metal−silicon bond.[29,30] The formation of dehydrogenated products in hydrosilylation reactions is explained by insertion of the unsaturated substrate into a metal−silicon bond, followed by β-hydrogen elimination from the newly formed metal alkyl species. Direct observations of metal-containing insertion products are limited in number, with late-metal examples including platinum[31,32] and ruthenium.[33]

We have previously discussed the synthesis of the silylene complexes $[Cp^*(PMe_3)Ir(SiMes_2)(H)][OTf]$ (**4**) and $[Cp^*(PMe_3)Ir(SiPh_2)(H)][B(C_6F_5)_4]$ (**5**),[20,34] along with evidence that these complexes are likely intermediates in rearrangement reactions at silicon. Here we present an investigation of the stoichiometric and catalytic reactivity of these new metal silylene complexes.

Results

Stoichiometric Reactivity of $[Cp^*(PMe_3)Ir(SiMes_2)(H)][OTf]$ (4). Treatment of $[Cp^*(PMe_3)Ir(SiMes_2)(H)][OTf]$ (**4**) with 1 equiv of *p*-tolualdehyde results in the clean formation of $\{Cp^*(PMe_3)Ir(H)[\kappa_2\text{-}Si(2\text{-}CH_2\text{-}4,6\text{-}(CH_3)_2C_6H_2)(Mes)(OCH_2(p\text{-tolyl}))]\}[OTf]$ (**6**), which was isolated in 85% yield (eq 4). The ^1H NMR spectrum of **6**



(4)

displays the expected resonances for the Cp* (δ 1.67, d, J_{P-H} = 2 Hz) and PMe_3 ligands (δ 1.45, d, J_{P-H} = 11 Hz), as well as resonances for the diastereotopic protons on the metalated carbon (δ 3.49, d, J_{H-H} = 14 Hz; δ 2.90, vt, J_{H-H} = 14 Hz) and diastereotopic benzylic ether protons (δ 4.83, d, J_{P-H} = 12 Hz; δ 4.43, d, J_{P-H} = 12 Hz). Additional spectroscopic evidence for the proposed structure includes the phosphorus-coupled ^{13}C NMR resonance for the metalated carbon (δ 13.0, d, J_{P-C} = 10 Hz), and an infrared stretch for the iridium−hydride bond (ν_{Ir-H} = 2163 cm^{-1}).

Reactions of dimesitylsilylene complex **4** with unsaturated hydrocarbon substrates were subsequently investigated. However, no reaction was observed when **4** was treated with 1 equiv of ethylene after heating to 45 °C for 4 d. Further heating led only to decomposition, and reaction of **4** with 2-butyne showed no conversion after 30 min at 25 °C. Presumably, complex **4** is too crowded to undergo migratory insertion reactions with these substrates.

The reactivity of dimesitylsilylene complex **4** was also examined toward substrates not expected to react via insertion. Upon addition of MeOH to a CD_2Cl_2 solution of **4**, the bright yellow color immediately bleaches and $[Cp^*(PMe_3)Ir(H)_3][OTf]$ is observed by ^1H and ^{31}P NMR spectroscopy as the only organometallic product.[35] The major silicon-containing product of this reaction is presumably $Mes_2Si(OMe)_2$, although ^1H NMR and GC/MS analysis after extraction into pentane indicates a mixture of organic products which could not be purified by crystallization. Addition of CCl_4 to **4** does not result in the formation of $[Cp^*(PMe_3)Ir(SiMes_2)(Cl)][OTf]$ after heating to 45 °C for 24 h, presumably due to steric hindrance. In fact, complex **4** displayed a surprising lack of reactivity with added Lewis bases such as pyridine

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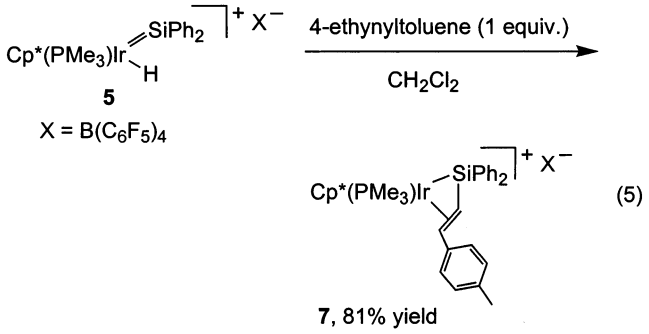
and CH_3CN. The bulky environment around silicon also accounts for the fact that **4** is the first cationic transition metal silylene complex that does not coordinate triflate. Treatment of **4** with other Lewis bases, such as CN^tBu and CO, led to the formation of multiple products.

An effort was made to prepare the neutral iridium silylene complex $Cp^*(PMe_3)Ir(SiMes_2)$ by deprotonation of **4**. Reaction with either $KN(SiMe_3)_2$ or lithium 2,2,6,6-tetramethylpiperidide led to production of a deep red solution that was found to contain multiple products by ^1H and ^{31}P NMR spectroscopy. To assess the possibility that the putative neutral silylene complex might be inherently unstable, attempts were made to trap it. However, inclusion of an excess (10 equiv) of diphenylacetylene, benzophenone, *p*-tolyl disulfide, or diphenylsilane had little effect on the decomposition induced by added lithium 2,2,6,6-tetramethylpiperidide.

Stoichiometric Reactivity of $[Cp^*(PMe_3)Ir(SiPh_2)(H)][B(C_6F_5)_4]$ (5). Although studies of dimesitylsilylene complex **4** revealed a number of new metal silyl tranformations, its limited reactivity with Lewis bases suggested that a more reactive complex could be found if the size of the substituents at silicon was reduced. Because of the propensity of tertiary iridium silyl complexes to cyclometalate in this system,[20,36] the synthesis of a new iridium silylene complex was approached by using a secondary silane. The less hindered silylene complex $[Cp^*(PMe_3)Ir(SiPh_2)(H)][B(C_6F_5)_4]$ (**5**) is readily available by treatment of $Cp^*(PMe_3)Ir(Me)OTf$ with H_2SiPh_2, followed by anion metathesis with $(Et_2O)_2LiB(C_6F_5)_4$.[12]

Silylene complex **5** reacts with 4-ethynyltoluene at 25 °C within minutes to give spectroscopically pure $\{Cp^*(PMe_3)Ir[SiPh_2(\eta^2\text{-}CHCH(p\text{-tolyl}))]\}[B(C_6F_5)_4]$ (**7**) in 81% isolated yield (eq 5). As cationic 16-electron iridium silyl



(5)

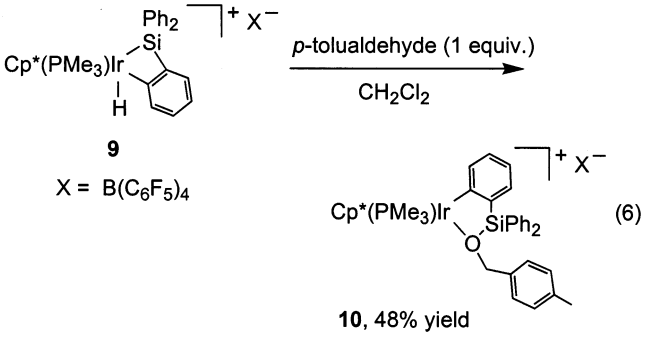
complexes are electron deficient, it is not too surprising that the carbon−carbon double bond in the styrenyl ligand coordinates to the metal center. The ^{13}C NMR spectrum for this complex contains upfield resonances at δ 66.3 and 38.6, which are consistent with a coordinated olefin. Structural evidence for the olefinic group can also be found in the ^1H NMR spectrum (δ 5.29, vt, J_{H-H} = 14 Hz; δ 3.52, d, J_{H-H} = 15 Hz).

The base-free silylene complex **5** is expected to be more reactive than dimesitylsilylene complex **4** because the substituents on silicon are smaller. This was found to be the case experimentally, although competing side reactions often led to production of multiple products. For example, reaction of **5** with 1 equiv of *p*-tolualdehyde led to a dark brown mixture containing numerous unidentified compounds. Similarly, treatment of **5** with 1 equiv of either 2-butyne or 1,2-propadiene led to formation of at least three products. Reaction of **5** with di-*p*-tolylcarbodiimide also did not result in clean reaction behavior.

Deprotonation was considered as a possible synthetic route to $Cp^*(PMe_3)Ir(SiPh_2)$ as either a stable entity or a species that could be trapped, as was described for silylene complex **4**. However, reaction of **5** with the hindered base $KN(SiMe_3)_2$ led to formation of $Cp^*(PMe_3)Ir[SiPh_2N(SiMe_3)_2](H)$ (**8**) in 41% isolated yield. This complex is readily soluble in nonpolar solvents such as pentane and Et_2O, and exhibits the expected ^1H NMR spectroscopic characteristics. Unfortunately, addition of lithium 2,2,6,6-tetramethylpiperidide to **5** led only to decomposition, and use of an excess (10 equiv) of diphenylacetylene, benzophenone, *p*-tolyl disulfide, or diphenylsilane had little effect on the outcome of the reaction.

Reactivity of $[Cp^*(PMe_3)Ir(\eta^2\text{-}SiPh_2C_6H_4)(H)][B(C_6F_5)_4]$ (9). As previously described, cyclometalated complex **9** is obtained by treating $Cp^*(PMe_3)Ir(SiPh_2OTf)(Ph)$ with $(Et_2O)_2LiB(C_6F_5)_4$.[20] Studying the reactivity of this species could provide insight into the behavior of the 16-electron iridium silyl complex "$[Cp^*(PMe_3)Ir(SiPh_3)][B(C_6F_5)_4]$" if C−H reductive elimination to form the triphenylsilyl ligand is facile for **9**.

The insertion behavior of cyclometalated silyliridium complex **9** toward a carbonyl-containing substrate was examined. Reaction of **9** with *p*-tolualdehyde is complete within 10 min at 25 °C, and $\{Cp^*(PMe_3)Ir[\kappa^2\text{-}(C_6H_4\text{-}2\text{-}SiPh_2)(OCH_2(p\text{-tolyl}))]\}[B(C_6F_5)_4]$ (**10**) is obtained in 48% recrystallized yield (eq 6). A ^1H NMR spectrum of **10**



(6)

indicates resonances for the Cp* (δ 1.41, d, J_{P-H} = 2 Hz) and PMe_3 (δ 1.23, d, J_{P-H} = 10 Hz) ligands, as well as diagnostic resonances for the diastereotopic protons of the benzylic methylene group (δ 5.55, d, J_{H-H} = 12 Hz; δ 4.80, d, J_{H-H} = 12 Hz). This complex was also characterized by X-ray crystallography, providing definitive evidence for a bonding interaction between oxygen and iridium (2.251(3) Å). An ORTEP diagram of the cationic portion of **10** is seen in Figure 1, and representative bond lengths and angles are found in Table 1.

Reaction of $Cp^*(PMe_3)Ir(SiPh_2OTf)(Ph)$ with $NaBAr_f$ (BAr_f = (3, 5-$(CF_3)_2C_6H_3)_4B$), followed by addition of acetonitrile, provides $[Cp^*(PMe_3)Ir(NCCH_3)(SiPh_3)][BAr_f]$ (**11a**) in high yield.[20] Similarly, reaction of **9** with acetonitrile was found to be an effective method for

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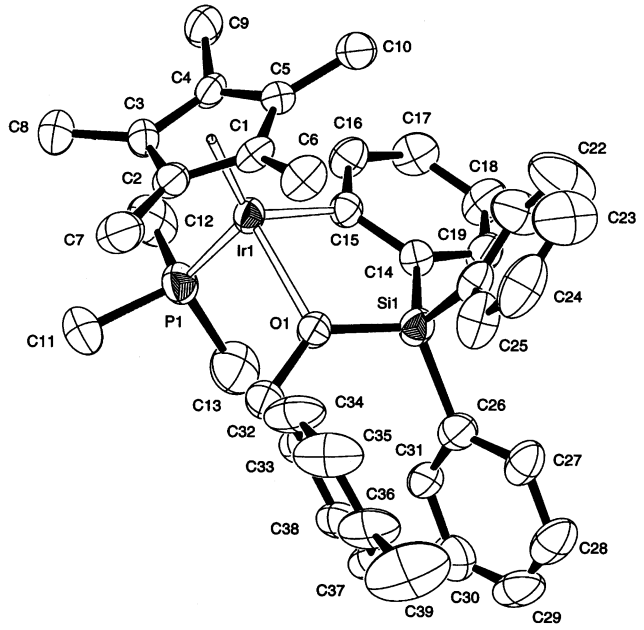


Figure 1. ORTEP diagram of the cationic portion of {Cp*-(PMe$_3$)Ir[κ^2-(C$_6$H$_4$-2-SiPh$_2$)(OCH$_2$(*p*-tolyl))]}[B(C$_6$F$_5$)$_4$] (**10**). Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms have been omitted for clarity.

Table 1. Selected Bond distances (Å) and Angles (deg) for 10

bond	distance	bond	angle
Ir−P	2.284(2)	P−Ir−C15	86.1(1)
Ir−O	2.251(3)	P−Ir−O	91.85(9)
Ir−C15	2.083(5)	O−Ir−C15	82.4(2)
Ir−C100	1.7438(2)	P−Ir−C100	127.76(4)
Si−O	1.701(4)	Si−O−C32	128.4(3)

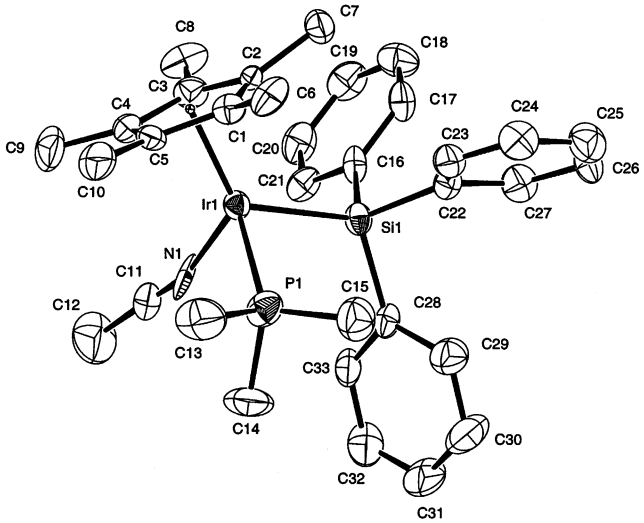


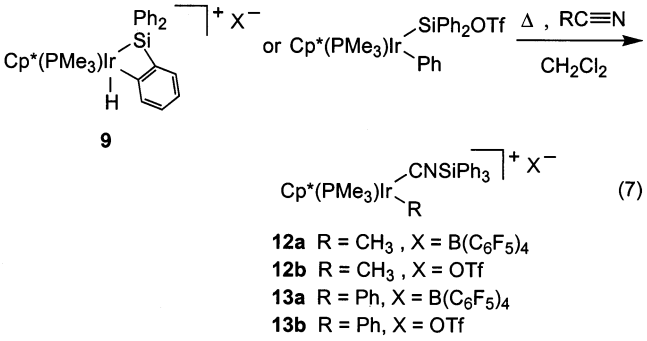
Figure 2. ORTEP diagram of the cationic portion of [Cp*-(PMe$_3$)Ir(NCCH$_3$)(SiPh$_3$)][BAr$_f$] (**11a**). Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms have been omitted for clarity.

generating [Cp*(PMe$_3$)Ir(NCCH$_3$)(SiPh$_3$)][B(C$_6$F$_5$)$_4$] (**11b**). Complex **11a** was characterized crystallographically through an X-ray diffraction study, and an ORTEP diagram of the cationic portion of it is shown in Figure 2. Representative bond angles and lengths are found in Table 2.

Table 2. Selected Bond distances (Å) and Angles (deg) for 11a

bond	distance	bond	angle
Ir−P	2.312(3)	P−Ir−Si	91.15(10)
Ie−Si	2.411(2)	P−Ir−N	89.5(3)
Ir−N	2.042(9)	Si−Ir−N	90.5(2)
Ir−C100	1.9033(4)	P−Ir−C100	129.41(7)
N−C11	1.106(11)	Si−Ir−C100	124.60(8)

Heating a CD_2Cl_2 solution of acetonitrile complex **11b**, which is formed in situ by reaction of **9** with acetonitrile, to 75 °C for 24 h leads to nitrile cleavage and production of isocyanide complex [Cp*(PMe$_3$)Ir(CH$_3$)(CNSiPh$_3$)][B(C$_6$F$_5$)$_4$] (**12a**) (eq 7). This complex exhibits the

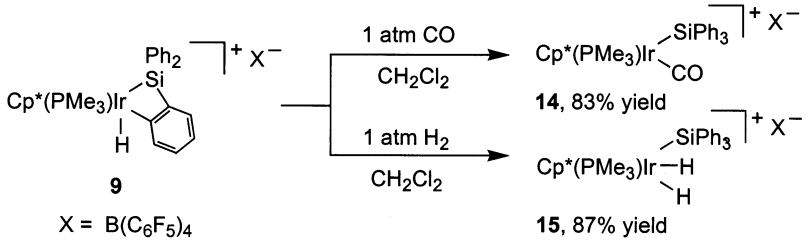


expected ^{1}H NMR spectroscopic resonances, including a resonance typical of an iridium-bound methyl group (δ 0.44, d, J_{P-C} = 6 Hz). Concurrent work involving an X-ray crystallographic study of the related rhodium species [Cp*(PMe$_3$)Rh(CH$_3$)(CNSiPh$_3$)][B(3,5-(CF$_3$)$_2$-C$_6$H$_3$)$_4$] suggests the formulation of **12a** as an isonitrile complex, rather than a nitrile complex.[37] A similar nitrile cleavage reaction was observed when cyclometalated complex **9** was treated with benzonitrile. This reaction occurs more rapidly than does the analogous reaction with acetonitrile, as [Cp*(PMe$_3$)Ir(Ph)(CNSiPh$_3$)][B(C$_6$F$_5$)$_4$] (**13a**) was produced cleanly after heating to 45 °C for 4 h.

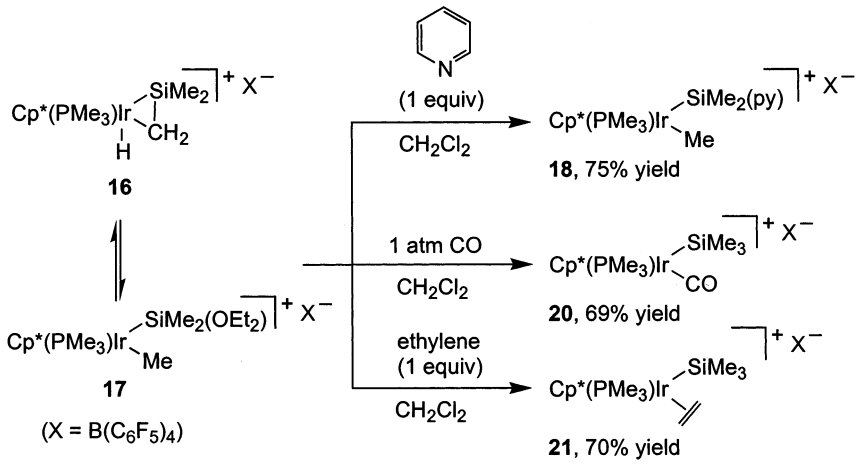
It might be suspected that the B(C$_6$F$_5$)$_4^-$ anion is essential to these C−C activation reactions, given the increased reactivity observed for similar Ir(III) complexes upon replacing the triflate anion with a more weakly coordinating anion. However, treatment of Cp*-(PMe$_3$)Ir(SiPh$_2$OTf)(Ph) with 1.2 equiv of acetonitrile in CH_2Cl_2 at 75 °C for 24 h leads to formation of the C−C activated product [Cp*(PMe$_3$)Ir(CH$_3$)(CNSiPh$_3$)][OTf] (**12b**). Additionally, reaction of benzonitrile at 45 °C for 4 h with Cp*(PMe$_3$)Ir(SiPh$_2$OTf)(Ph) also leads to C−C activation and production of [Cp*(PMe$_3$)Ir(Ph)(CNSiPh$_3$)][OTf] (**13b**). Because the anions of these C−C activated products are outer-sphere, it is not surprising that the borate and triflate complexes exhibit nearly identical NMR spectroscopic shifts. Therefore, the nitrile cleavage products were fully characterized as their more crystalline triflate salts. Interestingly, nitrile cleavage is not observed upon heating a CD_2Cl_2 solution of Cp*-(PMe$_3$)Ir(SiPh$_2$OTf)(H) with acetonitrile to 75 °C for 3 h; the adduct [Cp*(PMe$_3$)Ir(SiPh$_2$H)(NCCH$_3$)][OTf] was also not spectroscopically observable in this case. This

(37) This experiment was inspired by a similar observation made by F.L. Taw in the corresponding cationic rhodium system. See: Taw, F. L.; Brookhart, M.; Bergman, R. G. *J. Am. Chem. Soc.* **2002**, *124*, 4192.

Scheme 1



Scheme 2



lack of reactivity is attributed to the apparently unfavorable process of iridium-hydride migration back to silicon.

Given that silyliridium complexes were active in nitrile cleavage reactions, it seemed reasonable to expect that the corresponding methyliridium complexes would undergo similar transformations. In that case, the known acetonitrile complex $[Cp^*(PMe_3)Ir(CH_3)(NCCH_3)][OTf]$[12] would be expected to undergo a degenerate reaction upon thermolysis that would exchange the iridium-bound methyl group with the methyl group of the bound acetonitrile. To investigate this possibility, the complex $[Cp^*(PMe_3)Ir(CH_3)(NCCD_3)][OTf]$ was prepared from reaction of $Cp^*(PMe_3)Ir(CH_3)(OTf)$ with CD_3CN in CD_2Cl_2. However, there was no observable isotopic scrambling upon heating $[Cp^*(PMe_3)Ir(CH_3)(NCCD_3)][OTf]$ in CD_2Cl_2 at 105 °C for 15 h, and thermolysis at 135 °C for days led to decomposition with no evidence of nitrile cleavage. The ability of the silyliridium complexes to undergo C−C activation might therefore be due to the energetic accessibility of a silicon-stabilized Ir(V) intermediate on the pathway.

Cyclometalated complex $[Cp^*(PMe_3)Ir(\eta^2\text{-}SiPh_2C_6H_4)(H)][B(C_6F_5)_4]$ (**9**) is also reactive toward carbon monoxide and dihydrogen. The reaction with CO affords the Ir(III) carbonyl complex $[Cp^*(PMe_3)Ir(CO)(SiPh_3)][B(C_6F_5)_4]$ (**14**) in 83% yield (Scheme 1). The iridium−carbonyl functionality is evident from ^{13}C NMR (δ 169.3, d, $J_{P-C} = 11$ Hz) and IR ($\nu_{CO} = 2029$ cm^{-1}) spectroscopy. Addition of 1 atm of dihydrogen to complex **9** leads to formation of the Ir(V) complex $[Cp^*(PMe_3)Ir(H)_2(SiPh_3)][B(C_6F_5)_4]$ (**15**) in 87% yield after recrystallization (Scheme 1). A similar complex may also be generated by treating the cationic iridium monohydride complex $[Cp^*(PMe_3)Ir(H)(CD_2Cl_2)][CH_3B(C_6F_5)_3]$ with Ph_3SiH.[38]

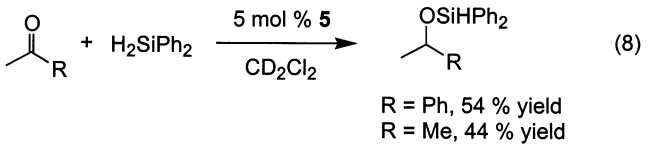
Because of the readily reversible nature of the 1,2-phenyl migration in the complex $Cp^*(PMe_3)Ir(SiPh_2OTf)(Ph)$, it has the potential to behave as "$Cp^*(PMe_3)Ir(SiPh_3)(OTf)$" when engaged in reactions with added ligands. When $Cp^*(PMe_3)Ir(SiPh_2OTf)(Ph)$ is treated with 1 equiv of *p*-tolualdehyde in CD_2Cl_2 the solution darkens over the course of 2 min, and a complicated mixture of products is detected by ^1H and ^{31}P NMR spectroscopy. This reaction outcome stands in contrast to that observed with the silyliridium complex containing a more weakly coordinating anion, which, as described, reacts with the aldehyde to afford cyclometalated species **10**.

Reactivity of $[Cp^*(PMe_3)Ir(\eta^2\text{-}CH_2SiMe_2)(H)][B(C_6F_5)_4]$ (16). As mentioned previously, reaction of $Cp^*(PMe_3)Ir(SiMe_2OTf)(Me)$ with 1 equiv of $(Et_2O)_2LiB(C_6F_5)_4$ in CH_2Cl_2 at 25 °C produced an equilibrium mixture of silene complex $[Cp^*(PMe_3)Ir(\eta^2\text{-}CH_2SiMe_2)(H)][B(C_6F_5)_4]$ (**16**) and base-stabilized silylene complex $[Cp(PMe_3)Ir(SiMe_2(Et_2O))(Me)][B(C_6F_5)_4]$ (**17**).[36] Treatment of a mixture of **16** and **17** with pyridine produced $[Cp^*(PMe_3)Ir(Me)(SiMe_2(py))][B(C_6F_5)_4]$ (**18**) in 75% isolated yield as a bright yellow crystalline solid (Scheme 2). The related complex, $[Cp^*(PMe_3)Ir(Me)(SiMe_2(py))][OTf]$ (**19**), was prepared in 98% isolated yield by treating the migrated triflate species $Cp^*(PMe_3)Ir(Me)(SiMe_2OTf)$ (**2**) with 1 equiv of pyridine. In contrast to the reaction with pyridine, treatment of **16** and **17** with carbon monoxide provided the nonmigrated silyl carbonyl complex $[Cp^*PMe_3Ir(SiMe_3)(CO)][B(C_6F_5)_4]$ (**20**) in 69% recrystallized yield (Scheme 1). This change in

(38) Golden, J. T. Ph.D. Thesis, University of California, Berkeley, 2001.

selectivity is probably due to the fact that as a strong π-acid, CO prefers coordination to the electron-rich Ir center, while pyridine, a good σ donor like Et_2O, prefers to bind to the silicon center. Ethylene reacts with a mixture of **16** and **17** like CO rather than pyridine, leading to the silyl ethylene complex $[Cp^*(PMe_3)Ir(SiMe_3)(C_2H_4)][B(C_6F_5)_4]$ (**21**) in 70% isolated yield as pale yellow crystals. This appears to be the first reported *cationic* silyl ethylene complex, and it provides circumstantial evidence for the existence of $[Cp^*(P(OMe)_3)Co(SiEt_3)(olefin)]^+$, a postulated intermediate in the catalytic hydrosilylation of olefins by $[Cp^*(P(OMe)_3)CoCH_2CH_2\text{-}\mu\text{-}H]\{B[3,5\text{-}(CF_3)_2C_6H_3]_4\}$.[29]

Catalytic Studies. Reduction of acetophenone with H_2SiPh_2 in CD_2Cl_2 using 5 mol % $[Cp^*(PMe_3)Ir(SiPh_2)(H)][B(C_6F_5)_4]$ (**5**) leads to formation of the corresponding alkoxysilane in 54% yield after 18 h at 25 °C (eq 8).



(8)

R = Ph, 54 % yield
R = Me, 44 % yield

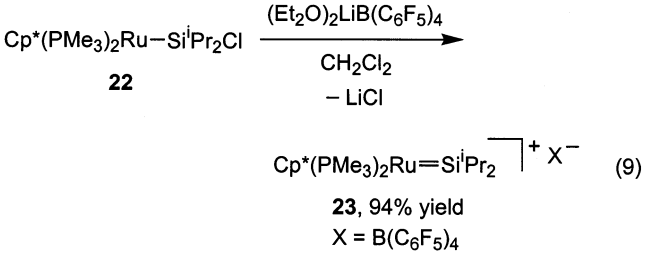
Ethylbenzene, the product of overreduction, was detected in 20% yield. Although it is not very common, overreduction of acetophenone has been observed previously in other hydrosilation reactions.[41] Acetone could be reduced under similar conditions, with formation of $Ph_2Si(H)(O^iPr)$ occurring in 33% yield after 3 h. The major product formed in this reaction is $Ph_2Si(O^iPr)_2$ (40% yield), formed from further reaction of $Ph_2Si(H)(O^iPr)$ with acetone. The remaining unreacted H_2SiPh_2 (27%) was spectroscopically observed. Monitoring the reaction mixture after 5 min by ^{31}P NMR spectroscopy at room temperature indicates complete conversion of **5** to a mixture of products. It was not possible to determine the resting state of the catalyst due to the number of different organometallic species present in solution.

The success of using silylene complex **5** as a precatalyst in room temperature reductions of ketones led us to investigate the catalytic properties of another Ir(III) silylene complex. The more sterically hindered silylene complex $[Cp^*(PMe_3)Ir(SiMes_2)(H)][OTf]$ (**4**) offered the possibility of stabilization against catalyst decomposition. However, when 5 mol % of **4** was combined with acetophenone and diphenylsilane no productive hydrosilylation was observed after 3 d at room temperature. At that time, the ^{31}P NMR spectrum indicated the presence of at least four organometallic complexes and no **4**.

The catalytic hydrosilylation activity of the cyclometalated species $[Cp^*(PMe_3)Ir(\eta^2\text{-}SiPh_2C_6H_4)(H)][B(C_6F_5)_4]$ (**9**) was studied because of its potential to function in a fashion mechanistically similar to that of **5**. As described previously, complex **9** has been shown to readily undergo C−H reductive elimination in the presence of added Lewis bases, and therefore hydrosilylation by **9** could involve insertion of the ketone into the iridium−silyl bond of a putative $[Cp^*(PMe_3)Ir(SiPh_3)][B(C_6F_5)_4]$ complex. When 5 mol % of cyclometalated complex **9** is combined with acetophenone and $HSiPh_3$ at room temperature in CD_2Cl_2, formation of the hydrosilylated product occurs in 27% yield after 24 h. Only one organometallic species is evident at this time. This species was unambiguously identified as $[Cp^*(PMe_3)Ir(SiPh_3)(H)_2][B(C_6F_5)_4]$ (**14**) by addition of an authentic sample to the mixture and analysis by ^1H NMR spectroscopy. Surprisingly, when **14** was independently prepared from **9** and dihydrogen (Scheme 1), it was not an active catalyst for hydrosilylation of acetophenone with triphenylsilane. This indicates that the true catalyst must be present in a very small amount and must be highly active. Further reaction of the hydrosilylation mixture at 75 °C for 24 h leads to an increase of the amount of hydrosilylated material (50% overall) and formation of ethylbenzene in 19% yield.

The role of the weakly coordinating anion was probed by examining triflate-stabilized silylene complexes as catalysts for room temperature ketone hydrosilylation. A catalyzed hydrosilylation was attempted by treating acetophenone with diphenylsilane in CD_2Cl_2 in the presence of 5 mol % $Cp^*(PMe_3)Ir(SiPh_2OTf)(H)$. No reaction was observed after allowing the reaction mixture to stand for 5 h. A small amount (30% against an internal standard) of hydrosilylated product was observed upon heating the mixture to 75 °C for 4 h. Under these conditions, $Cp^*(PMe_3)Ir(SiPh_2OTf)(H)$ is converted to an approximately 1:1:1 mixture of unidentified products. The low reactivity of the triflate suggests that anion dissociation is crucial to catalyst activity.

The possibility that 1,2-hydride migration in $[Cp^*(PMe_3)Ir(SiPh_2)(H)][B(C_6F_5)_4]$ (**5**) leads to catalyst decomposition led us to synthesize and examine ruthenium complexes of the type $[Cp^*(PMe_3)_2Ru(SiR_2)][B(C_6F_5)_4]$ (R = thiolate, alkyl). A ruthenium silylene complex bearing carbon substituents on silicon was synthesized and examined first, as this should be a close analogue of the iridium silylene complex **5**. Heating a toluene solution of $Cp^*(PMe_3)_2Ru(CH_2SiMe_3)$ and $HSi(^iPr)_2Cl$ to 105° C for 5 h produced $Cp^*(PMe_3)_2Ru[Si(^iPr)_2Cl]$ (**22**) in 76% yield as yellow crystals after recrystallization from Et_2O at −35 °C. Related ruthenium complexes have been previously synthesized.[28] Chlorosilyl derivative **22** was converted to the corresponding silylene complex $[Cp^*(PMe_3)_2Ru(Si^iPr_2)][B(C_6F_5)_4]$ (**23**) in 94% isolated yield by treatment with $(Et_2O)_2LiB(C_6F_5)_4$ (eq 9). Ruthenium silylene complex



(9)

23 exhibits a ^{29}Si NMR resonance of +437.4 ppm, the furthest downfield shift yet measured for a silylene complex. This verifies the existence of a base-free three-

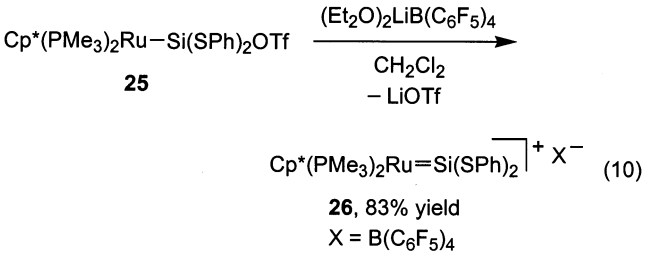
(39) Hollis, T. K.; Robinson, N. P.; Bosnich, B. *Tetrahedron Lett.* **1992**, *33*, 6423.
(40) Grumbine, S. K.; Straus, D. A.; Tilley, T. D.; Rheingold, A. L. *Polyhedron* **1995**, *14*, 127.
(41) Parks, D. J.; Blackwell, J. M.; Piers, W. E. *J. Org. Chem.* **2000**, *65*, 3090.

coordinate silicon center. Ruthenium silylene complex **23** was observed to undergo 22% decomposition to multiple products after 16 h at room temperature. This indicates a higher kinetic stability for **23** than for [Cp*-(PMe_3)$_2$Ru($SiMe_2$)][$B(C_6F_5)_4$], which is known to decompose at room temperature with a half-life of 7 h.[28]

Employing [Cp*(PMe_3)$_2$Ru(Si^iPr_2)][$B(C_6F_5)_4$] (**23**) as a hydrosilylation catalyst for the reduction of acetophenone with diphenylsilane led to no detectable product formation after 4 h at room temperature. Analysis of the reaction mixture during and after the hydrosilylation catalysis indicated that silylene complex **23** was converted to a number of unidentified organometallic complexes. Interestingly, silylene complex **23** is a catalytically active (5 mol %) precursor for the addition of 1-ethoxy-1-(trimethylsilyloxy)ethene to acetophenone, a reaction catalyzed by Lewis acids.[39] The addition product is formed in 53% yield after 20 min. Unfortunately, complete decomposition of the catalyst was also observed after 20 min.

The thermal instability of silylene complex **23** and its ready decomposition under catalytic conditions led us to explore ruthenium silylene complexes with differing substitution at silicon. Tilley and co-workers have measured the activation parameters for acetonitrile exchange in complexes of the type [Cp*(PMe_3)$_2$Ru(SiR_2)-(NCMe)][BPh_4], and used these data to compare the stabilization offered by various donor substituents at silicon. It was found that the stability offered followed the trend S(*p*-tolyl) > O(*p*-tolyl) > Me > Ph.[40] This suggested that employing thiolate substitution at silicon might lead to a catalytically active silylene complex that was more stable to the reaction conditions.

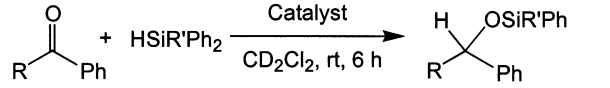
Reaction of Cp*(PMe_3)$_2$Ru(CH_2SiMe_3) with $HSi(SPh)_3$ at 105 °C for 6 h in benzene produces the silyl derivative Cp*(PMe_3)$_2$Ru[$Si(SPh)_3$] (**24**) in 64% isolated yield as off-white crystals. Treatment of silyl complex **24** with 1.1 equiv of TMSOTf in benzene at 45 °C for 5 h led to isolation of Cp*(PMe_3)$_2$Ru[$Si(SPh)_2$OTf] (**25**) in 45% yield. The pale yellow silyltriflate complex **25** could then be treated with 1 equiv of $Li(Et_2O)_2B(C_6F_5)_4$ in CH_2Cl_2 to afford the deep yellow silylene complex {Cp*(PMe_3)$_2$-Ru[$Si(SPh)_2$]}[$B(C_6F_5)_4$] (**26**) in 83% isolated yield (eq 10). The ^{29}Si NMR spectrum of **26** consists of one



resonance at 262.0 ppm, establishing the presence of a three-coordinate silicon center. It was found that combining 5 mol % of thiolate-substituted silylene complex **26** with acetophenone and diphenylsilane in CD_2Cl_2 led to no observable ketone reduction after 20 min, and <10% yield of the desired product after 12 h.

A direct comparison of [Cp*(PMe_3)Ir($SiPh_2$)(H)][B-(C_6F_5)$_4$] (**5**) with $B(C_6F_5)_3$ in hydrosilylation reactions was made because these two compounds are both strong electrophiles and may use a similar mechanism for

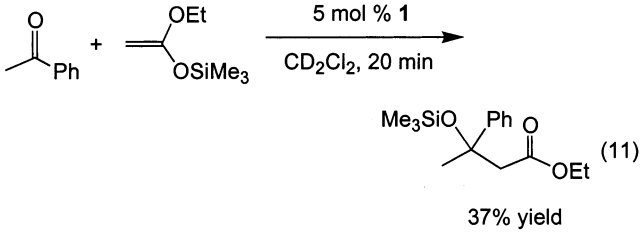
Table 3. Comparison of Hydrosilylation Catalysts



catalyst	R = Me; R′ = H	R = Ph; R′ = H	R = Ph; R′ = Ph
5	44	54	<10
$B(C_6F_5)_3$	0	21	>95

hydrosilylation. The use of this borane for ketone reductions has been reported recently.[41] The combined results for the hydrosilyation comparison are summarized in Table 3. It can be seen that in reactions catalyzed by 10 mol % $B(C_6F_5)_3$, use of $HSiPh_3$ leads to an excellent yield (>95%) of the hydrosilylated product for the reduction of acetophenone. In contrast, using H_2-$SiPh_2$ as the reductant led to substantially lower yields of hydrosilylated product for both acetophenone (21%) and acetone (<5%). All reactions were carried out at room temperature in CD_2Cl_2 for 6 h. Intriguingly, a completely different reactivity pattern is observed with 5 mol % of silylene complex [Cp*(PMe_3)Ir($SiPh_2$)(H)]-[$B(C_6F_5)_4$] (**5**) under otherwise identical conditions. There it is found that using triphenylsilane as the reductant leads to very little hydrosilylated product (<10%), but diphenylsilane led to increased reactivity for both acetophenone and acetone.

The possibility that iridium silylene complex **5** catalyzes ketone hydrosilylation through a metal-centered Lewis acid mechanism deserved further attention. This was probed by using the corresponding methyliridium complex Cp*(PMe_3)Ir(Me)OTf (**1**) as a precatalyst. Studying the hydrosilylation reactions in this context is not feasible because reaction with the silane to produce the corresponding silyliridium species is extremely rapid. Therefore, another reaction commonly catalyzed by Lewis acids, the addition of a silyl ketene acetal to a ketone,[39] was examined. When 5 mol % of methyliridium complex **1** was combined with acetophenone and 1-ethoxy-1-(trimethylsilyloxy)ethene a 37% yield of the addition product was detected after 20 min (eq 11).

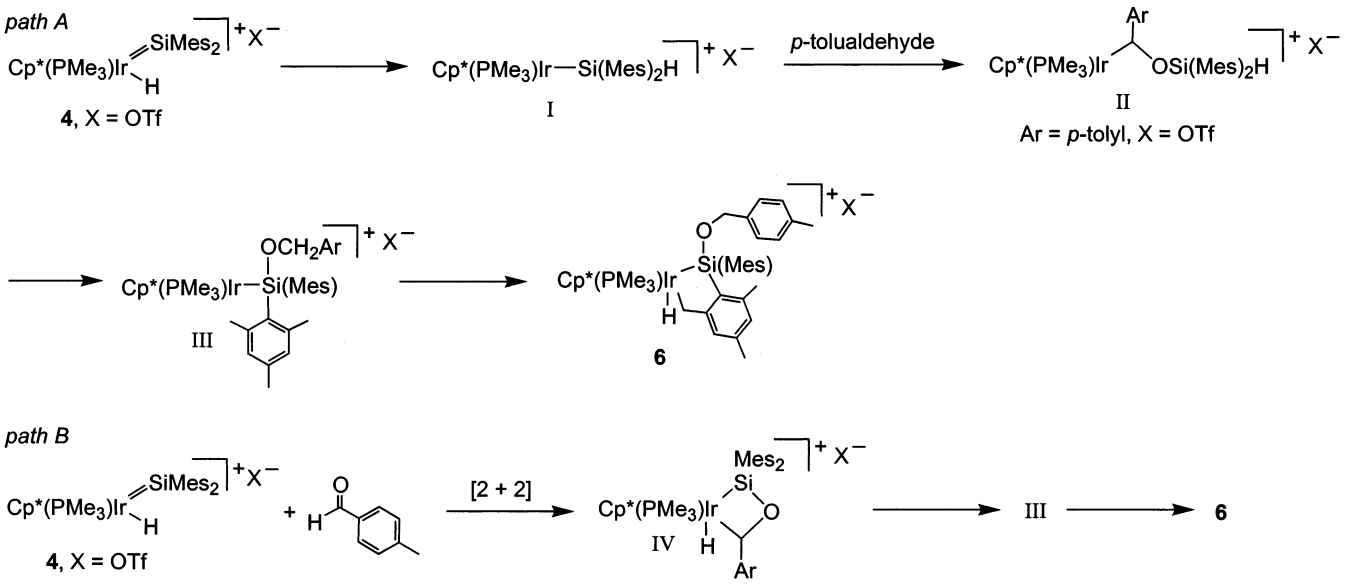


Again, however, complete conversion of **1** to a complex mixture of at least four new organometallic complexes was observed by ^{31}P NMR spectroscopy.

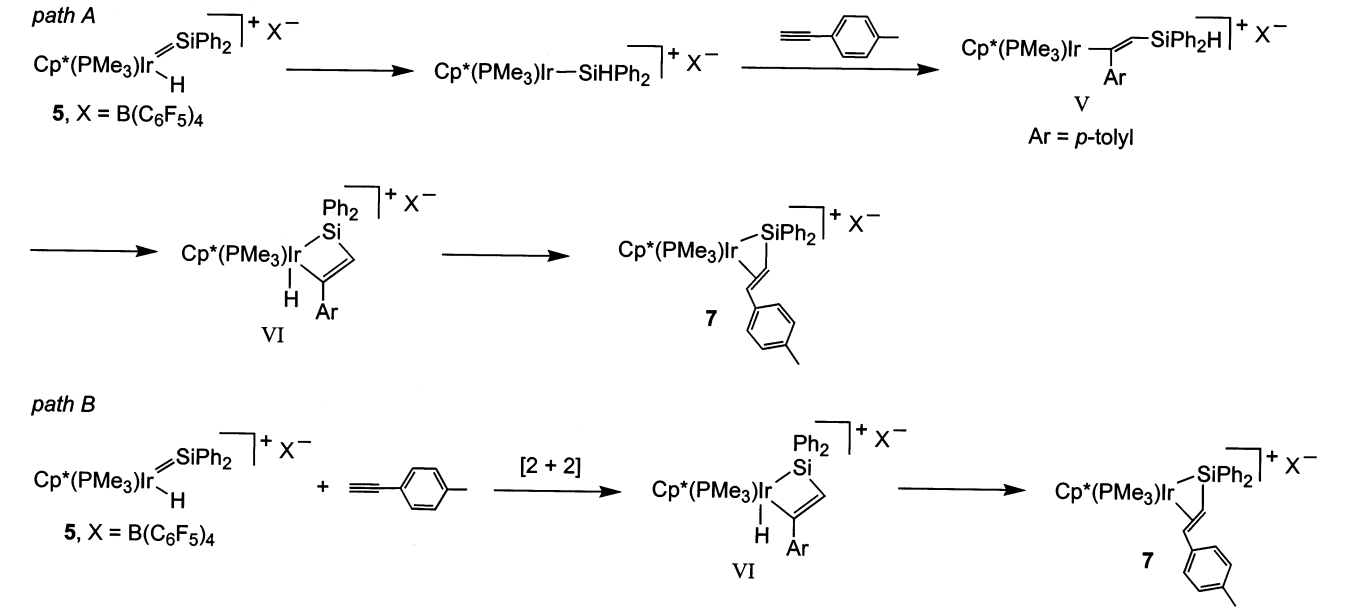
Discussion

Stoichiometric Reactivity. An insertion reaction that may have relevance as a step in catalytic hydrosilylation was discovered upon reaction of dimesitylsilylene complex **4** with *p*-tolualdehyde to give cyclometalated Ir(V) complex **6**. This reaction is rapid ($t_{1/2}$ < 5 min), and no intermediates are observed by ^{1}H and ^{31}P NMR spectroscopy. One mechanism for the formation of **6** involves a 1,2-hydride migration to produce an iridium silyl complex (**I**), which is capable of inserting

Scheme 3



Scheme 4



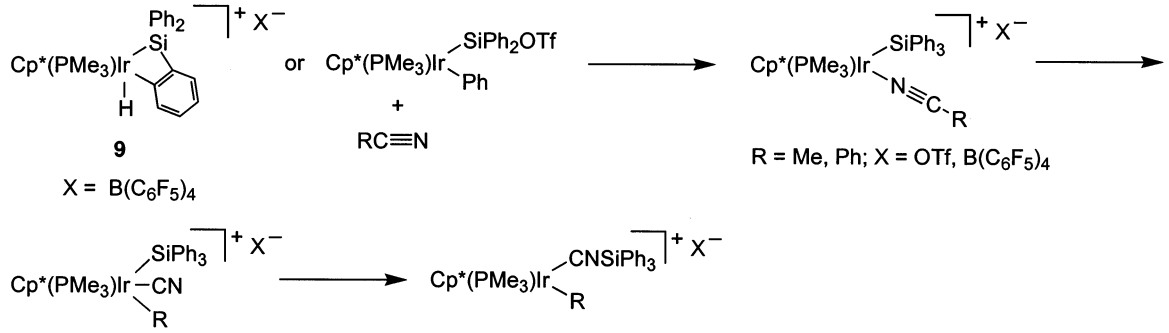
the aldehyde to form an Ir(III) alkyl complex (**II**) (Path A in Scheme 3). This species can then react with the pendant Si−H bond by oxidative addition, and then reductive elimination from the iridium center will form a new C−H bond and produce silyl intermediate **III**. The observed product **6** is then formed by cyclometalation of a silicon-bound mesityl group by oxidative addition. An alternative mechanism involves a [2+2] cycloaddition of the iridium silylene group with the carbonyl functionality to produce intermediate **IV** (Path B in Scheme 3). Carbon−hydrogen reductive elimination would provide intermediate **III** (as in Path A), which can then form the product as described. There is no evidence at this time to favor either of the mechanisms.[42] It should be noted that the degree of double bond character in late-metal silylene complexes such as **4** is predicted to be low,[43,44] making the possibility of a concerted [2+2] cycloaddition somewhat unlikely. Instead, reactions involving these polar metal−silicon bonds with unsaturated substrates can be expected to take place in two steps. In fact, there has been only one report involving cycloaddition reactions of silylene complexes, and evidence was presented that it proceeds in a stepwise fashion.[26]

Similar mechanistic steps can be proposed for the formation of pendant olefin complex **7** from diphenylsilylene complex **5** and 4-ethynyltoluene (eq 5). Again, insertion and cycloaddition mechanisms are both possible for this transformation (Scheme 4). For the insertion mechanism (Path A), a 1,2-hydride migration of **5** produces an iridium silyl intermediate that undergoes insertion to form an iridium alkenyl species (**V**). Activa-

(42) A referee has suggested an alternative mechanism involving coordination of *p*-tolualdehyde through its oxygen to the silylene ligand of **4**, followed by hydride migration to the carbonyl carbon of the aldehyde to give intermediate **III**. We cannot rule out this possibility on the basis of our observations at the present time.

(43) Cundari, T. R.; Gordon, M. S. *J. Phys. Chem.* **1993**, *96*, 631.
(44) Arnold, F. P. *Organometallics* **1999**, *18*, 4800.

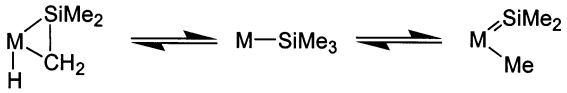
Scheme 5



tion of the Si−H bond by oxidative addition to produce an Ir(V) intermediate (**VI**), followed by C−H reductive elimination and olefin coordination, affords the observed product. An alternative mechanism involves cycloaddition to form an iridacycle (**VI**, Path B), which is capable of C−H reductive elimination to form an iridium silyl complex. Olefin coordination then results in formation of **7**.

The observation that cyclometalated iridium complex **9** can cleave the carbon−carbon bond of alkyl and aryl nitrile substrates follows closely the reactivity of the isostructural rhodium complex [Cp*(PMe$_3$)Rh(η^2-SiPh$_2$-(C$_6$H$_4$))(H)][B(C$_6$F$_5$)$_4$].[37] The postulated mechanism for nitrile cleavage can be seen in Scheme 5. It is likely that after the silyliridium acetonitrile complex is produced, C−C activation occurs to yield an iridium(V) species, [Cp*(PMe$_3$)Ir(SiPh$_3$)(CN)(CH$_3$)][B(C$_6$F$_5$)$_4$]. Migration of the silyl group to the nitrogen atom of the cyanide ligand completes the mechanism. The iridium complexes require elevated temperatures for this transformation, presumably because the acetonitrile ligand of the intermediate [Cp*(PMe$_3$)Ir(NCMe)(SiPh$_3$)][B(C$_6$F$_5$)$_4$] is more tightly bound in the third row transition metal complex. As a possible mechanism for the reaction of **9** with *p*-tolualdehyde, we suggest it may begin by insertion of the aldehyde into the Ir−Si bond to afford an iridium alkyl complex, followed by cyclometalation of a phenylsilicon C−H bond, alkyl C−H reductive elimination, and coordination of the oxygen to iridium to give product **10**.

Reactivity studies of the iridium silene complex **13** revealed an observable rearrangement to a cationic, base-stabilized iridium silylene complex. Berry and co-workers recently reported the first direct observation of intramolecular activation (or β-hydrogen elimination) of aliphatic C−H bonds in a 16-electron metal silyl complex to generate a silene complex, showing that a silene complex can be derived from a silyl complex.[4,45] Likewise, it has been shown that observable base-free silylene ligands may be derived from silyl ligands by α-migration.[28] Reactivity studies in the iridium system described here provide evidence for a third type of isomerization, involving silene and silylene ligands (eq 12). Whereas the free silene/silylene interconversion



(12)

between SiMe$_2$ and H$_2$C=Si(H)Me has been the topic of considerable experimental and theoretical investigation,[14] this is the first report of such a process within the coordination sphere of a transition metal.

Catalytic Reactivity. Catalytic transformations involving C−H bond activation and/or insertion at Ir(III) centers are exceedingly rare. One example involves use of [Cp*(PMe$_3$)Ir(H)(CH$_2$Cl$_2$)][HB(C$_6$F$_5$)$_3$] as a catalyst for transferring deuterium from C$_6$D$_6$ to organic substrates.[46] Another is the more recent isotopic labeling system comprised of Cp*(PMe$_3$)IrCl$_2$ and D$_2$O.[47] Smith and co-workers recently reported an iridium-catalyzed arene borylation method for which they propose an Ir(III)/Ir(V) oxidation state couple.[48] The slow development of C−H functionalization processes based on Ir(III) complexes is due in part to the reluctance of Ir(III) alkyl complexes to undergo insertion reactions. For example, once the β-H elimination products [Cp*(PMe$_3$)Ir(R)-(olefin)][X] are formed from C−H activation, neither olefin dissociation nor insertion are observed as clean reaction pathways.[13] In fact, high barriers for olefin insertion into the iridium−methyl bonds of [Cp(PH$_3$)-Ir(Me)]$^+$ have been calculated.[49,50] Since the complexes described here have the potential to behave as 16-electron Ir(III) silyl complexes, it was hoped that an examination of the insertion reactivity of these species would lead to a catalytic hydrosilylation processes involving an Ir(III)/Ir(V) oxidation state couple.

The iridium silylene complexes tested for catalytic hydrosilylation of ketones were clearly more active than the ruthenium silylene complexes. Although this may be due to a more readily accessed metal-mediated "Chalk−Harrod" mechanism,[14] the mixtures of organometallic products that result from catalytic hydrosilylation initiated by both the silyliridium and silylruthenium complexes have so far prevented extensive mechanistic insight into the reactions. Another likely possibility, Lewis acid catalysis that is either silicon- or iridium-centered, is considered based on a report by Piers and co-workers that the strong electrophile B(C$_6$F$_5$)$_3$ can catalyze ketone hydrosilylation.[41] Back-bonding in transition metal silylene complexes is predicted to be low.[43,44] In the limit that there is no back-bonding, the silylene complexes feature 6-electron silicon centers, which are isoelectronic with boranes, and would there-

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(49) Han, Y.; Deng, L.; Ziegler, T. *J. Am. Chem. Soc.* **1997**, *119*, 5939.
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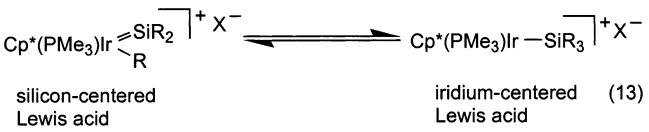
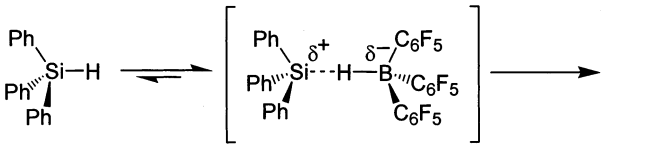
fore be referred to as metal-substituted silylium cations. Note that three-coordinate silyl cations which are not substituted by metal centers are very unstable,[51] with $[Mes_3Si][B(C_6F_5)_4]$ being the only well-established example.[52] The silicon- and iridium-centered Lewis acidic centers are interchanged by a 1,2-migration that is known to be facile[20] in this system (eq 13).



(13)

A direct comparison of the iridium silylene complexes with $B(C_6F_5)_3$ in hydrosilylation reactions offered an aid to our understanding of the reaction mechanism. Interestingly, it was found that catalysis by $B(C_6F_5)_3$ was substantially improved upon changing the reductant from H_2SiPh_2 to $HSiPh_3$. The iridium silylene complex **5** behaved in the opposite manner, with the less substituted silane giving superior performance. The results for borane catalysis can be interpreted upon consideration of the hydrosilylation mechanism advanced by Piers and co-workers,[41] which invokes an intermediate with positive charge buildup on silicon (eq 14). Such an intermediate would be more stabilized



Reduction (14)

through resonance if the silicon center were substituted by three, rather than two, phenyl rings. Although the iridium results are most readily interpreted by using steric arguments that would suggest reaction with a less hindered silane is more feasible, distinguishing between a metal-mediated and a Lewis acid mechanism appears to be difficult.

Conclusion

The reactivity of unsaturated organic substrates with late metal silyl complexes has not been fully developed, especially when compared to metal alkyl complexes.[14] The studies described here offer new findings in the stoichiometric reaction chemistry of Ir(III) silyl and silylene complexes, which hopefully can be used to develop new catalytic processes involving silanes. For example, a nitrile cleavage reaction was also discovered while studying the reactivity of silyliridium complexes. In the course of these reactivity studies, subsequent rearrangement of the initially formed insertion products made it difficult to learn the details of the putative insertion step.

The chemistry of metal complexes containing reactive silicon-based fragments is believed to be highly relevant to a number of catalytic processes. For example, a newly discovered dehydropolymerization of silanes to carbosilanes appears to involve silene complexes.[53] Also, considerable speculation has centered on the potential role of silylene complexes in the dehydrocoupling of silanes to polysilanes, and Berry has presented convincing evidence for participation of a germylene complex formed via α-migration in the demethanitive coupling of germanes to polygermanes.[54] Clearly, an understanding of the factors controlling the pathway for elimination reactions in metal silyl derivatives (e.g., α vs β) are key to development of catalytic reactions in these systems. In this context, the observed interconversion of the silene and silylene ligands is interesting in that it provides information regarding factors that might be used to control the course of reactions from a metal silene/silylene equilibrium manifold.

Iridium silyl and silylene complexes are catalysts for the hydrosilylation of ketones under mild conditions. The formation of multiple organometallic products during the catalysis made it difficult to study the mechanism of these catalyses, however, and in one case it was shown that the only detectable organometallic species in solution was not catalytically active. The facile decomposition of these silyliridium catalysts is a result of the large number of different reaction pathways available to them, including 1,2-migration to produce silylene complexes and cyclometalation to give Ir(V) complexes. If these complexes can be stabilized effectively against decomposition, an extension of this work to include catalytic, enantioselective reductions may be possible using chiral silylene complexes.

Experimental Section

General Procedures. Unless otherwise noted, reactions and manipulations were performed at 25 °C in an inert atmosphere (N_2) glovebox or with standard Schlenk and high vacuum or pressure techniques. Glassware was dried for a minimum of 12 h at temperatures of 150 °C or greater. All NMR spectra were obtained on Bruker AMX-400, AMX-300, and DRX-500 MHz spectrometers. The temperature for NMR experiments was controlled with BVT-1000 or BVT-3000 units. ^{1}H NMR chemical shifts (δ) are reported in parts per million (ppm) relative to tetramethylsilane and referenced to residual protiated solvent. Infrared (IR) spectra were recorded on a Mattson Instruments Galaxy 3000 Fourier transform spectrometer, and samples were prepared as KBr pellets. Mass spectrometric (MS) analyses were obtained at the University of California, Berkeley mass spectrometry facility on Micromass VG Quattro (equipped with ESI source), VT ProSpec, ZAB2-Eq, and 70-FE mass spectrometers. Elemental analyses were performed at the University of California, Berkeley Microanalytical facility on a Perkin-Elmer 2400 Series II CHNO/S Analyzer.

Sealed NMR tubes were prepared by attaching Cajon adapters directly to Kontes vacuum stopcocks and flame sealing. Reactions with gases and low-boiling liquids involved condensation of a calculated pressure of gas from a bulb of known volume into the reaction vessel at −196 °C. These vacuum transfers were accomplished with a digital MKS Baratron gauge attached to a high-vacuum line.

Materials. Unless otherwise noted, reagents were purchases from commercial suppliers and used without further purification. Celite (Aldrich) and alumina (Brockman I, Ald-

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rich) were dried at 250 °C for 48 h under vacuum. Pentane, hexanes, and benzene were passed through a column of activated alumina (A2, 12 × 32, Purifry Co.) collected under and sparged with N_2 prior to use.[55] Diethyl ether and tetrahydrofuran were distilled from sodium/benzophenone ketyl under N_2 and sparged with N_2 prior to use. Dichloromethane (Fisher) was either distilled from CaH_2 (Aldrich) under N_2 or passed through a column of activated alumina and collected under and sparged with N_2 prior to use. Deuterated solvents (Cambridge Isotope Laboratories) were purified by the same procedures used for their protiated analogues and vacuum transferred prior to use. Cp*$(PMe_3)_2RuCH_2SiMe_3$[56] and Cp*(PMe_3)Ir(Me)OTf[11] were made according to literature procedures. The Boulder Scientific Company is our supplier of $(Et_2O)_2LiB(C_6F_5)_4$.

{Cp*(PMe$_3$)Ir(H)[κ^2-Si(2-CH$_2$-3,5-(CH$_3$)$_2$C$_6$H$_2$)(Mes)(OCH$_2$-(*p*-tolyl))]}[OTf] (6). A solution of Cp*(PMe_3)Ir(Me)OTf (120 mg, 0.212 mmol) in 5 mL of CH_2Cl_2 was pipetted into a vial containing solid H_2SiMes_2 (56.8 mg, 0.212 mmol) and a magnetic stir bar. This solution was stirred for 24 h, and then *p*-tolualdehyde (24.9 μL, 0.212 mmol) was added by syringe. The solution was stirred an additional 30 min, and the solvent was then removed in vacuo. This afforded 169 mg (0.180 mmol, 85%) of **6** as an analytically pure yellow foam. ^{1}H NMR (500 MHz) δ 7.16 (s, 1H, Ar-*H*), 7.09 (m, 4H, Ar-*H*), 6.97 (s, 1H, Ar-*H*), 6.87 (s, 1H, Ar-*H*), 6.82 (s, 1H, Ar-*H*), 4.83 (d, J_{H-H} = 12 Hz, 1H, diastereotopic OC*H*$_2$Ar), 4.43 (d, J_{H-H} = 12 Hz, 1H, diastereotopic O-C*H*$_2$Ar), 3.49 (d, J_{H-H} = 14 Hz, 1H, diastereotopic Ir-C*H*$_2$), 2.90 (vt, J_{H-H} = 14 Hz, 1H, diastereotopic Ir−C*H*$_2$), 2.74 (s, 3H, Ar-*Me*), 2.34 (s, 3H, Ar-*Me*), 2.30 (m, 9H, overlapping Ar-*Me*), 1.75 (s, 3H, Ar-*Me*), 1.67 (d, J_{P-H} = 1.6 Hz, 15H, C$_5$*Me*$_5$), 1.45 (d, J_{P-H} = 11 Hz, 9H, P*Me*$_3$), −14.7 (d, J_{P-H} = 20 Hz, 1H, Ir-*H*). ^{13}C{^{1}H} NMR (126 MHz) (the CF_3 group was not detectable within a reasonable number of scans) δ 152.9 (s, Ar-*C*), 145.0 (s, Ar-*C*), 144.3 (s, Ar-*C*), 142.3 (s, Ar-*C*), 140.9 (s, Ar-*C*), 140.8 (s, Ar-*C*), 139.7 (s, Ar-*C*), 137.7 (s, Ar-*C*), 137.1 (s, Ar-*C*), 130.4 (s, Ar-*C*H), 130.2 (s, Ar-*C*H), 129.5 (s, Ar-*C*H), 129.0 (s, Ar-*C*H), 127.5 (s, Ar-*C*H), 104.4 (d, J_{P-C} = 1.3 Hz, *C*$_5$Me$_5$), 67.8 (s, O*C*H$_2$Ar), 25.0 (s, Ar-*Me*), 23.7 (s, Ar-*Me*), 23.0 (s, Ar-*Me*), 21.3 (s, Ar-*Me*), 21.3 (s, Ar-*Me*), 16.7 (d, J_{P-C} = 43 Hz, P*Me*$_3$), 13.0 (d, J_{P-C} = 10 Hz, Ir-*C*H$_2$), 8.9 (s, C$_5$*Me*$_5$). ^{31}P{^{1}H} NMR (162 MHz) δ −33.4. ^{29}Si NMR (INEPT, 99 MHz) 32.9 (d, J_{Si-P} = 14 Hz). ^{19}F{^{1}H} NMR (376 MHz) δ −77.0. IR 2980, 2871, 2920, 2163 (Ir-H), 1601, 1452, 1274, 1154, 1078, 1032, 949, 854, 799, 745, 637 cm^{-1}. Anal. Calcd for $C_{40}H_{55}PIrSiO_4SF_3$: C, 51.10; H, 5.90. Found: C, 51.37, H, 6.13.

{Cp*(PMe$_3$)Ir[SiPh$_2$(η^2-CHCH(*p*-tolyl))]}[B(C$_6$F$_5$)$_4$] (7). To a 1 mL CH_2Cl_2 solution of Cp*(PMe_3)Ir(Me)OTf (**1**) (50.0 mg, 0.0881 mmol) was added H_2SiPh_2 (16.4 mL, 0.0881 mmol) by syringe, and the solution mixed well with a pipet. This solution was added to solid $(Et_2O)_2LiB(C_6F_5)_4$ (73.5 mg, 0.0881 mmol). The resulting slurry was mixed for 30 s with a pipet, and then filtered through fiberglass into a vial. The fiberglass and solids were washed with an additional 1 mL of CH_2Cl_2. To the filtrate was added 4-ethynyltoluene (11.2 mL, 0.0881 mmol) by syringe, and the reaction mixed with a pipet for 10 s. The reaction mixture was allowed to stand for 30 min, and then the solvent was removed in vacuo. This afforded 116 mg (0.0842 mmol, 95%) of **7** as an analytically pure pale yellow foam. ^{1}H NMR (500 MHz) δ 7.83 (m, 2H, Ar-*H*), 7.70 (d, J_{H-H} = 6.8 Hz, 2H, Ar-*H*), 7.15−7.50 (m, 10H, Ar-*H*), 5.29 (vt, J_{H-H} = 14 Hz, 1H, alkenyl), 3.52 (d, J_{H-H} = 15 Hz, 1H, alkenyl), 2.37 (s, 3H, Ar-*Me*), 1.42 (d, J_{P-H} = 9.8 Hz, 9H, P*Me*$_3$), 1.38 (d, J_{P-H} = 1.6 Hz, 15H, C$_5$*Me*$_5$). ^{13}C{^{1}H} NMR (126 MHz) δ 149.8 (m, B(*C*$_6$F$_5$)), 147.9 (m, B(*C*$_6$F$_5$)), 139.8 (m, B(*C*$_6$F$_5$)), 139.1 (s, Ar-*C*), 137.9 (m, B(*C*$_6$F$_5$)), 136.4 (s, Ar-*C*H), 135.4 (s, Ar-*C*), 135.2 (s, Ar-*C*H), 131.5 (s, Ar-*C*H), 131.5 (s, Ar-*C*), 131.3 (s, Ar-*C*H), 130.0 (s, Ar-*C*H), 129.9 (s, Ar-*C*H), 129.3 (s, Ar-*C*H), 129.0 (s, Ar-*C*), 128.3 (s, Ar-*C*H), 100.8 (d, J_{P-C} = 1.3 Hz, *C*$_5$-Me$_5$), 66.3 (s, alkenyl-*C*H), 38.6 (s, alkenyl-*C*H), 21.4 (s, Ar-*Me*), 19.5 (d, J_{P-C} = 42 Hz, P*Me*$_3$), 9.31 (s, C$_5$*Me*$_5$). ^{31}P{^{1}H} NMR (162 MHz) δ −46.2. ^{19}F{^{1}H} NMR (376 MHz) δ −133 (s), −164 (t, J_{B-F} = 19 Hz), −167 (s). ^{29}Si NMR (INEPT, 99 MHz) −5.1 (d, J_{Si-P} = 15 Hz). ^{19}F{^{1}H} NMR (376 MHz) δ −133 (s), −164 (t, J_{B-F} = 19 Hz), −167 (s). IR 3016, 2919, 2149, 1642, 1512, 1459, 1380, 1275, 1098, 950, 773, 705, 488 cm^{-1}. Anal. Calcd for $C_{58}H_{43}PIrSiBF_{20}$: C, 50.41; H, 3.14. Found: C, 50.14, H, 2.98.

Cp*(PMe$_3$)[SiPh$_2$N(SiMe$_3$)$_2$]H (8). To a vial containing 4 mL of a CH_2Cl_2 solution of Cp*(PMe_3)Ir(Me)OTf (98.9 mg, 0.174 mmol) was added H_2SiPh_2 (32.4 μL, 0.174 mmol) by syringe. After the resulting yellow solution was manually agitated for 10 s, the solvent was removed in vacuo. The residue was dissolved in 3 mL of THF and to this was added a THF (2 mL) solution of $KN(TMS)_2$ (34.8 mg, 0.174 mmol). The color of the solution changed to a dark amber yellow and the solution was allowed to stand for 5 min. The solvent was then removed in vacuo, producing a light brown residue, which was extracted with pentane (3 × 2 mL). The extracts were filtered through a fiberglass plug, and the filtrate solvent removed in vacuo. The resulting oil was redissolved in 2 mL of pentane and filtered through a plug (2 cm × 0.5 cm) of silanized silica gel, and the plug was washed with 2 × 2 mL of fresh pentane. The filtrate was removed in vacuo to afford 99.3 mg of a light amber oil (0.133 mmol, 76%). Material obtained in this fashion is 80% pure by ^{1}H NMR integration of the product resonances against those of an internal standard. Conditions could not be found to induce crystallization, and satisfactory elemental analysis could not be obtained. ^{1}H NMR (500 MHz) δ 7.61 (d, J_{P-H} = 7 Hz, 4 H, Ar-*H*), 7.24 (m, 6H, Ar-*H*), 1.75 (s, 15 H, C$_5$*Me*$_5$), 1.48 (d, J_{P-H} = 10 Hz, P*Me*$_3$), 0.083 (s, 18 H, Si*Me*$_3$), −18.1 (d, J_{P-H} = 28 Hz, Ir-*H*). ^{13}C{^{1}H} NMR (126 MHz) δ 146.4 (s, Ar-*C*), 145.4 (s, Ar-*C*), 135.5 (s, Ar-*C*H), 135.3 (s, Ar-*C*H), 126.8 (s, Ar-*C*H), 126.8 (s, Ar-*C*H), 126.4 (s, Ar-*C*H), 126.4 (s, Ar-*C*H), 94.2 (d, J_{P-C} = 3 Hz, *C*$_5$-Me$_5$), 22.4 (d, J_{P-C} = 38 Hz, P*Me*$_3$), 10.1 (s, C$_5$*Me*$_5$), 1.8 (s, Si*Me*$_3$). ^{31}P{^{1}H} NMR (162 MHz) δ −50.9. ^{29}Si NMR (INEPT, 99 MHz) δ 3.9. IR 3050, 2966, 2919, 2861, 2128 (Ir-H), 1477, 1426, 1379, 1254, 1105, 1027, 953, 835, 738, 679, 531, 491, 442 cm^{-1}.

[Cp*(PMe$_3$)Ir(Me)(CNSiPh$_3$)][OTf] (11b). A solution of Cp*(PMe_3)Ir(Me)OTf (91.2 mg, 0.161 mmol) in 4 mL of CH_2Cl_2 was added to a solution of $HSiPh_3$ (41.9 mg, 0.161 mmol) in 1 mL of CH_2Cl_2. To the resulting light yellow solution was added acetonitrile (10.0 μL, 0.193 mmol) by syringe, and the entire solution was then transferred to a 25-mL glass vessel sealed to a Kontes vacuum adapter that contained a magnetic stir bar. The stirred solution was heated to 75 °C for 24 h. After cooling to room temperature, the reaction mixture was transferred to a vial and the solvent was removed in vacuo. An attempted recrystallization of the resulting pale yellow foam from CH_2Cl_2/pentane at −35 °C yielded a light yellow oil that was separated by removing the supernatant with a pipet. This oil was triturated with Et_2O (3 × 2 mL) to give 97.5 mg of a light yellow solid (0.114 mmol, 71%). ^{1}H NMR (500 MHz) δ 7.61 (m, 8H, Ar-*H*), 7.53 (m, 7H, Ar-*H*), 1.86 (d, J_{P-H} = 2 Hz, 15H, C$_5$*Me*$_5$), 1.47 (d, J_{P-H} = 11 Hz, 9H, P*Me*$_3$), 0.44 (d, J_{P-H} = 7 Hz, 3H, Ir-*Me*). ^{13}C{^{1}H} NMR (126 MHz) δ 151.9 (d, J_{P-C} = 14 Hz, Ir-*C*NSiPh$_3$), 135.4 (s, Ar-*C*H), 132.4 (s, Ar-*C*H), 129.7 (s, Ar-*C*), 129.2 (s, Ar-*C*H), 99.5 (d, J_{P-C} = 3 Hz, *C*$_5$Me$_5$), 15.4 (d, J_{P-C} = 41 Hz, P*Me*$_3$), 9.3 (s, C$_5$*Me*$_5$), −26.2 (d, J_{P-C} = 8 Hz, Ir-*Me*). ^{31}P{^{1}H} NMR (162 MHz) δ −37.0. ^{29}Si NMR (INEPT, 99 MHz) δ −151.1. ^{19}F{^{1}H} NMR (376 MHz) δ −77.0. IR 2961, 2917, 2057, 1429, 1291, 1230, 1160, 1117, 1029, 955, 857, 743, 709, 638, 516 cm^{-1}. Satisfactory elemental analysis could not be obtained, despite several attempts.

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[Cp*(PMe$_3$)Ir(Ph)(CNSiPh$_3$)][OTf] (12b). A solution of Cp*(PMe$_3$)Ir(Me)OTf (105.5 mg, 0.1859 mmol) in 4 mL of CH_2Cl_2 was added to a solution of $HSiPh_3$ (48.4 mg, 0.186 mmol) in 1 mL of CH_2Cl_2. To the resulting light yellow solution was added benzonitrile (18.9 μL, 0.186 mmol) by syringe, and the entire solution was transferred to a 25-mL glass vessel sealed to a Kontes vacuum adapter that contained a magnetic stir bar. The stirred solution was heated to 45 °C for 5 h. After cooling to room temperature, the reaction mixture was transferred to a vial and the solvent was removed in vacuo. The resulting pale yellow foam was recrystallized at −35 °C from CH_2Cl_2/pentane to give a single crop of off-white crystals (95.0 mg, 0.104 mmol) in 56% yield. ^{1}H NMR (500 MHz) δ 7.62−7.71 (m, 9H, Ar-*H*), 7.54 (m, 6H, Ar-*H*), 7.20 (d, J_{H-H} = 8 Hz, 2H, Ar-*H*), 7.02 (t, J_{H-H} = 8 Hz, 2H, Ar-*H*), 6.96 (t, J_{H-H} = 8 Hz, 2H, Ar-*H*), 1.80 (d, J_{P-H} = 2 Hz, 15H, C$_5$*Me*$_5$), 1.42 (d, J_{P-H} = 11 Hz, 9H, P*Me*$_3$). ^{13}C{^{1}H} NMR (126 MHz) δ 139.5 (s, Ar-*C*), 135.0 (s, Ar-CH), 132.1 (s, Ar-CH), 129.2 (s, Ar-CH), 128.8 (s, Ar-CH), 128.6 (s, Ar-C), 127.7 (s, Ar-CH), 125.5 (d, J_{P-C} = 16 Hz, Ir-*C*), 124.2 (s, Ar-CH), 100.4 (s, *C*$_5$Me$_5$), 15.1 (d, J_{P-C} = 43 Hz, P*Me*$_3$), 8.9 (s, C$_5$*Me*$_5$). ^{31}P{^{1}H} NMR (162 MHz) δ −35.8. ^{29}Si NMR (INEPT, 99 MHz) −17.6. ^{19}F{^{1}H} NMR (376 MHz) δ −77.0. IR 3063, 2986, 2917, 2067 (C-N), 1570, 1428, 1366, 1274, 1201, 1156, 1031, 951, 858, 740, 705, 635, 512 cm^{-1}. Anal. Calcd for $C_{39}H_{44}PIrNSiO_3SF_3$: C, 51.19; H, 4.85; N, 1.53; S, 3.50. Found: C, 50.85; H, 4.68; N, 1.48; S, 3.81.

[Cp*(PMe$_3$)Ir(SiPh$_3$)(CO)][B(C$_6$F$_5$)$_4$] (13). To solid $HSiPh_3$ (53.1 mg, 0.204 mmol) was added 5 mL of a CH_2Cl_2 solution of Cp*(PMe$_3$)Ir(Me)OTf (**1**) (116 mg, 0.204 mmol). The resulting pale yellow solution was mixed thoroughly with a pipet for 20 s, then added to solid $(Et_2O)_2LiB(C_6F_5)_4$ (170 mg, 0.204 mmol). The slurry produced was mixed for 10 s with a pipet, then filtered through a Celite/fiberglass plug to give a golden solution. This solution was diluted to a total volume of 10 mL with added CH_2Cl_2 and transferred to a 50-mL glass vessel sealed to a Kontes vacuum adapter. The solution was degassed and placed under CO (1 atm). The solution was stirred for 24 h and the solvent was removed in vacuo. Attempted crystallization from CH_2Cl_2/pentane at −35 °C produced a light yellow oil that was isolated by decanting the supernatant and washing with 2 mL of fresh pentane. The oil was dried in vacuo, producing 232 mg (0.169 mmol, 83%) of **13** as an analytically pure off-white foam. ^{1}H NMR (500 MHz) δ 7.54 (m, 6H, Ar-*H*), 7.41 (m, 9H, Ar-*H*), 1.79 (d, J_{P-H} = 2 Hz, 15 H, C$_5$*Me*$_5$), 1.41 (d, J_{P-H} = 11 Hz, 9H, P*Me*$_3$). ^{13}C{^{1}H} NMR (126 MHz) δ 169.3 (d, J_{P-C} = 11 Hz, Ir-*C*O), 149.9 (m, B(*C*$_6$F$_5$), 138.0 (m, B(*C*$_6$F$_5$)), 137.2 (s, Ar-*C*H), 136.8 (s, Ar-*C*), 136.0 (m, B(*C*$_6$F$_5$)), 129.8 (s, Ar-*C*H), 128.0 (s, Ar-*C*H), 124.0 (m, B(*C*$_6$F$_5$)), 104.9 (d, J_{P-C} = 2 Hz, *C*$_5$Me$_5$), 18.1 (d, J_{P-C} = 42 Hz, P*Me*$_3$), 9.2 (s, C$_5$*Me*$_5$). ^{31}P{^{1}H} NMR (162 MHz) δ −49.2. ^{29}Si NMR (INEPT, 99 MHz) δ −7.5. ^{19}F{^{1}H} NMR (376 MHz) δ −133 (s), −164 (t, J_{B-F} = 19 Hz), −167 (s). IR 3073, 3015, 2964, 2920, 2029 (Ir−CO), 1643, 1512, 1480, 1275, 1087, 972, 773, 704, 661, 496 cm^{-1}. Anal. Calcd for $C_{56}H_{39}PIrSiOBF_{20}$: C, 49.10; H, 2.87. Found: C, 48.94, H, 3.09.

[Cp*(PMe$_3$)Ir(SiPh$_3$)(H)$_2$][B(C$_6$F$_5$)$_4$] (14). To solid $HSiPh_3$ (40.3 mg, 0.155 mmol) was added a 5 mL CH_2Cl_2 solution of Cp*(PMe$_3$)Ir(Me)OTf (**1**) (87.9 mg, 0.155 mmol). A pipet was used to mix the resulting pale yellow solution thoroughly for 20 s, followed by addition of the reaction mixture to solid $(Et_2O)_2LiB(C_6F_5)_4$ (131 mg, 0.155 mmol). The slurry produced was mixed for 10 s with a pipet and filtered through a Celite/fiberglass plug to give a golden solution. This solution was diluted to a total volume of 10 mL with fresh CH_2Cl_2 and transferred to a 50-mL glass vessel sealed to a Kontes vacuum adapter. Three freeze−pump−thaw cycles were used to degas the solution, which was then placed under H_2 (1 atm). The solution was stirred for 24 h and the solvent was removed in vacuo. Attempted crystallization from CH_2Cl_2/pentane at −35 °C produced a light yellow oil that was isolated by decanting the supernatant and washing with 2 mL of fresh pentane. The oil was dried in vacuo, producing 181 mg (0.135 mmol, 87%) of **14** as an analytically pure off-white foam. ^{1}H NMR (500 MHz) δ 7.64 (m, 6H, Ar-*H*), 7.41 (m, 9H, Ar-*H*), 1.78 (s, 15 H, C$_5$*Me*$_5$), 1.41 (d, J_{P-H} = 11 Hz, 9H, P*Me*$_3$), −14.5 (d, J_{P-H} = 24 Hz, 2H, Ir-*H*). ^{13}C{^{1}H} NMR (126 MHz) δ 149.9 (m, B(*C*$_6$F$_5$), 138.0 (m, B(*C*$_6$F$_5$)), 137.7 (s, Ar-*C*), 136.7 (s, Ar-*C*H), 136.0 (m, B(*C*$_6$F$_5$)), 130.5 (s, Ar-*C*H), 128.8 (s, Ar-*C*H), 124.0 (m, B(*C*$_6$F$_5$)), 103.1 (s, *C*$_5$Me$_5$), 20.2 (d, J_{P-C} = 44 Hz, P*Me*$_3$), 9.2 (s, C$_5$*Me*$_5$). ^{31}P{^{1}H} NMR (162 MHz) δ −42.7. ^{29}Si NMR (INEPT, 99 MHz) δ −3.3. ^{19}F{^{1}H} NMR (376 MHz) δ −133 (s), −164 (t, J_{B-F} = 19 Hz), −167 (s). IR 3074, 3013, 2917, 2142 (Ir-H), 1642, 1510, 1490, 1382, 1275, 1098, 975, 861, 755, 684, 504 cm^{-1}. Anal. Calcd for $C_{55}H_{41}PIrSiBF_{20}$: C, 49.15; H, 3.08. Found: C, 48.77; H, 3.45.

{Cp*(PMe$_3$)Ir[κ_2-(C$_6$H$_4$-2-SiPh$_2$)(OCH$_2$(*p*-tolyl))]}-[B(C$_6$F$_5$)$_4$] (15). To 1 mL of a CH_2Cl_2 solution of Cp*(PMe$_3$)Ir(Me)OTf (**1**, 115 mg, 0.203 mmol) was added 2 mL of a CH_2Cl_2 solution of $HSiPh_3$ (52.8 mg, 0.203 mmol) in a 20-mL scintillation vial. The resulting pale yellow solution was well mixed with a pipet, and then was added to solid $(Et_2O)_2LiB(C_6F_5)_4$ (169 mg, 0.203 mmol) in another vial. The resulting yellow slurry was mixed for 30 s with a pipet, then filtered through fiberglass into a 5-mL vial. To this was added *p*-tolualdehyde (23.9 μL, 0.203 mmol) by syringe. The solution was mixed with a pipet for 30 s and allowed to stand for 20 min. The solvent was removed in vacuo, leaving a light yellow residue. The residue was dissolved in 1 mL of Et_2O then eluted through a pipet column (0.5 cm × 3 cm) of silanized silica gel with Et_2O, and the yellow band was collected. The solvent was removed in vacuo and the resulting yellow residue was recrystallized from Et_2O/pentane, yielding 143 mg (0.0974 mmol, 48%) of analytically pure **15**. ^{1}H NMR (500 MHz) δ 7.15−7.58 (m, 15H, Ar-*H*), 6.95 (d, J_{H-H} = 8 Hz, 2H, Ar-*H*), 6.75 (d, J_{H-H} = 8 Hz, 2H, Ar-*H*), 5.55 (d, J_{H-H} = 12 Hz, 1H, diastereotopic OC*H*$_2$), 4.80 (d, J_{H-H} = 12 Hz, 1H, diastereotopic OC*H*$_2$), 2.23 (s, 3H, Ar-*Me*), 1.41 (d, J_{P-H} = 2 Hz, 15H, C$_5$*Me*$_5$), 1.23 (d, J_{P-H} = 10 Hz, 9H, P*Me*$_3$). ^{13}C{^{1}H} NMR (126 MHz) δ 156.8 (d, J_{P-C} = 15 Hz, Ir-*C*), 149.9 (m, B(*C*$_6$F$_5$), 141.1 (s, Ar-*C*), 139.7 (Ar-*C*), 138.0 (m, B(*C*$_6$F$_5$)), 137.1 (s, Ar-*C*H), 136.9 (s, Ar-*C*H), 136.2 (s, Ar-*C*H), 136.2 (s, Ar-*C*H), 136.0 (m, B(*C*$_6$F$_5$)), 133.5 (s, Ar-*C*), 132.9 (s, Ar-*C*), 132.5 (s, Ar-*C*), 132.3 (s, Ar-*C*H), 131.9 (s, Ar-*C*H), 131.9 (s, Ar-*C*H), 130.2 (Ar-*C*H), 130.0 (s, Ar-*C*H), 129.3 (s, Ar-*C*H), 129.0 (s, Ar-*C*H), 124.0 (m, B(*C*$_6$F$_5$)), 124.0 (s, Ar-*C*H), 95.5 (d, J_{P-C} = 3 Hz, *C*$_5$Me$_5$), 77.6 (s, O*C*H$_2$), 21.3 (s, Ar-*Me*), 14.9 (d, J_{P-C} = 39 Hz, P*Me*$_3$), 9.6 (s, C$_5$*Me*$_5$). ^{31}P{^{1}H} NMR (162 MHz) δ −23.4. ^{29}Si NMR (INEPT, 99 MHz) δ 14.0. ^{19}F{^{1}H} NMR (376 MHz) δ −133 (s), −164 (t, J_{B-F} = 19 Hz), −167 (s). IR 3034, 2922, 2036, 1643, 1512, 1460, 1380, 1273, 1090, 1022, 978, 811, 756, 700, 582, 518, 479 cm^{-1}. Anal. Calcd for $C_{63}H_{47}PIrSiOBF_{20}$: C, 51.75; H, 3.24. Found: C, 51.35; H, 3.53.

[Cp*(PMe$_3$)Ir(SiMe$_2$(py))(Me)][B(C$_6$F$_5$)$_4$] (18). A 50-mL glass vessel sealed to a Kontes vacuum adapter was charged with 5 mL of a CH_2Cl_2 solution of Cp*(PMe$_3$)Ir(Me)OTf (147.7 mg, 0.2603 mmol). The vessel was then degassed with 3 freeze−pump−thaw cycles. Into the vessel was condensed $HSiMe_3$ (74 Torr, 0.26 mmol) at −196 °C, using a bulb of known volume (66 mL). The vessel was then warmed to 25 °C, and the solvent was removed in vacuo to afford Cp*(PMe$_3$)Ir(SiMe$_2$OTf)(Me) as a light yellow oil. This oil (134 mg, 0.214 mmol) was dissolved in 4 mL of CH_2Cl_2 and pipetted onto solid $(Et_2O)_2LiB(C_6F_5)_4$ (179 mg, 0.214 mmol). The resulting light yellow slurry was agitated with a pipet for 20 s and then filtered through a fiberglass plug. Pyridine (17.3 mL, 0.214 mmol) was then added to the filtrate. After the reaction mixture was allowed to stand for 5 min, the solution was concentrated to 2 mL, and then Et_2O was added until precipitation occurred. The slurry was then filtered through a fiberglass plug and stored at −35 °C for 36 h. Yellow crystals (69 mg) were then isolated by removing the mother liquors

with a pipet, washing the crystals with 3 mL of pentane, and drying in vacuo. A second crop of crystals was grown by concentrating the mother liquors to 1 mL in vacuo, adding Et_2O until precipition occurred, filtering the slurry through a fiberglass plug, and storing the resulting solution at −35 °C for 36 h. The combined yield of analytically pure yellow crystals from the two crops was 200 mg (0.162 mmol, 75%). ^{1}H NMR (400 MHz) δ 8.67 (d, ^3J = 5.2 Hz), 2H, py), 8.36 (t, J_{H-H} = 7.5 Hz, 1H, py), 7.95 (t, J_{H-H} = 7.0 Hz, 2H, py), 1.58 (d, J_{P-H} = 1.7 Hz, 15 H, C_5Me_5), 1.50 (d, J_{P-H} = 9.6 Hz, 9 H, PMe_3), 0.74 (s, 3H, Si-*Me*), 0.53 (s, 3H, Si-*Me*), 0.26 (d, J_{P-H} = 6.3 Hz, 3H, Ir-*Me*). ^{13}C{^{1}H} NMR (126 MHz) δ 149 (m, B(C_6F_5), 146.3 (s, py), 144.1 (s, py), 139 (m, B(C_6F_5)), 136 (m, B(C_6F_5)), 124 (m, B(C_6F_5)),127.2 (s, py), 96.5 (s, C_5Me_5), 18.1 (d, J_{P-C} = 40 Hz, P*Me*$_3$), 9.3(C_5Me_5), 7.4 (s, Si-*Me*), 6.7 (s, Si-*Me*), −10.1 (d, J_{P-C} = 8.8 Hz, Ir-*Me*). ^{31}P NMR (162 MHz) δ −44.3 (s). ^{19}F NMR (376 MHz) δ −133 (s), −164 (t, J_{B-F} = 19 Hz), −167 (s). ^{29}Si NMR (99 MHz) δ 49.0 (d, J_{P-Si} = 20 Hz). IR 2924, 1643, 1514, 1466, 1277, 1085, 979, 956, 833, 792, 770, 755, 682, 660. Anal. Calcd for $C_{45}H_{38}F_{20}IrNPSi$: C, 43.77; H, 3.10; N, 1.13. Found: C, 43.73; H, 3.04; N, 1.09.

[Cp*(PMe$_3$)Ir(SiMe$_2$(py))(Me)][OTf] (19). A 20-mL scintillation vial was charged with 2 mL of a CH_2Cl_2 solution of Cp*(PMe$_3$)Ir(SiMe$_2$OTf)(Me) (41.3 mg, 0.0660 mmol) and a magnetic stir bar. To this stirred solution was added pyridine (8.0 mL, 0.990 mmol) by syringe, and the reaction mixture was stirred for 90 min. The volatile materials were removed in vacuo and the resulting foam washed with 1:1 Et_2O/pentane (2 × 5 mL). The product was then dried in vacuo, affording 45.4 mg (0.647 mmol, 98%) of **19** as an analytically pure yellow oil. ^{1}H NMR (400 MHz) δ 8.67 (d, J_{H-H} = 5.2 Hz, 2H, py), 8.36 (t, J_{H-H} = 7.5 Hz, 1H, py), 7.95 (t, J_{H-H} = 7.0 Hz, 2H, py), 1.58 (d, J_{P-H} = 1.7 Hz, 15H, C_5Me_5), 1.50 (d, J_{P-H} = 9.6 Hz, 9H, P*Me*$_3$), 0.74 (s, 3H, Si-*Me*), 0.53 (s, 3H, Si-*Me*), 0.26 (d, J_{P-H} = 6.3 Hz, 3H, Ir-*Me*). ^{13}C{^{1}H} NMR (126 MHz) δ 146.3 (s, py), 144.4 (s, py), 127.5 (s, py), 96.3 (s, C_5Me_5), 18.1 (d, J_{P-C} = 40 Hz, P*Me*$_3$), 9.3(s, C_5Me_5), 7.4 (s, Si-*Me*), 6.5 (s, Si-*Me*), −10.1 (d, J_{P-C} = 8.8 Hz, Ir-*Me*). ^{31}P{^{1}H} NMR (162 MHz) δ −44.3 (s). ^{19}F{^{1}H} NMR (376 MHz): δ −78.9 (s). ^{29}Si{^{1}H} NMR (99 MHz) δ 49.0 (d, J_{P-Si} = 20 Hz). IR 2923, 1780, 1646, 1599, 1448, 1320, 1259, 1025, 697. Anal. Calcd for $C_{22}H_{38}F_3IrNPO_3SSi$: C, 37.49; H, 5.43; N, 1.99. Found: C, 37.62; H, 5.77; N, 1.64.

[Cp*(PMe$_3$)Ir(SiMe$_3$)(CO)][B(C$_6$F$_5$)$_4$] (20). A 50-mL glass vessel sealed to a Kontes vacuum adapter was charged with 5 mL of a CH_2Cl_2 solution of Cp*(PMe$_3$)Ir(Me)OTf (119.5 mg, 0.2106 mmol). The vessel was then degassed with 3 freeze−pump−thaw cycles. Into the vessel was condensed $HSiMe_3$ (59 Torr, 0.21 mmol) at −196 °C, using a bulb of known volume (66 mL). The vessel was then warmed to 25 °C, and the resulting solution was pipetted onto solid $(Et_2O)_2LiB(C_6F_5)_4$ (175.7 mg, 0.2106 mmol). The slurry produced in this manner was mixed for 20 s with a pipet and then filtered through fiberglass into another 50-mL glass vessel sealed to a Kontes vacuum adapter that contained a magnetic stir bar. This vessel was degassed with 3 freeze−pump−thaw cycles and filled with 1 atm of CO. The contents of the vessel were allowed to stir for 24 h, transferred to a vial, and then reduced in volume to 1 mL in vacuo. Pentane was added until precipitation occurred, and then CH_2Cl_2 was added until the solution was again homogeneous. The resulting solution was filtered through a fiberglass plug and cooled to −35 °C for 12 h. The supernatant was removed with a pipet, and the crystals were washed with 3 mL of pentane and dried in vacuo. A second crop of crystals was grown by concentrating the mother liquors, adding pentane until precipitation occurred, filtering the solution through a fiberglass plug, and cooling the resulting solution to −35 °C for 24 h. The combined yield of analytically pure off-white crystals was 172 mg (0.146 mmol, 69%). ^{1}H NMR (400 MHz) δ 2.10 (d, J_{P-H} = 2.1 Hz, 15H, C_5Me_5), 1.79 (d, J_{P-H} = 10.7 Hz, 9H, P*Me*$_3$), 0.56 (s, 3H, Si*Me*$_3$). ^{13}C{^{1}H} NMR (126 MHz) δ 168.9 (s, *C*O), 149 (m, B(C_6F_5), 139 (m, B(C_6F_5)), 136 (m, B(C_6F_5)), 124 (m, B(C_6F_5)), 104.6 (s, C_5Me_5), 19.0 (d, J_{P-C} = 41 Hz, P*Me*$_3$), 10.4(s, C_5Me_5), 6.1(s, $SiMe_3$). ^{31}P{^{1}H} NMR (162 MHz) δ −49.4 (s). ^{19}F{^{1}H} NMR (376 MHz) δ −133 (s), −164 (t, J_{B-F} = 19 Hz), −167 (s). ^{29}Si{^{1}H} NMR INEPT (99 MHz) δ −1.2 (d, J_{P-Si} = 9.4 Hz). IR 2981, 2018, 1643, 1519, 1471, 1383, 1273, 1087, 1029, 985, 955, 833, 772, 662. Anal. Calcd for $C_{41}H_{33}BF_{20}IrOPSi$: C, 41.60; H, 2.81. Found: C, 41.50; H, 2.98.

[Cp*(PMe$_3$)Ir(SiMe$_3$)(C$_2$H$_4$)][B(C$_6$F$_5$)$_4$] (21). To solid $(Et_2O)_2LiB(C_6F_5)_4$ (0.126 mg, 0.151 mmol) was added 10 mL of a CH_2Cl_2 solution of Cp*(PMe$_3$)Ir(Me)OTf (94.4 mg, 0.151 mmol). The resulting pale yellow slurry was mixed for 20 s with a pipet and filtered through a fiberglass plug. The filtrate was transferred to a 50-mL glass vessel sealed to a Kontes vacuum adapter and degassed with 3 freeze−pump−thaw cycles. Ethylene (43 Torr, 0.15 mmol) was condensed into the vessel at −196 °C, using a bulb of known volume (66 mL). The flask was allowed to warm to 25 °C, and was then shaken vigorously for 30 s. After the reaction mixture was allowed to sit for 15 min, the contents of the vessel were transferred to a vial and reduced in volume to 1 mL in vacuo. Pentane was added dropwise until precipitation occurred, and then CH_2Cl_2 was added until the solution was again homogeneous. Et_2O (1 mL) was added, and the solution was filtered through a fiberglass plug. The filtrate was stored at −35 °C for 15 h, and the mother liquors were removed with a pipet. The crystals were washed with 2 mLof pentane, and this pentane was then added to the mother liquors. The remaining solvent was then removed in vacuo. A second crop of crystals was grown by cooling the mother liquors to −35 °C for 24 h, and isolated as described for the first crop. The combined yield of the crops of analytically pure off-white crystals was 126 mg (0.106 mmol, 70%). ^{1}H NMR (400 MHz) δ 2.20 (br, 2H, C_2H_4), 1.90, (br, 2H, C_2H_4), 1.74 (d, J_{P-H} = 2 Hz, 15H, C_5Me_5), 1.40 (d, J_{P-H} = 12 Hz, 9H, P*Me*$_3$), 0.36 (s, 3H, Si*Me*$_3$). ^{13}C{^{1}H} NMR (126 MHz) δ 149 (m, B(C_6F_5), 139 (m, B(C_6F_5)), 136 (m, B(C_6F_5)), 124 (m, B(C_6F_5)), 101.9 (s, C_5Me_5), 37.0, (br, C_2H_4), 16.1 (d, J_{P-C} = 41 Hz, P*Me*$_3$), 9.3 (s, C_5Me_5), 5.7 (s, Si*Me*$_3$). ^{31}P{^{1}H} NMR (162 MHz) δ −41.2 (s). ^{19}F{^{1}H} NMR (376 MHz) δ −133 (s), −164 (t, J_{B-F} = 19 Hz), −167 (s). ^{29}Si{^{1}H} NMR INEPT (99 MHz) δ −3.8 (d, J_{P-Si} = 9.4 Hz). IR 1644, 1514, 1464, 1405, 1274, 1093, 980. Anal. Calcd for $C_{42}H_{37}BF_{20}IrPSi$: C, 42.61; H, 3.15. Found: C, 42.28; H, 3.46.

Cp*(PMe$_3$)$_2$Ru(Si^{i}Pr$_2$Cl) (22). A 50-mL glass vessel sealed to a Kontes vacuum adapter containing a magnetic stir bar was charged with 10 mL of a toluene solution of Cp*(PMe$_3$)$_2$Ru(CH_2SiMe_3) (300 mg, 0.631 mmol) and HSi(^{i}Pr)$_2$Cl (108 μL, 0.631 mmol). The stirred solution was heated to 105 °C for 6 h. The solvent was then removed in vacuo, and a total of 3 crops of crystals were grown from concentrated Et_2O solutions at −35 °C. This afforded analytically pure yellow crystals of **22** in a combined yield of 257 mg (0.480 mmol, 76%). ^{1}H NMR (500 MHz) δ 1.55 (d, J_{P-C} = 1 Hz, C_5Me_5), 1.49 (s, 8H, ^{i}Pr), 1.42 (d, J_{P-C} = 6 Hz, 6H, ^{i}Pr), 1.21 (m, 18H, P*Me*$_3$). ^{13}C{^{1}H} NMR (126 MHz) δ 93.9 (s, C_5Me_5), 24.7 (dd, J_{P-C} = 13 Hz, J_{P-C} = 15 Hz, P*Me*$_3$), 23.2 (s, ^{i}Pr), 22.9 (s, ^{i}Pr), 20.2 (s, ^{i}Pr), 12.6 (s, C_5Me_5). ^{31}P{^{1}H} NMR (162 MHz) δ 3.2. ^{29}Si NMR (INEPT, 99 MHz) δ 102.1. IR 2949, 2896, 2848, 1441, 1375, 1275, 1026, 943, 853, 702, 664, 608, 562, 478 cm^{-1}. Anal. Calcd for $C_{22}H_{47}P_2RuSiCl$: C, 49.10; H, 8.80. Found: C, 49.19; H, 8.90.

[Cp*(PMe$_3$)$_2$Ru(Si^{i}Pr$_2$)]B(C$_6$F$_5$)$_4$] (23). A solution of Cp*(PMe$_3$)$_2$Ru(Si(^{i}Pr)$_2$Cl) (**22**) (18.6 mg, 0.0346 mmol) in 1 mL of CH_2Cl_2 was added to a vial containing solid $(Et_2O)_2LiB(C_6F_5)_4$ (28.8 mg, 0.0346 mmol). The resulting slurry was filtered through a fiberglass plug, and the plug was washed with 1 mL of fresh CH_2Cl_2 that was added to the filtrate. The solvent was removed to afford 38.3 mg (0.0325 mmol, 94%) of **23** as an analytically pure yellow foam. ^{1}H NMR (500 MHz) δ 2.44 (septet, J_{H-H} = 7 Hz, ^{i}Pr), 1.86 (s, 15 H, C_5Me_5), 1.53 (m, 18

H, P*Me*$_3$), 1.25 (d, J_{H-H} = 7 Hz, ^{i}Pr). ^{13}C{^{1}H} NMR (126 MHz) δ 149.9 (m, B(C_6F_5), 138.0 (m, B(C_6F_5)), 136.0 (m, B(C_6F_5)), 124.0 (m, B(C_6F_5)), 97.4 (s, C_5Me$_5$), 25.1 (dd, J_{P-C} = 15 Hz, J_{P-C} = 17 Hz, P*Me*$_3$), 17.4 (s, ^{i}Pr), 15.6 (s, ^{i}Pr), 12.0 (s, C$_5$*Me*$_5$). ^{31}P{^{1}H} NMR (162 MHz) δ 1.1. ^{29}Si NMR (INEPT, 99 MHz) δ 437.4. ^{19}F{^{1}H} NMR (376 MHz) δ −133 (s), −164 (t, J_{B-F} = 19 Hz), −167 (s). IR 2942, 2868, 2140, 2103, 1643, 1514, 1442, 1382, 1278, 1089, 958, 854, 773, 684, 662, 611, 574 cm^{-1}. Anal. Calcd for $C_{46}H_{47}P_2RuSiBF_{20}$: C, 46.75; H, 4.01. Found: C, 46.61, H, 4.09.

Cp*(PMe$_3$)$_2$Ru[Si(SPh)$_3$] (24). A 50-mL glass vessel sealed to a Kontes vacuum adapter containing a magnetic stir bar was charged with a 10 mL toluene solution of Cp*(PMe$_3$)$_2$Ru-(CH_2SiMe_3) (300 mg, 0.631 mmol) and HSi(SPh)$_3$ (225 mg, 0.631 mmol). The stirred solution was heated to 105 °C for 6 h. The solvent was then removed in vacuo, and a single crop of crystals was grown from a concentrated Et$_2$O solution at −35 °C. This afforded 300 mg (0.404 mmol, 64%) of **24** as analytically pure pale yellow crystals. ^{1}H NMR (500 MHz, C_6D_6) δ 7.62 (dd, J_{H-H} = 2 Hz, J_{H-H} = 8 Hz, 6 H, S*Ph*), 6.85 (m, 9H, S*Ph*), 1.75 (s, 15 H, C$_5$*Me*$_5$), 1.25 (dd, J_{P-H} = 8 Hz, J_{P-H} = 4 Hz, 9H, P*Me*$_3$). ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2) δ 138.4 (s, Ar-*C*), 134.5 (s, Ar-*C*H), 128.3 (s, Ar-*C*H), 125.6 (s, Ar-*C*H), 95.7 (s, C_5Me$_5$), 24.5 (dd, J_{P-C} = 16 Hz, J_{P-C} = 13 Hz, P*Me*$_3$), 12.4 (s, C$_5$*Me*$_5$). ^{31}P{^{1}H} NMR (162 MHz, C_6D_6) δ 0.4. ^{29}Si NMR (INEPT, 99 MHz, CD_2Cl_2) δ 48.8. IR 3045, 2980, 2912, 1578, 1475, 1434, 1279, 1066, 1024, 956, 851, 739, 688, 462 cm^{-1}. Anal. Calcd for $C_{34}H_{48}P_2RuSiS_3$: C, 54.89; H, 6.50. Found: C, 54.59, H, 6.45.

Cp*(PMe$_3$)$_2$Ru[Si(SPh)$_2$OTf] (25). A 50-mL glass vessel sealed to a Kontes vacuum adapter containing a magnetic stir bar was charged with 10 mL of a toluene solution of Cp*-(PMe$_3$)$_2$Ru(Si(SPh)$_3$) (**24**) (275 mg, 0.370 mmol) and HSi(SPh)$_3$ (73 μL, 0.407 mmol). The stirred solution was heated to 45 °C for 12 h. The solvent was then removed in vacuo, and a single crop of crystals was grown from a concentrated Et$_2$O solution at −35 °C. This afforded 124 mg (0.164 mmol, 45%) of **25** as analytically pure pale yellow crystals. An attempt to grow a second crop of crystals produced impure material. ^{1}H NMR (500 MHz) δ 7.48 (m, 4 H, S*Ph*), 7.14 (m, 6 H, S*Ph*), 1.86 (d, J_{P-H} = 1 Hz, 15 H, C$_5$*Me*$_5$), 1.38 (m, 18 H, P*Me*$_3$). ^{13}C{^{1}H} NMR (126 MHz) (the CF_3 group was not detectable within a reasonable number of scans) δ 135.6 (s, Ar-*C*H), 134.8 (s, Ar-*C*), 128.7 (s, Ar-*C*H), 127.0 (s, Ar-*C*H), 95.9 (s, C_5Me$_5$), 24.2 (dd, J_{P-C} = 15 Hz, J_{P-C} = 17 Hz, P*Me*$_3$), 11.8 (s, C$_5$*Me*$_5$). ^{31}P-{^{1}H} NMR (162 MHz) δ −0.9. ^{29}Si NMR (INEPT, 99 MHz) δ 67.3. ^{19}F{^{1}H} NMR (376 MHz) δ −77.5. IR 1580, 1479, 1275, 1154, 1029, 946, 741, 638 cm^{-1}. Anal. Calcd for $C_{29}H_{43}P_2$-$RuSiS_3O_3F_3$: C, 44.43; H, 5.53. Found: C, 44.18, H, 5.39.

{Cp*(PMe$_3$)$_2$Ru[Si(SPh)$_2$]}[B(C$_6$F$_5$)$_4$] (26). A solution of Cp*(PMe$_3$)$_2$Ru(Si(SPh)$_2$OTf) (**25**) (32.7 mg, 0.0433 mmol) in 0.5 mL of CD_2Cl_2 was added to a vial containing solid (Et$_2$O)$_2$LiB-(C_6F_5)$_4$ (36.1 mg, 0.0433 mmol). The resulting slurry was filtered through a fiberglass plug. The solvent was removed to afford 47.1 mg (0.0359 mmol, 83%) of **26** as an analytically pure yellow foam. ^{1}H NMR (500 MHz) δ 7.31 (m, 10H, S*Ph*), 1.92 (d, J_{P-H} = 2 Hz, 15 H, C$_5$*Me*$_5$), 1.40 (m, 9 H, P*Me*$_3$). ^{13}C-{^{1}H} NMR (126 MHz) δ 149.9 (m, B(C_6F_5), 138.0 (m, B(C_6F_5)), 136.0 (m, B(C_6F_5)), 134.9 (s, Ar-*C*H), 130.8 (s, Ar-*C*), 130.3 (s, Ar-*C*H), 129.7 (s, Ar-*C*H), 124.0 (m, B(C_6F_5)), 97.0 (s, C_5Me$_5$), 24.2 (m, P*Me*$_3$), 11.6 (s, C$_5$*Me*$_5$). ^{31}P{^{1}H} NMR (162 MHz) δ −2.9. ^{29}Si NMR (INEPT, 99 MHz) δ 262.0. ^{19}F{^{1}H} NMR (376 MHz) δ −133 (s), −164 (t, J_{B-F} = 19 Hz), −167 (s). IR 2990, 2914, 1643, 1513, 1461, 1380, 1275, 1086, 979, 755, 684, 467 cm^{-1}. Anal. Calcd for $C_{52}H_{43}P_2RuSiS_2BF_{20}$: C, 47.54; H, 3.30. Found: C, 47.21, H, 3.33.

Sample Procedure for Hydrosilylation Catalysis. All silylene complexes were generated in situ under an inert atmosphere at room temperature and used immediately. In the case of iridium silylene complex **5**, an external standard (sealed in a capillary) of 1,3,5-trimethoxybenzene in C_6D_6 was used as an integration reference. The internal standard used for the other catalyses was 1,3,5-trimethoxybenzene. The following is a sample protocol with [Cp*(PMe$_3$)Ir(H)(SiPh$_2$)]-[B(C_6F_5)$_4$]. A 5-mL vial was charged with Cp*(PMe$_3$)Ir(Me)-OTf (8.6 mg, 0.015 mmol) and 0.5 mL of CD_2Cl_2. To this solution was added 2.8 μL (0.015 mmol) of H_2SiPh_2, and the contents of the vial were mixed with a pipet. The reaction mixture was pipetted onto solid (Et$_2$O)$_2$LiB(C_6F_5)$_4$ (12.6 mg, 0.015 mmol), producing a light yellow slurry that was filtered through a fiberglass plug after 20 s of agitation with a pipet. This solution was transferred to a J. Young NMR tube, which contained an external capillary standard of 1,3,5-trimethoxybenzene in C_6D_6, and a ^{1}H NMR spectrum was acquired. To this tube were added H_2SiPh_2 (56.3 μL, 0.303 mmol) and then acetophenone (35.4 μL, 0.303 mmol), each by syringe. A ^{1}H NMR spectrum was immediately acquired and reaction progress monitored periodically, with integrations of the hydrosilylation product resonances made against resonances of the standard. One-pulse spectra were acquired in all cases to ensure accurate integration.

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Supporting Information Available: Procedures and characterization data for all new compounds and X-ray structural data for complexes **10** and **11a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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