Reactions of Cp*(PMe$_3$)Ir(Me)OTf with Silanes: Role of Base-Free Silylene Complexes in Rearrangements of the Resulting Silicon-Based Ligands

Steven R. Klei, T. Don Tilley,* and Robert G. Bergman*

Department of Chemistry, University of California, and Chemical Sciences Division,
Lawrence Berkeley National Laboratory, Berkeley, California 94720

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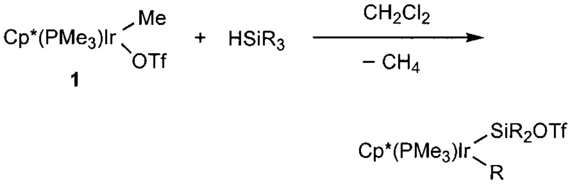
The mechanisms of silicon−hydrogen activation by Cp*(PMe$_3$)Ir(Me)OTf (Cp* = η^5-C$_5$Me$_5$, OTf = OSO$_2$CF$_3$; **1**) and rearrangements of the resulting silyliridium complexes were investigated. The scope of this reaction has been studied for silanes with a variety of substituents. Silylene complexes of the type [Cp*(PMe$_3$)Ir(SiR$_2$)(H)][X] (X = OTf, R = Mes, **6**; X = B(C$_6$F$_5$)$_4$, R = Ph, **16**) have been isolated, and the likelihood of their involvement in the rearrangements is discussed. The kinetics of the isomerization reaction of the cyclometalated iridium(V) complex {Cp*(PMe$_3$)Ir(H)[κ^2-SiH(Mes)(2-CH$_2$-4,6-Me$_2$C$_6$H$_2$)]}[OTf] (**5**) to the iridium silylene [Cp*(PMe$_3$)Ir(SiMes$_2$)(H)][OTf] (**6**) were examined using NMR spectroscopic techniques. The primary kinetic isotope effect (Si−H vs Si−D bond) for this process was determined to be 1.4 ± 0.1, implying a rate-limiting hydride migration from silicon to iridium. The activation parameters for this isomerization have also been measured: $\Delta H^\ddagger$ = 23 ± 2 kcal/mol and $\Delta S^\ddagger$ = 0.1 ± 0.01 eu. Slow hydride migration to produce a silylene complex from either Cp*(PMe$_3$)Ir(Me)OTf (**1**) or [Cp*(PMe$_3$)Ir(Me)(CH$_2$Cl$_2$)][B(C$_6$F$_5$)$_4$] (**17**) is observed for large substituents on silicon. However, production of the sterically less crowded complex [Cp*(PMe$_3$)Ir(SiPh$_2$)(H)][B(C$_6$F$_5$)$_4$] (**16**) is extremely rapid upon reaction of **17** with H$_2$SiPh$_2$. This argues for the intermediacy of a three-coordinate silicon species.

Introduction

The phenomenon of substituent metathesis, or redistribution, has been observed for many main-group and transition-metal systems.[1] Redistribution at silicon centers occurs more easily than at carbon, yet not as readily as at tin, and can be catalyzed by acids, bases, and metals.[2] Silicon redistribution reactions are utilized industrially to convert unwanted byproducts from the synthesis of functionalized silanes into useful materials.[1] The transition-metal-catalyzed pathway is believed to involve 1,2-shifts of groups between the metal and silicon and 1,3-shifts between metal-bound silicon centers. Evidence for intramolecular 1,3-shifts between silicon atoms,[3−5] and for an intermolecular exchange between transition-metal silylene and silyl complexes, has been documented.[6] It was recently reported that a silylene complex can be accessed by the 1,2-migration of hydrogen from silicon to platinum.[7]

The reactivity of methyliridium(III) salts, including stoichiometric and catalytic C−H activation reactions, has been studied recently.[8] Relevant to these investigations is the reactivity of methyliridium salts with silanes. The complex Cp*(PMe$_3$)Ir(Me)OTf (Cp* = η^5-C$_5$Me$_5$, OTf = OSO$_2$CF$_3$; **1**) is known to activate the Si−H bonds of tertiary silanes (HSiR$_3$) to liberate methane and produce organometallic compounds of the general formula Cp*(PMe$_3$)Ir(SiR$_2$OTf)(R), the result of an apparent 1,2-shift of a group from silicon to the metal center (eq 1).[9] This 1,2-group migration models a



$$\underset{\mathbf{1}}{\mathrm{Cp^*(PMe_3)Ir(Me)(OTf)}} + \mathrm{HSiR_3} \xrightarrow[-\,\mathrm{CH_4}]{\mathrm{CH_2Cl_2}} \mathrm{Cp^*(PMe_3)Ir(SiR_2OTf)(R)} \qquad (1)$$

potential key step in metal-mediated redistribution reactions. Moreover, the migration and cyclometalation chemistry reported here adds to the growing number of transformations observed after bond activation in the Ir(III) system. Previously it has been reported that alkyl and acyl complexes formed from C−H activation undergo α- and β-elimination and decarbonylation reactions, respectively.[10,11]

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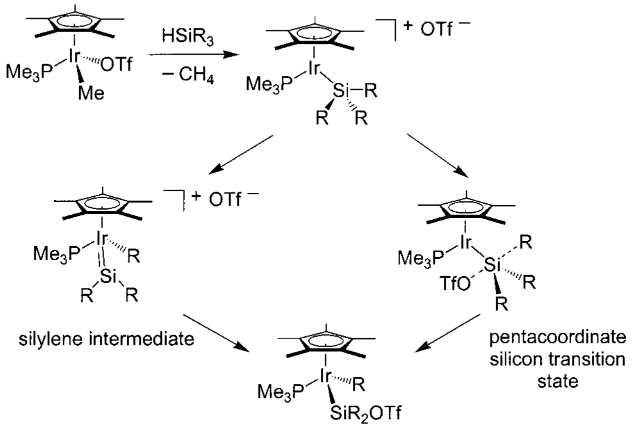
Scheme 1



We wished to ascertain whether base-free silylene intermediates are formed in the 1,2-shift, or if the rearrangement proceeds instead via a triflate-assisted pathway involving a pentacoordinate silicon species (Scheme 1). Although a number of base-stabilized silylene complexes are known,[12–14] base-free silylene complexes are rare.[7,15–19] We reported in preliminary form the isolation of a rare iridium–silylene complex kinetically stabilized by incorporation of bulky groups on the silicon center.[20] Although H_2SiMes_2 underwent Si–H activation and migration of a substituent from silicon to iridium upon treatment with **1**, our inability to access similar silylene complexes from anion metathesis reactions of $Cp^*(PMe_3)Ir(SiPh_2OTf)(Ph)$ (**2**) and $Cp^*(PMe_3)Ir(SiMe_2OTf)Me$[21] (**3**) made us suspicious of the generalization that silylene complexes were intermediates in reactions of less hindered silanes. We now report the full details of our investigation of 1,2-group migrations resulting from a presumed 16-electron cationic iridium center. Reactions of $Cp^*(PMe_3)Ir(Me)OTf$ with a variety of silanes provided evidence for distinguishing between the two mechanisms illustrated in Scheme 1.

Results

X-ray Crystal Structure of $Cp^*(PMe_3)Ir(SiPh_2OTf)$(Ph) (2). As reported by Burger et al., addition of $HSiPh_3$ to an orange solution of **1** affords $Cp^*(PMe_3)Ir(SiPh_2OTf)(Ph)$ (**2**) in 95% yield. Although this complex had been fully characterized, a crystal structure had not yet been obtained. Single crystals of **2** were grown by slow evaporation of a CH_2Cl_2 solution into pentane at room temperature, and an X-ray diffraction study was performed. An ORTEP diagram of complex **2** is shown in Figure 1. There are two crystallographically unique but chemically identical molecules in the asymmetric unit. The bond lengths of the two molecules are essentially the same; representative bond lengths are given in Table 1.[22] Comparison to the data reported by Oro and co-workers for $IrH_2(SiPh_2OTf)(TFB)(P^iPr_3)$ (TFB = tetrafluorobenzobarrelene, Ir–Si = 2.337(2) Å) indicates that the Ir–Si bond length observed for **2** is not unusual. Both the Oro compound and **2** are produced by Si–H activation strategies, although the starting material is Ir(I) for the former and Ir(III) for the latter.

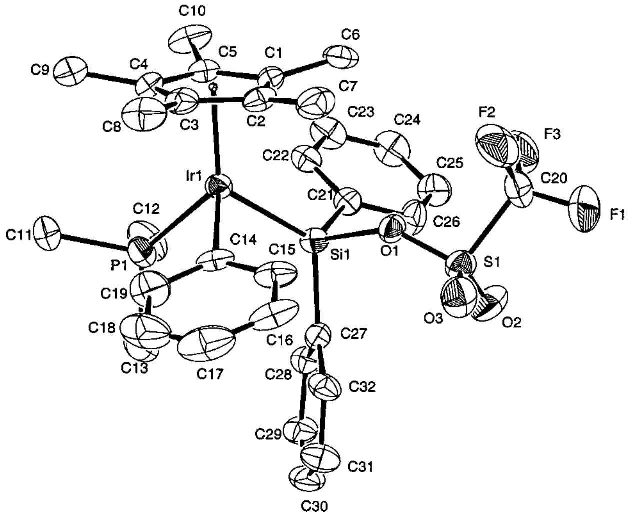
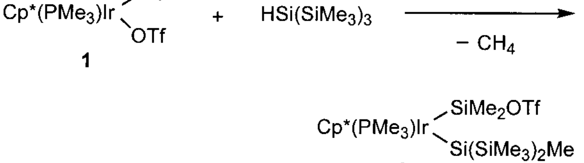


Figure 1. ORTEP diagram of $Cp^*(PMe_3)Ir(SiPh_2OTf)(Ph)$ (**2**). Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms have been omitted for clarity.

Table 1. Selected Bond Distances (Å) and Angles (deg) for 2

bond	distance	bond	angle
Ir–P	2.281(2)	P–Ir–Si	90.95(8)
Ir–Si	2.317(2)	P–Ir–C14	90.3(2)
Ir–C14	2.065(8)	Si–Ir–C14	92.5(2)
Ir–C100	1.9488(3)	C14–Ir–C100	117.3(2)
Si–O	1.819(5)	Si–Ir–C100	125.86(6)

Further Reactivity of $Cp^*(PMe_3)Ir(Me)OTf$ (1) toward Silanes. To probe the nature of steric and electronic factors on migrations in $[Cp^*(PMe_3)IrSiR_3]^+$ systems, we examined the reactivity of **1** with a variety of silanes. Addition of the bulky hydrosilane $HSi(SiMe_3)_3$ to $Cp^*(PMe_3)Ir(Me)OTf$ (**1**) in CH_2Cl_2 affords $Cp^*(PMe_3)Ir[Si(SiMe_3)_2Me](SiMe_2OTf)$ (**4**; eq 2) in 82%



$$\underset{\mathbf{1}}{Cp^*(PMe_3)Ir\begin{matrix}Me\\OTf\end{matrix}} + HSi(SiMe_3)_3 \xrightarrow[-\,CH_4]{CH_2Cl_2} \underset{\mathbf{4}}{Cp^*(PMe_3)Ir\begin{matrix}SiMe_2OTf\\Si(SiMe_3)_2Me\end{matrix}} \quad (2)$$

isolated yield after 5 h at 25 °C. Diastereotopic trimethylsilyl groups (δ 0.17 and 0.15) and three types of Si–Me groups (δ 0.96, 0.78, and 0.44) are evident from the ^1H NMR spectrum. Cooling a concentrated CH_2Cl_2 solution of **4** to –35 °C for 2 weeks afforded X-ray-

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[22] For complete details of this X-ray diffraction study, see the Supporting Information.

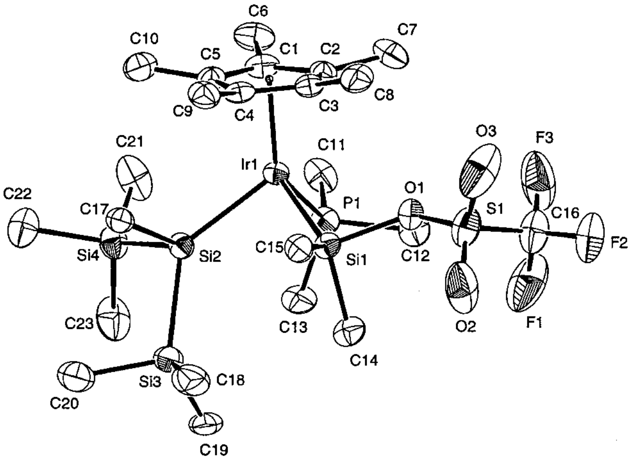


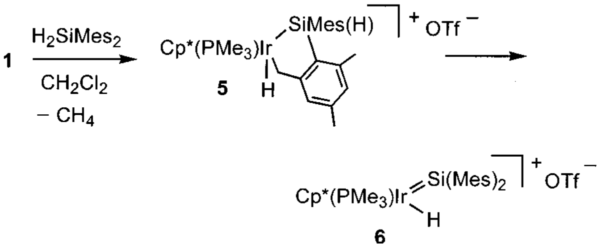
Figure 2. ORTEP diagram of Cp*$(PMe_3)Ir(SiMe_2OTf)(Si(SiMe_3)_2(Me)$ (**4**). Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms have been omitted for clarity.

Table 2. Selected Bond Distances (Å) and Angles (deg) for 4

bond	distance	bond	angle
Ir−P	2.2532(18)	P−Ir−Si1	89.95(9)
Ir−Si1	2.2987(18)	P−Ir−Si2	94.85(7)
Ir−Si2	2.446(2)	Si1−Ir−Si2	88.12(9)
Ir−C100	1.9622(3)	Si1−Ir−C100	123.49(6)
Si−O	1.837(5)	Si2−Ir−C100	122.84(5)

quality crystals. A crystallographic study confirmed the structure, and an ORTEP diagram is shown in Figure 2. The Ir−Si bond length for the silicon bound to two silyl groups and a methyl group is 2.446(2) Å, whereas the Ir−Si bond length of the silicon bound to the triflate is 2.2987(18) Å (Table 2). This comparison is informative, as it implies partial multiple-bond character in the latter case. The ^{29}Si NMR spectrum contains resonances at 62.2 and −79.0 ppm for the two silicon atoms attached to iridium, suggesting very different silicon environments. Although the reaction takes 5 h to proceed to completion, no intermediates were observed by room-temperature ^{1}H and ^{31}P{^{1}H} NMR spectroscopy. Attempts to observe an iridium silylene complex directly by the addition of either NaBAr$_f$ (BAr$_f$ = B(3,5-$(CF_3)_2C_6H_3)_4$) or $(Et_2O)_2LiB(C_6F_5)_4$ to the final product **4** led to intractable products.

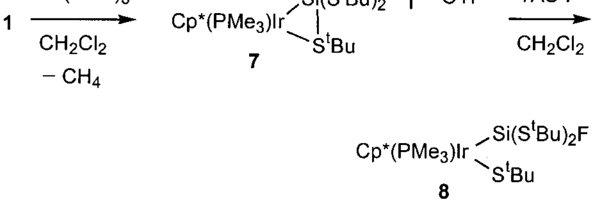
Addition of a CD_2Cl_2 solution of Cp*$(PMe_3)Ir(Me)OTf$ (**1**) to H_2SiMes_2 (Mes = 2,4,6-$Me_3C_6H_2$) results in rapid evolution of CH_4, and the solution adopts a pale yellow color. This Si−H activation reaction, like all those described subsequently except the reaction with $HSi(SiMe_3)_3$, occurs immediately at room temperature. The presence of an iridium hydride was confirmed by ^{1}H NMR spectroscopy (δ −14.56, J_{P-H} = 24 Hz); the diastereotopic protons of the iridium−methylene unit resonate at 3.79 and 2.67 ppm. The combined spectroscopic data for this new material conclusively show that it is a cyclometalated Ir(V) alkyl hydride, {Cp*$(PMe_3)Ir(H)[\kappa^2$-SiH(Mes)(2-CH_2-4,6-$Me_2C_6H_2$)]}[OTf] (**5**; eq 3), formed apparently by intramolecular benzyl C−H bond activation in the iridium silyl complex [Cp*$(PMe_3)Ir(SiHMes_2)$][OTf]. Complex **5** isomerizes to the bright yellow base-free silylene complex [Cp*$(PMe_3)Ir(SiMes_2)$(H)][OTf] (**6**) over the course of 12 h, with no intermediates observed by ^{1}H or ^{31}P NMR spectroscopy. The ^{29}Si NMR signal of **6** resonates at +301 ppm downfield of $SiMe_4$, clearly indicating that the silicon center is three-coordinate.[18] This is the first known example of a silylene complex which does not coordinate triflate, and we believe that steric congestion at the silicon center is responsible for this observation.



(3)

Previous work has shown that heteroatom substituents have a stabilizing effect on metal silylene complexes, on the basis of activation parameters for acetonitrile exchange.[23] With this in mind, the reactivity of silanes of the type $HSi(ER)_3$ (E = S, O) with **1** was examined with the hope that intermediate silyl or silylene complexes would be sufficiently long-lived that they could be observed.

Addition of 1 equiv of $HSi(S^tBu)_3$ to a CH_2Cl_2 solution of **1** produces [Cp*$(PMe_3)Ir(\kappa^2$-$Si(S^tBu)_2S^tBu$)][OTf] (**7**) in 88% isolated yield (eq 4). Unlike the reactions of alkyl- and aryl-substituted silanes, complete migration of a thiolato group to iridium is not observed. The ^{31}P{^{1}H} NMR spectrum contains a broad resonance at δ −45.4, and one of the ^{13}C{^{1}H} NMR spectral resonances is broad (δ 40.1, S*C*(Me)$_3$). The ^{1}H NMR spectrum, which contains three chemically inequivalent *tert*-butyl thiolato groups, is consistent with the structure shown in eq 4. However, it is also supportive both of an unmigrated species in which hindered rotation renders the thiolato groups inequivalent and also of a fully migrated species. X-ray-quality crystals of **7** were grown from CH_2Cl_2/pentane at −35 °C, and a structural study was carried out. An ORTEP diagram of the cationic portion of this compound is shown in Figure 3, and representative bond lengths and angles for complex **7** are found in Table 3. The structure involves a dative interaction between one of the *tert*-butyl thiolato groups on silicon and the iridium center. Attempts to observe equilibration of the thiolato groups by NMR spectroscopy at elevated temperatures (60 °C) in $ClCD_2CD_2Cl$ led to decomposition.



(4)

The bonding motif revealed by the crystal structure of **7** suggests an "arrested" migration. We therefore believed that it might be possible to complete the migration if a suitable donor could be found to bind

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(23) Grumbine, S. K.; Straus, D. A.; Tilley, T. D. *Polyhedron* **1995**, *14*, 127.

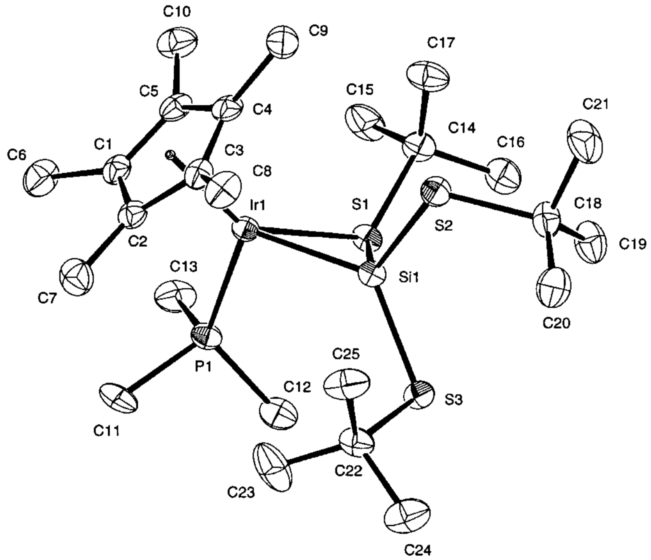


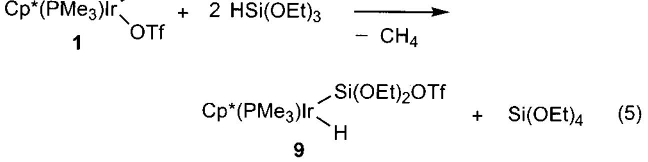
Figure 3. ORTEP diagram of the cationic portion of [Cp*(PMe$_3$)Ir(κ^2-Si(S^{t}Bu)$_2$S^{t}Bu)][OTf] (**7**). Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms have been omitted for clarity.

Table 3. Selected Bond Distances (Å) and Angles (deg) for 7

bond	distance	bond	angle
Ir−P	2.3290(15)	P−Ir−S1	79.94(5)
Ir−Si	2.3044(16)	P−Ir−Si	100.66(6)
Ir−S1	2.4357(15)	Si−Ir−S1	55.73(5)
Si−S1	2.219(2)	S2−Si−S1	115.20(9)
Si−S2	2.124(2)	S2−Si−S3	111.92(9)

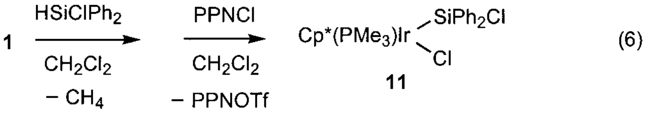
preferentially to silicon. Addition of acetonitrile to **7** led to the liberation of isobutylene and formation of an unidentified iridium complex. However, treatment of **7** with 1 equiv of a soluble fluoride source, TAS-F (tris(dimethylamino)sulfur (trimethylsilyl)difluoride)), produced [Cp*(PMe$_3$)Ir[Si(S^{t}Bu)$_2$F](S^{t}Bu)][OTf] (**8**) in 82% isolated yield (eq 4). The ^{29}Si NMR resonance (δ 9.1, dd, $J_{\text{Si-F}} = 400$ Hz, $J_{\text{Si-P}} = 25$ Hz) is supportive of this formulation, as is the detection of a stoichiometric amount of Me$_3$SiF by ^{1}H NMR spectroscopy (δ 0.02, d, $J_{\text{H-F}} = 7.2$ Hz). A driving force for this reaction is presumed to be the formation of the strong Si−F bond.

The products formed when **1** was treated with 2 equiv of HSi(OEt)$_3$ in CH$_2$Cl$_2$ were identified as Cp*(PMe$_3$)Ir[Si(OEt)$_2$OTf](H) (**9**; 85% isolated yield) and Si(OEt)$_4$ (eq 5). The presence of Si(OEt)$_4$ was confirmed by comparison of the volatile materials from the reaction with an authentic sample using GC/MS and ^{1}H NMR spectroscopy. Using 1 equiv or less of HSi(OEt)$_3$ did not alter the course of the reaction; only the starting material **1** and product **9** were observed by ^{1}H NMR spectroscopy under these conditions. Conversion of the product to the corresponding chloride Cp*(PMe$_3$)Ir[Si(OEt)$_2$OTf](Cl) (**10**) in 80% isolated yield was accomplished by treatment of **9** with CCl$_4$. As expected, no Ir−H resonances were observed for chloride complex **10** by ^{1}H NMR spectroscopy; 1 equiv of chloroform was detected by ^{1}H NMR analysis of the crude reaction mixture.



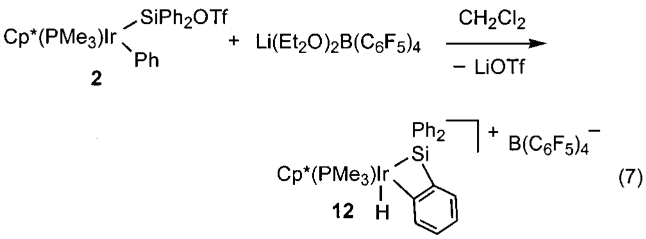
$$\mathrm{Cp^*(PMe_3)Ir(Me)(OTf)}\ (\mathbf{1}) + 2\ \mathrm{HSi(OEt)_3} \xrightarrow[-\ \mathrm{CH_4}]{\mathrm{CH_2Cl_2}} \mathrm{Cp^*(PMe_3)Ir(Si(OEt)_2OTf)(H)}\ (\mathbf{9}) + \mathrm{Si(OEt)_4} \quad (5)$$

Reaction of **1** with HClSiPh$_2$ gives an inseparable mixture of two products by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy. Treatment of this mixture with [PPN]Cl led to the formation of Cp*(PMe$_3$)Ir(SiPh$_2$Cl)Cl (**11**) in 49% recrystallized yield (eq 6). Attempts to reduce this species with common reducing agents (Na, Na(Hg), and Riecke Mg), in hopes of accessing the neutral silylene complex Cp*(PMe$_3$)Ir(SiPh$_2$), led to the formation of multiple products. A similar route has provided the silene complex Cp$_2$W(η^2-Me$_2$Si=CH$_2$) by reduction of Cp$_2$W(Cl)(CH$_2$SiMe$_2$Cl) with Riecke Mg.[24]



$$\mathbf{1} \xrightarrow[\mathrm{CH_2Cl_2}\ -\ \mathrm{CH_4}]{\mathrm{HSiClPh_2}} \xrightarrow[\mathrm{CH_2Cl_2}\ -\ \mathrm{PPNOTf}]{\mathrm{PPNCl}} \mathrm{Cp^*(PMe_3)Ir(SiPh_2Cl)(Cl)}\ (\mathbf{11}) \quad (6)$$

Anion Metathesis Reactions of the Iridium Silyl Triflate Complexes. The possibility of base-free silylene complex involvement in the rearrangement reactions of iridium silyl complexes was probed using anion metathesis reactions. The reaction of Cp*(PMe$_3$)Ir(SiPh$_2$OTf)(Ph) with (Et$_2$O)$_2$LiB(C$_6$F$_5$)$_4$ yields the crystallographically characterized cyclometalated Ir(V) complex [Cp*(PMe$_3$)Ir(κ^2-SiPh$_2$(C$_6$H$_4$))(H)][B(C$_6$F$_5$)$_4$] (**12**) (eq 7).[20]



$$\mathrm{Cp^*(PMe_3)Ir(SiPh_2OTf)(Ph)}\ (\mathbf{2}) + \mathrm{Li(Et_2O)_2B(C_6F_5)_4} \xrightarrow[-\ \mathrm{LiOTf}]{\mathrm{CH_2Cl_2}} [\mathrm{Cp^*(PMe_3)Ir(H)(\kappa^2\text{-}SiPh_2C_6H_4)}]^+\ \mathrm{B(C_6F_5)_4^-}\ (\mathbf{12}) \quad (7)$$

When Cp*(PMe$_3$)Ir(SiPh$_2$OTf)(Ph) is treated with 1 equiv of NaBAr$_f$ (BAr$_f$ = 3,5-(CF$_3$)$_2$C$_6$H$_3$)$_4$B), the reaction mixture immediately adopts a dark blue-green color, with one major product observed by ^{1}H and ^{31}P{^{1}H} NMR. This species decomposes over the course of hours to multiple products. Only by using the soluble salt (Et$_2$O)$_2$LiB(C$_6$F$_5$)$_4$ was it possible to isolate an iridium-containing product free of impurities; this was shown to be [Cp*(PMe$_3$Ir(H)(κ^2-SiPh$_2$(C$_6$H$_4$))][B(C$_6$F$_5$)$_4$] (**12**), which is pale yellow. This complex displays an Ir−H NMR resonance at δ −12.7 (d, $J_{\text{P-H}} = 20$ Hz) and an infrared $\nu_{\text{Ir-H}}$ stretching frequency at 2084 cm^{-1}. The identity of the highly colored impurity present in the reactions with NaBAr$_f$ is currently unknown, as are the identities of the decomposition products.

The novelty of this unprecedented Ir(III) to Ir(V) C−H oxidative addition reaction led us to examine whether the cyclometalation was limited to aryl substitution at silicon. Specifically, metalation of the intermediate trimethylsilyl−iridium complex "[Cp*(PMe$_3$)Ir(SiMe$_3$)(CH$_2$Cl$_2$)][B(C$_6$F$_5$)$_4$]" would lead to a cationic iridium−silene complex, a previously unknown structural type. This expectation was confirmed on treatment of Cp*-

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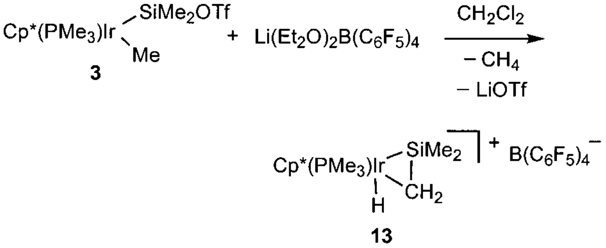
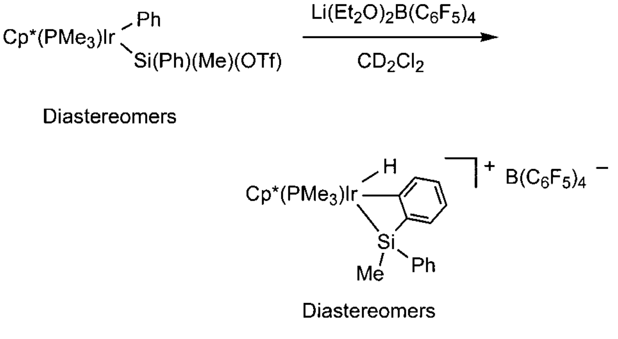
$(PMe_3)Ir(SiMe_2OTf)(Me)$ (**3**) with $(Et_2O)_2LiB(C_6F_5)_4$, which generated a mixture of $[Cp^*(PMe_3)Ir(\eta^2\text{-}CH_2\text{-}SiMe_2)(H)][B(C_6F_5)_4]$ (**13**) and $[Cp^*(PMe_3)Ir(SiMe_2(Et_2O))(Me)][B(C_6F_5)_4]$ (**14**) (eq 8).[21] The silene complex **13** could



(8)

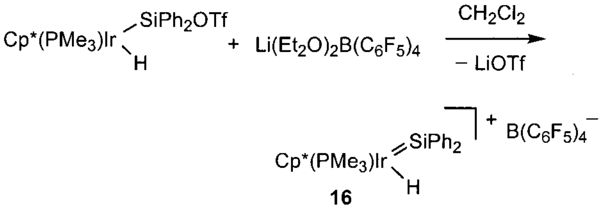
be purified by crystallization from CH_2Cl_2/pentane at −35 °C in 43% isolated yield. Campion and Tilley have previously reported the synthesis and reactivity of the charge-neutral analogue $Cp^*(PMe_3)Ir(\eta^2\text{-}CH_2SiPh_2)$ (**15**).[25]

An attempt was made to establish a synthetic link between silene complexes **13** and **15**. Reaction of $HSiMePh_2$ with $Cp^*(PMe_3)Ir(Me)OTf$, followed by metathesis with $(Et_2O)_2LiB(C_6F_5)_4$, should afford a protonated derivative of the Campion silene complex **15**. Deprotonation of **13** with a nonnucleophilic base should then give $Cp^*(PMe_3)Ir(\eta^2\text{-}CH_2SiPh_2)$. However, while the reaction of $HSiMePh_2$ with **1** produced a mixture of $Cp^*(PMe_3)Ir(SiMePhOTf)(Ph)$ diastereomers, the metathesis reaction of this mixture with $(Et_2O)_2LiB(C_6F_5)_4$ resulted in the production of two major and two minor products. The major products both exhibit iridium-hydride resonances in their ^1H NMR spectra (δ 12.85, J_{H-H} = 20 Hz; δ 12.94, J_{H-H} = 20 Hz). Neither of these products contains resonances in the expected chemical shift range for a metalated methylene unit. These combined data lead us to propose that the two major anion metathesis products are the diastereomers of $[Cp^*(PMe_3)Ir(H)(\eta^2\text{-}Si(Ph)(Me)(C_6H_4))][B(C_6F_5)_4]$, resulting from cyclometalation of the phenyl group attached to silicon (eq 9). Preferential attack on the C−H bond of the silicon-bound phenyl ring over attack on the silicon−methyl group is believed to be a result of thermodynamic considerations. Formation of a stronger Ir−C(aryl) bond over a weaker Ir−C(alkyl) bond has been considered as a driving force in the reaction of $Cp^*(PMe_3)IrMeOTf$ with benzene to produce $Cp^*(PMe_3)IrPhOTf$.[9]



(9)

Access to complexes of the type $[Cp^*(PMe_3)Ir(SiPh_2)(H)][X]$ was straightforward. Reaction of $(Et_2O)_2LiB(C_6F_5)_4$ with $Cp^*(PMe_3)Ir(SiPh_2OTf)(H)$ leads to the formation of the bright yellow silylene complex $[Cp^*(PMe_3)Ir(SiPh_2)(H)][B(C_6F_5)_4]$ (**16**; eq 10). The ^1H and



(10)

^{31}P NMR resonances for the silylene complex **16** are virtually identical with those of the iridium starting material, but the ^{19}F NMR spectrum indicates that a metathesis reaction has taken place. Furthermore, the ^{29}Si NMR spectrum contains a single resonance at 351.1 ppm. This remarkably downfield resonance for **16** is diagnostic of a three-coordinate silicon center; the ^{29}Si NMR resonance for the iridium silyl triflate starting material is 51.5 ppm. The lithium salts produced in the metathesis may be partially removed by filtration. However, samples isolated by this protocol typically contain 0.2−0.5 equiv of lithium salts. It should be noted that treating $[Cp^*(PMe_3)Ir(Me)(CH_2Cl_2)][BAr_f]$ with H_2SiPh_2 led to a complex mixture of products, as did reaction of $Cp^*(PMe_3)Ir(SiPh_2OTf)(H)$ with $NaBAr_f$. We suspect that undetectable impurities present from the preparation of $NaBAr_f$ are responsible for the latter observation. No new resonances in the ^{19}F NMR spectrum are observed, which would presumably result if the weakly coordinating anion had been attacked in the reaction.

Silylene complex **16** is very sensitive to adventitious moisture. As a result, reactions performed with $(Et_2O)_2LiB(C_6F_5)_4$ that has not been rigorously dried[26] yield a small amount of a hydrolysis product, which we speculate is $[Cp^*(PMe_3)Ir(SiPh_2OH)(H)_2][B(C_6F_5)_4]$. ^1H NMR spectroscopy reveals that the hydrolysis product contains an iridium−hydride resonance which gives an integration of two protons (δ −14.67, d, J_{P-H} = 20 Hz). However, evidence for the Si−OH functionality was not found using NMR or IR spectroscopy. That this new product is formed by hydrolysis was confirmed by adding a substoichiometric amount of H_2O to a sample containing it and silylene complex **16**. An increase in the quantity of the hydrolysis product was observed by integration of its resonance against those of an internal standard.

Isotope Effect and Rate Studies. Most of the silane activation reactions are extremely rapid and no intermediates were observed by ^1H or $^{31}P\{^1H\}$ NMR spectroscopy, even at −80 °C. Nevertheless, information concerning the activation/migration reaction mechanism can be gained experimentally by measurement of isotope effects and relative rates. The isotope effect for silane oxidative addition was probed using a competition experiment. Reaction of $Cp^*(PMe_3)Ir(Me)OTf$ with a mixture of 50 equiv of $HSiPh_3$ and 50 equiv of $DSiPh_3$ at 0 °C led to clean formation of $Cp^*(PMe_3)Ir(SiPh_2OTf)(Ph)$. Using ^1H NMR spectroscopy, the ratio of CH_4 to CH_3D was measured to determine that the kinetic

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(25) Campion, B. K.; Heyn, R. H.; Tilley, T. D. *J. Am. Chem. Soc.* **1990**, *112*, 4079.

(26) We have found that stirring a THF solution of $(Et_2O)_2LiB(C_6F_5)_4$ over 4 Å molecular sieves for 2 days, followed by filtration and removal of the solvent, is an effective way of producing the dry salt.

Table 4. Rate Data for the Conversion of 5 to 6

T (K)	rate constant (L mol^{-1})
287.73	$(2.43 \pm 0.05) \times 10^{-5}$
299.40	$(9.00 \pm 0.01) \times 10^{-5}$
309.75	$(3.85 \pm 0.05) \times 10^{-4}$
320.25	$(1.60 \pm 0.01) \times 10^{-3}$

isotope effect for the silicon−hydrogen activation was essentially unity ($k_H/k_D = 0.97 \pm 0.08$). It was then desirable to compare this value to the intramolecular kinetic isotope effect for the reaction of methyliridium complex **1** with $HDSiPh_2$. An attempt was made to synthesize $HDSiPh_2$ from $HClSiPh_2$ and $LiAlD_4$. However, a significant amount of redistribution to H_2SiPh_2 and D_2SiPh_2 was observed after workup. The redistribution is presumably catalyzed by aluminum before or during distillation of the product. This appears to contradict an earlier reported synthesis of $HDSiPh_2$.[27]

The isomerization reaction of cyclometalated complex **5** to iridium silylene **6** allows for a close examination of 1,2-hydride migration from silicon to iridium. To date, there have been no detailed kinetic analyses of reactions leading to base-free metal silylenes. Attempts were made to prevent isomerization to the silylene complex by trapping the cyclometalated iridium hydride complex as the corresponding chloride; however, the presence of CCl_4 had no effect on the isomerization reaction. Kinetic studies on the conversion of **5** to **6** revealed that the isomerization exhibited clean first-order kinetics. A rate constant of $(9.00 \pm 0.01) \times 10^{-5}$ L mol^{-1} was measured at 299.40 K in $ClCD_2CD_2Cl$. A similar protocol was implemented for the study of deuterium migration in $\{Cp^*(PMe_3)Ir(D)[\kappa^2\text{-}SiH(Mes)(2\text{-}CH_2\text{-}3,5\text{-}Me_2C_6H_2)]\}$-[OTf] (**5**-*d*), which was prepared by treating Cp*-(PMe₃)IrMeOTf with D_2SiMes_2. The first-order rate constant for the isomerization of **5-*d*** to **6-*d*** is $(6.54 \pm 0.01) \times 10^{-5}$ L mol^{-1} at 299.25 K. Using an Eyring plot (vide supra) to correct for the temperature difference in the measured rate constants, the primary kinetic isotope effect for this hydride/deuteride migration is 1.6 ± 0.1. Addition of triflate ion (4 equiv), in the form of $[NHex_4][OTf]$, had no effect on the first-order rate constant for the isomerization. This implies that the anion does not participate in the reaction.

The isomerization of **5** to silylene complex **6** was further examined with regard to the temperature dependence of the rate constant. The solvent chosen was $ClCD_2CD_2Cl$, as the elevated temperatures necessary for the study prevented the use of CD_2Cl_2. Although $CDCl_3$ was a potential solvent option, a small amount of an unidentified product was evident when it was used in the isomerization reaction. The rate constant for the conversion of **5** to **6** was monitored between 290 and 320 K; measured values can be found in Table 4. A plot of $\ln(k/T)$ vs $1/T$ fit well to a straight line, and the slope and intercept were used to determine $\Delta H^{\ddagger} = 23 \pm 2$ kcal/mol and $\Delta S^{\ddagger} = 0.1 \pm 0.01$ eu, respectively. The Eyring plot can be found in Figure 4.

Our ability to spectroscopically observe the formation of the iridium silylene complex **6** questioned the relevance of the reaction to the silyl migration behavior observed in reactions of Cp*(PMe₃)Ir(Me)OTf with silanes. For this reason, anion effects were examined. We have previously reported that, in general, C−H activation processes are faster for $[Cp^*(PMe_3)Ir(CH_3)(CH_2Cl_2)][B(C_6F_5)_4]$ (**17**) relative to **1**.[28] Treatment of methyliridium complex **17** with H_2SiMes_2 led to a rate that is very similar to that observed for the reaction of H_2SiMes with complex **1** to form **5**. It was found that the rate of intramolecular rearrangement of complexes with smaller substituents on silicon was very similar to the rate of reaction between **1** and H_2SiPh_2. That is, reaction of **17** with H_2SiPh_2 leads to immediate production of silylene complex **16**.

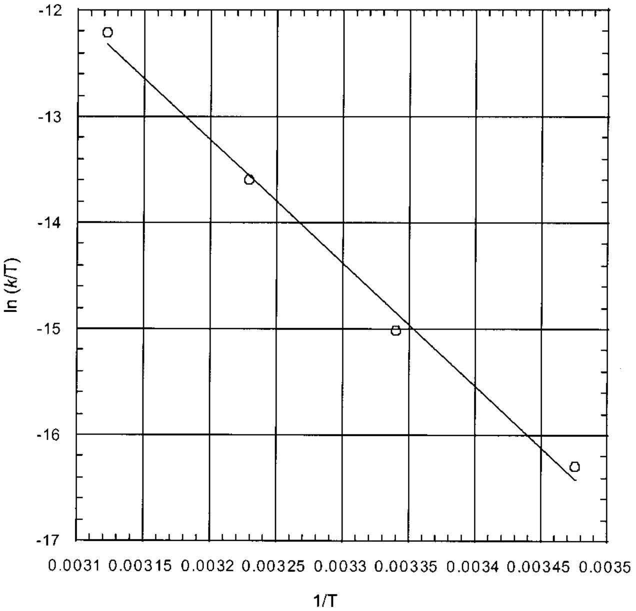

Figure 4. Eyring plot for the conversion of **5** to **6**.

Discussion

The silyl complexes described here were obtained from the corresponding alkyl derivatives. Although this methodology is somewhat uncommon, related examples are known for ruthenium,[29] osmium,[17] and rhodium,[30] in addition to those for iridium.[9,16] The circumstantial evidence in every case supports a dissociative mechanism in which a reactive 16-electron complex is involved. The distinction of complex **1** is that it accesses the coordinatively unsaturated intermediate via dissociation of an anionic,[31] rather than dative, ligand. Furthermore, **1** reacts with silanes under comparatively mild conditions. The synthesis of cationic ruthenium−silyl complexes has recently been effected under mild conditions through phosphine removal by borane abstraction.[32]

The rearrangement products obtained in this work could have the potential to serve as useful catalysts, given the reactivity of structurally similar compounds. For example, 16-electron silyl complexes of rhodium have been shown to be effective catalysts for C−F

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(27) Mayr, H.; Basso, N.; Hagen, G. *J. Am. Chem. Soc.* **1992**, *114*, 3060.

(28) Arndtsen, B. A.; Bergman, R. G. *Science* **1995**, *270*, 1970.

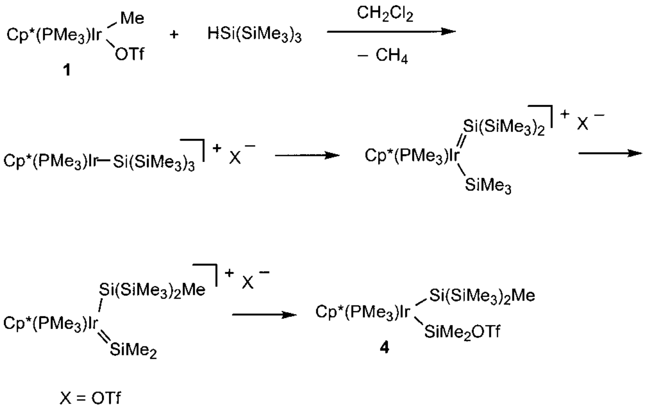
(29) Straus, D. A.; Tilley, T. D.; Rheingold, A. L.; Geib, S. J. *J. Am. Chem. Soc.* **1987**, *109*, 5872.

(30) Aizenberg, M.; Milstein, D. *Science* **1994**, *265*, 359.

(31) A full paper concerning mechanistic aspects of the Ir(III) C−H activation reaction has been written: Tellers, D. M.; Yung, C. M.; Arndtsen, B. A.; Adamson, D. R.; Bergman, R. G. *J. Am. Chem. Soc.*, in press.

(32) Dioumaev, V. K.; Plossl, K.; Carroll, P. J.; Berry, D. H. *J. Am. Chem. Soc.* **1999**, *121*, 8391.

Scheme 2

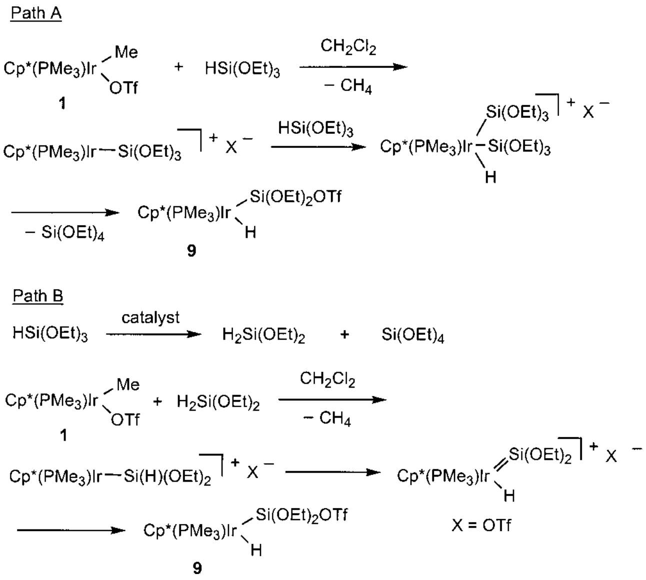


activation of aromatic fluorocarbons.[30] Brookhart and co-workers have shown that the related cationic 16-electron alkyl complexes of cobalt are useful for the polymerization of ethylene.[33] Also, cationic alkylrhodium complexes have been used for catalytic tail-to-tail dimerization of methyl acrylate,[34] and cationic alkylpalladium complexes are active for living alternating copolymerization of olefins and carbon monoxide.[35,36]

An interesting aspect of the silane activation products formed from methyliridium complex **1** is their propensity to undergo 1,2-rearrangement to form stable complexes of the type $Cp^*(PMe_3)Ir(SiR_2OTf)(R)$, in preference to structures of the form $Cp^*(PMe_3)Ir(SiR_3)(OTf)$. These migration reactions are especially facile when a comparison is made to the behavior of the corresponding alkyl derivatives. For example, very little evidence has been found for the interconversion of methyliridium species with $[Cp^*(PMe_3)Ir(=CH_2)(H)][X]$ (X = OTf, BAr_f).[8] This lower propensity for 1,2-migration may be one of the factors responsible for the previously mentioned reluctance of carbon to undergo transition-metal-catalyzed redistribution reactions.

All of our attempts to generate a complex of the type "$Cp^*(PMe_3)Ir(SiR_3)(OTf)$" have led to rearrangement to other structures. For example, the reaction of $Cp^*(PMe_3)Ir(Me)OTf$ with $HSi(SiMe_3)_3$ produces the more extensively rearranged product $Cp^*(PMe_3)Ir[Si(SiMe_3)_2Me](SiMe_2OTf)$. This reaction requires 5 h for completion, quite a bit longer than that required for reactions of $Cp^*(PMe_3)Ir(Me)OTf$ with $HSiPh_3$ and $HSiMe_3$. An apparent rate-determining Si–H activation step accounts for the lack of observable intermediates. A plausible mechanism for this apparent double migration is shown in Scheme 2; this mechanism invokes base-free iridium silylenes as key intermediates. Initial Si–H bond activation undoubtedly produces $[Cp^*(PMe_3)IrSi(SiMe_3)_3][OTf]$, which can then undergo 1,2-silyl migration to give $[Cp^*(PMe_3)Ir[Si(SiMe_3)_2](SiMe_3)][OTf]$, followed by 1,3-methyl migration to $[Cp^*(PMe_3)Ir[Si(SiMe_3)_2Me](SiMe_2)][OTf]$, which is trapped by triflate to give the observed products. The 1,3-methyl migration in this mechanism implies that a silicon-supported silylene complex is less stable than a silylene complex which is bonded to carbon. An intramolecular 1,3-group migration step involving silylene complexes has also been suggested in recent work by Sakaba et al. to explain redistribution reactions at a tungsten center.[37] A similar mechanism has been suggested for a migration reaction stemming from "$(PMe_3)_3RhSi(SiMe_3)_3$".[38]

Scheme 3



The reaction of $Cp^*(PMe_3)Ir(Me)OTf$ with $HSi(OEt)_3$ also exhibits rearrangements that are more complicated than simple 1,2-group migration. We have considered two mechanisms to account for formation of $Cp^*(PMe_3)Ir(H)[Si(OEt)_2OTf]$ and $Si(OEt)_4$; these are shown in Scheme 3. Path A involves oxidative addition of a Si–H bond to produce the presumed cationic silyl $[Cp^*(PMe_3)IrSi(OEt)_3][OTf]$, followed by oxidative addition of $HSi(OEt)_3$ to generate the Ir(V) complex $[Cp^*(PMe_3)Ir(H)(Si(OEt)_3)_2][OTf]$, which extrudes $Si(OEt)_4$ to give $[Cp^*(PMe_3)Ir(H)(Si(OEt)_2)][OTf]$. Charge neutralization by triflate coordination affords the product (**9**). An alternative explanation (path B) begins with a catalyzed redistribution of $HSi(OEt)_3$ to $Si(OEt)_4$ and $H_2Si(OEt)_2$. Reaction of the secondary silane with $Cp^*(PMe_3)Ir(Me)OTf$ followed by 1,2-migration of hydride from silicon to iridium and coordination of triflate would generate the observed products. Experimental verification of this latter hypothesis is hampered somewhat by the fact that $H_2Si(OEt)_2$ is not commercially or synthetically available. It is reasonable to suggest, however, that $Cp^*(PMe_3)Ir(Me)OTf$ is capable of mediating this redistribution, given that similar reactions are catalyzed by Lewis acids and bases and even proceed in the absence of a catalyst.[1,2] At this time there is no direct evidence available to distinguish between the two mechanisms.

At the time we began studying the rearrangement reactions in the $Cp^*(PMe_3)Ir$ system, there were no examples of base-free iridium silylene complexes. Since that time the synthesis of $[PhB(CH_2PPh_2)_3]Ir(H)_2(SiMes_2)$ has been described.[16] The methods by which

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[33] Schmidt, G. F.; Brookhart, M. *J. Am. Chem. Soc.* **1985**, *107*, 1443.

[34] Brookhart, M.; Sabo-Etienne, S. *J. Am. Chem. Soc.* **1991**, *113*, 2777.

[35] Brookhart, M.; Rix, F. C.; DeSimone, J. M.; Barborak, J. C. *J. Am. Chem. Soc.* **1992**, *114*, 5894.

[36] Brookhart, M.; Wagner, M. I. *J. Am. Chem. Soc.* **1996**, *118*, 7219.

[37] Sakaba, H.; Tsukamoto, M.; Hirata, T.; Kabuto, C.; Horino, H. *J. Am. Chem. Soc.* **2000**, *122*, 11511.

[38] Mitchell, G. P.; Tilley, T. D. *Organometallics* **1996**, *15*, 3477.

the silylene complexes are produced in these systems share some similarities. In the Cp* system, one synthetic approach involved anion metathesis with the silyliridium triflate complexes to provide cationic silylene complexes. An alternative method requires treating the more reactive complex [Cp*(PMe$_3$)Ir(CH$_3$)(CH$_2$Cl$_2$)][B(C$_6$F$_5$)$_4$] (**17**) with secondary silanes. The silylene complex [PhB(CH$_2$PPh$_2$)$_3$]Ir(H)$_2$(SiMes$_2$) is produced by treating the π-cyclooctenyl complex [PhB(CH$_2$PPh$_2$)$_3$]Ir(H)(η^3-C$_8$H$_{13}$) with secondary silanes. Both the Cp* and PhB(CH$_2$PPh$_2$)$_3$ systems have the potential to undergo the silane activation/1,2-migration transformation through coordinatively unsaturated cationic alkyl species. Olefin dissociation in the π-cyclooctenyl complex [PhB(CH$_2$PPh$_2$)$_3$]Ir(H)(η^3-C$_8$H$_{13}$) would produce an open coordination site, and CH$_2$Cl$_2$ dissociation is believed to occur in [Cp*(PMe$_3$)Ir(CH$_3$)(CH$_2$Cl$_2$)][B(C$_6$F$_5$)$_4$] (**17**).

Although the thermally sensitive methyliridium dichloromethane-solvated complex [Cp*(PMe$_3$)Ir(CH$_3$)(CH$_2$Cl$_2$)][BAr$_f$] has been isolated successfully,[28] the cationic silyl complex [Cp*(PMe$_3$)Ir(SiPh$_3$)][B(C$_6$F$_5$)$_4$] is apparently not stabilized sufficiently by CH$_2$Cl$_2$ ligation. Instead, activation of an ortho aryl C−H bond takes place to yield {Cp*(PMe$_3$)Ir(H)[η^2-SiPh$_2$(C$_6$H$_4$)]}[B(C$_6$F$_5$)$_4$] (**12**; eq 7). However, addition of the more strongly coordinating solvent acetonitrile to **12** permits the isolation of a cationic silyl complex, [Cp*(PMe$_3$)Ir(SiPh$_3$)(CH$_3$CN)][B(C$_6$F$_5$)$_4$], via a process which undoubtedly involves reductive elimination in **12**. Given the fact that reductive elimination is reversible, the cyclometalated complex **12** can be viewed as a masked version of the Ir(III) silyl complex [Cp*(PMe$_3$)Ir(SiPh$_3$)][B(C$_6$F$_5$)$_4$].[39]

The cyclometalation reaction was extended to tertiary silyliridium complexes which contain silicon−methyl bonds, as Cp*(PMe$_3$)Ir(SiMe$_2$OTf)(Me) gave [Cp*(PMe$_3$)Ir(H)(η^2-SiMe$_2$(CH$_2$))][B(C$_6$F$_5$)$_4$] (**13**) upon reaction with (Et$_2$O)$_2$LiB(C$_6$F$_5$)$_4$ (eq 8). In this case, the cyclometalation event may also be viewed as a β-hydride elimination. A comparison between silene complex **13** and a deprotonated analogue, the neutral iridium silene Cp*(PMe$_3$)Ir(η^2-CH$_2$SiPh$_2$) (**15**) prepared by Campion and Tilley, is warranted. As a result of its "extra proton", silene complex **13** has C−H reductive elimination as an accessible pathway. This reductive elimination is rapid and reversible, such that addition of soft donor ligands such as CO and ethylene to **13** traps the reductive elimination product by coordination to the metal center.[21] The neutral silene complex **15** does not have access to the reductive elimination pathway, however. As a result, treatment of Cp*(PMe$_3$)Ir(η^2-CH$_2$SiPh$_2$) with dative ligands such as PMe$_3$, even at 140 °C, leads to no observable reaction.[40]

The mechanism of C−H activation by Ir(III) complexes has received much attention, with two mechanistic postulates for the reaction being oxidative addition to an Ir(V) intermediate and a concerted σ-bond metathesis.[8,41] The reactions described here detail the only observable C−H activation reactions of Ir(III) materials to give stable Ir(V) aryl and alkyl hydride complexes. As such, they are important in their potential relevance to the intermolecular C−H activation reactions observed at cationic Ir(III) centers.[9] Consistent with our discovery of the cyclometalations reported here, theoretical studies performed on model Ir(III) systems supported the oxidative addition pathway.[42,43]

The ease with which the presumed 16-electron cationic silyliridium complexes underwent cyclometalation to Ir(V) species leaves open to question whether our ability to isolate the silylene complex [Cp*(PMe$_3$)Ir(SiMes$_2$)(H)][OTf] (**6**) was a result of steric effects or was due to the use of a secondary silane in the synthesis. The anion metathesis reaction of Cp*(PMe$_3$)Ir(SiPh$_2$OTf)(H) (the product of reaction of Cp*(PMe$_3$)Ir(Me)OTf with H$_2$SiPh$_2$) with (Et$_2$O)$_2$LiB(C$_6$F$_5$)$_4$ was therefore performed to distinguish these possibilities. The silylene complex [Cp*(PMe$_3$)Ir(SiPh$_2$)(H)][B(C$_6$F$_5$)$_4$] is formed in this reaction, and the ^{29}Si NMR signal of +351 ppm for this species demonstrates that it is base-free. This highlights the necessity of using secondary silanes in the preparation of silylene complexes of this kind. The possibility of interaction of the iridium-bound hydride ligand with the silylene moiety is ruled out by the ^{29}Si NMR shift of the complex.

Isomerization of the cyclometalated iridium complex **5** to silylene complex **6** allows careful study of the 1,2-migration from silicon to the metal center. In particular, the steric environment provides a base-free silylene complex with a triflate anion as the product. Therefore, the large mesityl substituents on silicon enable the study of an iridium silylene complex without salt metathesis. The most interesting aspect of this process is its long reaction time (12 h), compared to the essentially instantaneous reactions of Cp*(PMe$_3$)Ir(Me)OTf with HSiPh$_3$ and HSiMe$_3$. The slow isomerization (eq 3) might be attibuted to a slow reductive elimination step to produce [Cp*(PMe$_3$)Ir(SiHMes$_2$)][OTf] or a rate-limiting migration step to yield the silylene complex.

The kinetic isotope effect of 1.6 ± 0.1 for Si−H vs Si−D migration in **5** is believed to be a primary effect and is relevant to determining the rate-limiting step of the isomerization in eq 3. Isotope effects for other reactions which produce base-free silylene complexes have not yet been reported. A significant isotope effect here indicates that the rate-limiting step is the hydride/deuteride migration. Ruled out is the possibility of a rate-limiting reductive elimination step, because no isotope effect would be expected in that case. An alternative hydride transfer mechanism in which the silicon-bound hydride migrates directly to the metalated carbon atom was ruled out by the following labeling study. When Cp*(PMe$_3$)Ir(Me)OTf was treated with D$_2$SiMes$_2$, clean formation of {Cp*(PMe$_3$)Ir(D)[κ^2-SiH(Mes)(2-CH$_2$-4,6-Me$_2$C$_6$H$_2$)]}[OTf] (**5-*d***) was observed. Using ^{2}H NMR spectroscopy, it was possible to observe exclusive formation of [Cp*(PMe$_3$)Ir(D)(=SiMes)$_2$][OTf], with no label incorporated into the mesityl methyl groups. Since the rate-limiting step is group migration in the conversion of **5** to **6**, and this process necessarily takes place without triflate assistance, the long reaction time could indicate that triflate plays the role of

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(39) A full account of the reactivity of the iridium silyl and silylene complexes described here is in preparation.

(40) Campion, B. K. Ph.D. Thesis, University of California, San Diego, 1990.

(41) Alaimo, P. J.; Bergman, R. G. *Organometallics* **1999**, *18*, 2707.

(42) Strout, D. L.; Zaric, S.; Niu, S. Q.; Hall, M. B. *J. Am. Chem. Soc.* **1996**, *118*, 6068.

(43) Su, M. D.; Chu, S. Y. *J. Am. Chem. Soc.* **1997**, *119*, 5373.

accelerant in the other more rapid migration reactions. Alternatively, the much larger silyl ligand in this case may simply have difficulty achieving the proper orientation for hydride migration.

To distinguish these possibilities, $[Cp^*(PMe_3)Ir(Me)(CH_2Cl_2)][B(C_6F_5)_4]$ (**17**) was treated with H_2SiMes_2. The reaction rate was observed to be identical with that for conversion of **5** to **6**. This confirmed that the anion does not affect this process. If the group migration takes place with triflate assistance, it might then be expected that generation of $[Cp^*(PMe_3)Ir(SiPh_2H)(CH_2Cl_2)][B(C_6F_5)_4]$ would result in a long-lived species that gradually isomerized to $[Cp^*(PMe_3)Ir(H)(SiPh_2)][B(C_6F_5)_4]$ (**16**). However, treatment of methyliridium complex **17** with the sterically less demanding silane H_2SiPh_2 results in an immediate color change, and formation of silylene complex **16** is observed spectroscopically within 10 min. This indicates that hydride migration from any putative $[Cp^*(PMe_3)Ir(SiPh_2H)(CH_2Cl_2)][B(C_6F_5)_4]$ intermediate is rapid. Therefore, the best explanation for why the isomerization of **5** to **6** is slow is that the required conformation for hydride migration in $[Cp^*(PMe_3)Ir(SiMes_2H)(CH_2Cl_2)][OTf]$ is difficult to achieve.

Unlike the isotope effect for group migration, the isotope effect for silane oxidative addition is negligible and consistent with earlier findings. A primary kinetic isotope effect of 1.13 for the oxidative addition of Et_3SiH to $Cp_2Ta(\mu\text{-}CH_2)_2Ir(CO)_2$ to yield $Cp_2Ta(\mu\text{-}CH_2)_2Ir(SiEt_3)(H)(CO)_2$ has been reported previously.[44] Explanations offered for those results included a nonlinear transition state (η^2-bound Et_3SiH) and a preequilibrium involving a σ-complex (η^1-bound Et_3SiH). Graham and co-workers similarly reported a small primary kinetic isotope effect (1.05) for the oxidative addition of Ph_3SiH to $CpMn(CO)_2$ to give $CpMn(CO)_2(H)(SiPh_3)$.[45]

A limited amount of mechanistic information is available concerning the migration reactions which have thus far been reported to yield base-free silylene complexes,[3,4,7,15,16,18,37] compared to that for carbene complexes. Examples of α-hydride migration have been reported in which alkylidene complexes are generated for both early and late transition metals, and in a number of cases the mechanism of the reaction has been probed with isotope effects. An elegant study of this process was reported recently by Schrock et al., in which the primary kinetic isotope effect for molybdenum−alkylidene production was found to be $k_H/k_D(64\ °C) = 3.1 \pm 0.5$.[46] Similarly, Fryzuk et al. reported a primary kinetic isotope, $k_H/k_D(70\ °C) = 3.0(5)$, in the synthesis of a zirconium alkylidene.[47] Green and co-workers studied the reverse reaction, in which a tungsten methylidene hydride is converted to a tungsten methyl complex. They found that deuteration of the "active" methyl group led to an enhanced rate, with an inverse isotope effect of $k_H/k_D(70\ °C) = 0.80 \pm 0.02$.[48] Luecke and Bergman reported that Fischer type cationic alkylidene hydride complexes can be synthesized through a C−H bond activation/1,2-hydride migration strategy, although isotope effects were not reported in that work.[10] The comparatively lower isotope effect in our system suggests that there is less Si−H(D) bond breaking in the transition state for group migration.

Conclusion

After exploring the reaction scope of $Cp^*(PMe_3)Ir(Me)OTf$ with silanes, it is apparent that a rich variety of migration types are possible within this system. These include 1,3-migration in the case of $HSi(SiMe_3)_3$ and silane redistribution in the case of $HSi(OEt)_3$. Additionally, two reaction pathways that appear to be comparable in energy for 16-electron silyliridium(III) complexes are metalation to give Ir(V) products and 1,2-migration to afford silylene complexes. Base-free silylene complexes have been generated and characterized, and our data support a 1,2-migration mechanism that proceeds via these species as reactive intermediates. The similar rates of both the rearrangement reactions to $Cp^*(PMe_3)Ir(SiR_2OTf)(R)$ and the production of the silylene complex $[Cp^*(PMe_3)Ir(SiPh_2)(H)][B(C_6F_5)_4]$ from H_2SiPh_2 and $[Cp^*(PMe_3)Ir(CH_3)(CH_2Cl_2)]\ [B(C_6F_5)_4]$ (**17**) represents our most persuasive evidence for this conclusion.

Experimental Section

General Procedures. Unless otherwise noted, reactions and manipulations were performed at 25 °C in an inert-atmosphere (N_2) glovebox or using standard Schlenk and high-vacuum-line techniques. Except where noted, all NMR spectra were acquired at room temperature. In cases where assignment of the $^{13}C\{^1H\}$ NMR spectrum was ambiguous, resonances were assigned using standard DEPT 45, 90, and/or 135 pulse sequences. Infrared (IR) spectra were recorded using samples prepared as KBR pellets. Mass spectrometric (MS) analyses were obtained at the University of California, Berkeley Mass Spectrometry Facilty on 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. Melting points were determined with a Thomas-Hoover Unimelt capillary melting point apparatus using sealed capillary tubes under nitrogen, are uncorrected, and are reported in °C.

Sealed NMR tubes were prepared by attaching the NMR tube directly to a Kontes high-vacuum stopcock using a Cajon Ultra-Torr reducing union and then flame-sealing on a vacuum line. 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. Known-volume bulb vacuum transfers were accomplished with a digital MKS Baratron gauge attached to a high-vacuum line.

Materials. Unless otherwise noted, reagents were purchased from commercial suppliers and used without further purification. Potassium bromide (Aldrich), Celite (Aldrich), silica gel (Merck 60, 230−400 mesh), and alumina (Brockman I, Aldrich) were dried in vacuo at 250 °C for 48 h. Toluene, pentane, hexanes, methylene chloride, benzene, and toluene (Fisher) were passed through a column of activated alumina (type A2, size 12 × 32, Purifry Co.) under nitrogen pressure and sparged with N_2 prior to use.[49] Diethyl ether and tetra-

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hydrofuran (Fisher) were distilled from purple sodium/benzophenone ketyl under $\mathrm{N_2}$ prior to use. Deuterated solvents (Cambridge Isotope Laboratories) were purified by standard procedures.[50] Our supplier of lithium tetrakis(pentafluorophenyl)borate etherate is Boulder Scientific Co. $\mathrm{H_2SiMes_2}$ was prepared according to the literature procedure,[18] as were compounds **1**−**3**.[9]

Cp*(PMe$_3$)Ir[Si(SiMe$_3$)$_2$Me](SiMe$_2$OTf) (4). A 20 mL scintillation vial was charged with 5 mL of a $\mathrm{CH_2Cl_2}$ solution of Cp*(PMe$_3$)Ir(Me)OTf (95.8 mg, 0.169 mmol) and a magnetic stir bar. To this stirred orange solution was added a solution of HSi(SiMe$_3$)$_3$ (52.1 μL, 0.169 mmol) in $\mathrm{CH_2Cl_2}$ (2 mL) dropwise over a period of 10 s. The reaction mixture was stirred for 5 h, by which time the solution had turned yellow. Removal of the solvent in vacuo afforded 111 mg (82%) of **6** as a sticky, peach-colored foam. Mp: 138−140 °C dec. ^{1}H NMR (400 MHz): δ 1.89 (s, 15H, C$_5$*Me*$_5$), 1.61 (d, $J_{\mathrm{P-H}} = 9.8$ Hz, P*Me*$_3$), 0.96 (s, 3H, Si-*Me*), 0.78 (s, 3H, Si−*Me*), 0.44 (s, 3H, Si−*Me*), 0.17 (s, 9H, Si*Me*$_3$), 0.15 (s, 9H, Si*Me*$_3$). ^{13}C{^{1}H} NMR (126 MHz): the CF$_3$ group was not detectable within a reasonable number of scans; δ 99.4 (s, *C*$_5$Me$_5$), 21.1 (d, $J_{\mathrm{C-P}} =$ 40 Hz, P*Me*$_3$), 12.8 (s, *C*H$_3$), 10.3 (s, *C*H$_3$), 9.9 (s,*C*H$_3$), 4.0 (s, Si*Me*), 3.6 (s, Si*Me*), −1.1 (s, Si*Me*). ^{31}P{^{1}H} NMR (162 MHz): δ −54.0 (s). ^{19}F{^{1}H} NMR (376 MHz): δ −78.9 (s). ^{29}Si{^{1}H} NMR (99 MHz): δ 62.2 (d, $J_{\mathrm{Si-P}} = 21$ Hz, Ir−*Si*(Me$_2$OTf), −15.5 (s, *Si*Me$_3$), −17.2 (s, *Si*Me$_3$), −79.0 (d, $J_{\mathrm{Si-P}} = 12.9$ Hz, Ir−*Si*(SiMe$_3$)$_2$Me). IR: 1273, 1257, 1163, 1045, 952, 843, 773, 652 cm^{-1}. Anal. Calcd for $\mathrm{C_{23}H_{51}F_3O_3IrPSSi_4}$: C, 34.52; H, 6.42. Found: C, 34.63; H, 6.55.

[Cp*(PMe$_3$)Ir(SiMes$_2$)(H)][OTf] (6). A 20 mL scintillation vial was charged with 10 mL of a $\mathrm{CH_2Cl_2}$ solution of Cp*(PMe$_3$)Ir(Me)OTf (**1**; 250 mg, 0.441 mmol) and a magnetic stir bar. To this stirred orange solution was added a solution of $\mathrm{H_2SiMes_2}$ (118 mg, 0.441 mmol) in $\mathrm{CH_2Cl_2}$ (2 mL) dropwise over a period of 10 s. Removal of the solvent in vacuo and washing the resulting bright yellow foam with 10 mL of 1:1 ether/pentane afforded 259 mg (0.316 mmol, 72%) of analytically pure **6** as a yellow foam. ^{1}H NMR (500 MHz): δ 6.98 (s, 1H, Ar), 6.94 (s, 1H, Ar *H*), 6.82 (s, 1H, Ar *H*), 6.75(s, 1H, Ar *H*), 2.68 (s, 6H, coincident Ar *Me*), 2.32 (s, 3H, Ar *Me*), 2.27 (s, 3H, Ar *Me*), 2.17 (s, 3H, Ar *Me*), 2.15 (s, 3H, Ar *Me*), 1.90 (d, $J_{\mathrm{P-H}} = 1.5$ Hz, C$_5$*Me*$_5$), 1.58 (d, $J_{\mathrm{P-H}} = 10.8$ Hz, 9H, P*Me*$_3$), −15.90 (d, $J_{\mathrm{P-H}} = 28$ 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 143.8 (s, Ar *C*), 142.9 (s, Ar *C*), 142.9 (s, Ar *C*), 142.3 (s, Ar *C*), 141.9 (s, Ar *C*), 139.5 (s, Ar *C*), 139.4 (s, Ar *C*), 139.1 (s, Ar *C*), 130.6, (s, Ar *C*H), 129.7 (s, Ar *C*H), 129.3 (s, Ar *C*H), 129.1 (s, Ar *C*H), 100.2 (s, *C*$_5$Me$_5$), 24.8 (s, Ar *Me*), 23.9 (s, Ar *Me*), 23.3 (s, Ar *Me*), 23.1 (s, Ar *Me*), 22.1 (d, $J_{\mathrm{C-P}}$ = 43 Hz, P*Me*$_3$) 21.6 (s, Ar *Me*), 21.5 (s, Ar *Me*), 10.1 (s, C$_5$*Me*$_5$). ^{31}P{^{1}H} NMR (162 MHz): δ −45.1 (s). ^{19}F{^{1}H} NMR (376 MHz): δ −78.9 (s). ^{29}Si{^{1}H} NMR (99 MHz) δ 304.9 (dd, $J_{\mathrm{Si-H}}$ = 10 Hz, $J_{\mathrm{Si-P}} = 11$ Hz). IR: 2145, 1605, 1548, 1475, 1454, 1418, 1383, 1285, 1250, 1225, 1161, 1077, 1031, 959, 827, 638 cm^{-1}. Anal. Calcd for $\mathrm{C_{32}H_{47}F_3IrO_3PSSi}$: C, 46.87; H, 5.78. Found: C, 46.68; H, 6.07.

[Cp*(PMe$_3$)$\overline{\mathbf{Ir}(\kappa^2\text{-}\mathbf{Si(S^tBu)_2S}}$^{t}Bu)][OTf] (7). A 20 mL scintillation vial was charged with 5 mL of a $\mathrm{CH_2Cl_2}$ solution of Cp*(PMe$_3$)Ir(Me)OTf (**1**; 70.0 mg, 0.0123 mmol) and a magnetic stir bar. To this stirred solution was added dropwise over 10 s a solution of HSi(S^{t}Bu)$_3$ (36.6 mg, 0.0123 mmol) in $\mathrm{CH_2Cl_2}$ (2 mL). Gas evolution was observed upon mixing, and the solution was stirred for 10 min at room temperature. The solvent was removed in vacuo to give a yellow powder that could be recrystallized from $\mathrm{CH_2Cl_2}$/pentane at −35 °C to afford 92.0 mg (88%) of pure, bright yellow **7**. Mp: 116−120 °C dec. ^{1}H NMR (400 MHz): δ 2.05 (d, $J_{\mathrm{P-H}} = 2.2$ Hz, 15H, C$_5$*Me*$_5$), 1.70 (d, $J_{\mathrm{P-H}} = 10.2$ Hz, 9H, P*Me*$_3$), 1.68 (s, 9H, S^{t}Bu), 1.58 (s, 9H, S^{t}Bu), 1.45 (s, 9H, S^{t}Bu). ^{13}C{^{1}H} NMR (126 MHz: the CF$_3$ group was not detectable within a reasonable number of scans; δ 98.8 (s, *C*$_5$Me$_5$), 53.3 (s, SiS*C*(CH$_3$)$_3$), 52.6 (br s, IrS*C*(Me)$_3$), 52.5 (s, SiS*C*(Me)$_3$), 35.1 (s, SiSC(*Me*)$_3$), 35.0 (s, Si−SC(*C*H$_3$)$_3$), 32.5(s, IrSC(*Me*)$_3$), 17.8 (br s, P*Me*$_3$), 11.5 (s, C$_5$*Me*$_5$). ^{31}P{^{1}H} NMR (162 MHz): δ −45.4 (s). ^{19}F{^{1}H} NMR (376 MHz): δ −78.9 (s). ^{29}Si{^{1}H} NMR (99 MHz): δ −12.4 (d, $J_{\mathrm{Si-P}} = 14$ Hz). IR: 2965, 2922, 1460, 1277, 1255, 1160, 1031, 956, 638 cm^{-1}. Anal. Calcd for $\mathrm{C_{26}H_{51}F_3IrO_3PS_4Si}$: C, 36.82; H, 6.06. Found: C, 36.85; H, 6.28.

Cp*(PMe$_3$)Ir[Si(S^{t}Bu)$_2$F](S^{t}Bu) (8). A 20 mL scintillation vial was charged with 5 mL of a $\mathrm{CH_2Cl_2}$ solution of [Cp*(PMe$_3$)-$\overline{\mathrm{Ir}(\kappa^2\text{-}\mathrm{Si(S^tBu)_2S}}$^{t}Bu)][OTf] (**7**; 35.1 mg, 0.041 mmol), $\mathrm{CH_2Cl_2}$ (5 mL) and a magnetic stir bar. To this stirred solution was added dropwise over 10 s a solution of tris(dimethylamino)sulfur (trimethylsilyl)difluoride (11.4 mg, 0.041 mmol) in $\mathrm{CH_2Cl_2}$ (2 mL). The reaction mixture was stirred for 20 min at room temperature. The solvent was removed in vacuo to give a yellow powder that could be recrystallized from pentane/Et$_2$O at −35 °C to afford 24.2 mg (82%) of yellow **8**. Mp: 185−187 °C dec. ^{1}H NMR (500 MHz): δ 1.80 (d, $J_{\mathrm{P-H}} = 1.8$ Hz, 15H, C$_5$*Me*$_5$), 1.70 (d, $J_{\mathrm{P-H}} = 10.4$ Hz, 9H, P*Me*$_3$), 1.53 (s, 9H, S^{t}Bu), 1.52 (s, 9H, S^{t}Bu), 1.34 (s, 9H, S^{t}Bu). ^{13}C{^{1}H} NMR (126 MHz): δ 98.91 (d, $J_{\mathrm{P-C}} = 2.9$ Hz, *C*$_5$Me$_5$), 50.31 (s, Si−S*C*(Me)$_3$), 50.23 (s, SiS*C*(Me)$_3$), 40.12 (d, $J_{\mathrm{P-C}} = 4.6$ Hz, Ir−S*C*(CH$_3$)$_3$), 36.26 (s, SiSC(*Me*)$_3$), 35.64 (d, $J_{\mathrm{P-C}} = 1.5$ Hz, IrSC(*Me*)$_3$), 35.12(s, SiSC(*Me*)$_3$), 17.20 (d, $J_{\mathrm{P-C}} = 42.1$ Hz, P*Me*$_3$), 10.67 (s, C$_5$*Me*$_5$) ppm. ^{31}P{^{1}H} NMR (162 MHz): δ −45.5 (s). ^{19}F{^{1}H} NMR (376 MHz): δ −104 (s). ^{29}Si{^{1}H} NMR (99 MHz): δ 9.1 (dd, $J_{\mathrm{Si-F}} = 400$ Hz, $J_{\mathrm{P-Si}} = 25$ Hz). IR: 2560, 2909, 2856, 2365 (w), 1734 (w), 1454, 1361, 1277, 1156, 1026, 958, 938, 859, 792, 720, 677, 571, 511, 468 cm^{-1}. Anal. Calcd for $\mathrm{C_{25}H_{51}FIrPS_3Si}$: C, 41.81; H, 7.16. Found: C, 42.16; H, 7.38.

Cp*(PMe$_3$)Ir[Si(OEt)$_2$OTf](H) (9). A 20 mL scintillation vial was charged with 5 mL of a $\mathrm{CH_2Cl_2}$ solution of Cp*(PMe$_3$)-Ir(Me)OTf (52.2 mg, 0.0920 mmol) and a magnetic stir bar. To this stirred solution was added dropwise over 10 s a solution of HSi(OEt)$_3$ (60 μL, 0.32 mmol) in $\mathrm{CH_2Cl_2}$ (2 mL). The reaction mixture was stirred for 5 min at room temperature, and then the solvent was removed in vacuo to afford 52.5 mg (85%) of **9** as a sticky light yellow oil that was >95% pure by ^{1}H NMR spectroscopy. Repeated recrystallization attempts failed to produce a solid. ^{1}H NMR (400 MHz): δ 3.83 (m, 4H, Si−OEt), 2.03 (d, $J_{\mathrm{P-H}} = 1.5$ Hz, 15H, C$_5$*Me*$_5$), 1.60 (d, $J_{\mathrm{P-H}} = 10.5$ Hz, 9H, P*Me*$_3$), 1.21 (m, 6H, Si−OEt), −18.13 (d, $J_{\mathrm{P-H}} = 27$ Hz, 1H, Ir−H). ^{13}C{^{1}H} NMR (100 MHz): the CF$_3$ group was not detectable within a reasonable number of scans; δ 95.91 (d, $J_{\mathrm{P-C}} = 2.5$ Hz, *C*$_5$Me$_5$), 59.30 (s, O*C*H$_2$CH$_3$), 59.27 (s, O*C*H$_2$CH$_3$), 22.19 (d, $J_{\mathrm{P-C}} = 40$ Hz, P*Me*$_3$), 18.28 (s, OCH$_2$*C*H$_3$), 18.25 (d, OCH$_2$*C*H$_3$), 10.74 (s, C$_5$*Me*$_5$). ^{31}P{^{1}H} NMR (162 MHz): δ −46.1 (s). ^{19}F{^{1}H} NMR (376 MHz): δ −78.9 (s). ^{29}Si{^{1}H} NMR (99 MHz): δ −29.2 (d, $J_{\mathrm{P-Si}} = 27$ Hz). IR: 1280, 1245, 960, 800, 742, 652, 579, 519 cm^{-1}. MS (EI): *m/z* 672 (M$^+$). HRMS (EI): *m/z* (M$^+$) for $\mathrm{C_{18}H_{35}F_3IrO_5PSSi}$ calcd 672.1294, obsd 672.1288.

Cp*(PMe$_3$)Ir[Si(OEt)$_2$OTf](Cl) (10). A 20 mL scintillation vial was charged with 5 mL of a $\mathrm{CH_2Cl_2}$ solution of Cp*(PMe$_3$)Ir(H)(Si(OEt)$_2$OTf (**9**; 52.5 mg, 0.0781 mmol) and a magnetic stir bar. To this stirred solution was added neat $\mathrm{CCl_4}$ (30.1 μL, 0.31 mmol). The reaction mixture was stirred for 2 h at room temperature, and then the solvent was removed in vacuo. Subsequent extraction into ether/pentane (1:1) and removal of volatile materials in vacuo afforded 44.2 mg (0.0625 mmol, 80%) of **10** as a yellow oil that was >95% pure by ^{1}H NMR spectroscopy. Repeated recrystallization attempts failed to yield a solid. ^{1}H NMR (400 MHz): δ 3.97 (m, 4H, SiOEt), 1.76 (d, $J_{\mathrm{P-H}} = 1.8$ Hz, 15H, C$_5$*Me*$_5$), 1.64 (d, $J_{\mathrm{P-H}} = 10.8$ Hz, 9H, P*Me*$_3$), 1.22 (m, 6H, SiOEt). ^{13}C{^{1}H} NMR (126 MHz): the

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CF_3 group was not detectable within a reasonable number of scans; δ 97.5 (d, $J_{P-C} = 2.5$ Hz, C_5Me_5), 60.18 (s, OCH_2CH_3), 60.13 (OCH_2CH_3), 18.33 (s, OCH_2CH_3), 18.27 (s, OCH_2CH_3), 17.2 (d, $J_{P-C} = 40$ Hz, PMe_3), 9.64 (s, C_5Me_5). $^{31}P\{^1H\}$ NMR (162 MHz): δ −37.6 (s). $^{19}F\{^1H\}$ NMR (376 MHz): δ −78.9 (s). $^{29}Si\{^1H\}$ NMR (99 MHz): δ −40.0 (d, $J_{P-Si} = 35$ Hz). IR: 2921, 2857, 1642, 1599, 1449, 1260, 1105, 1019, 803, 695 cm^{-1}. MS (EI): *m/z* 706 (M^+). HRMS (EI): *m/z* for $C_{18}H_{34}F_3IrO_5PSSiCl$ calcd 706.0904, obsd 706.0907.

Cp*(PMe$_3$)Ir(SiPh$_2$Cl)Cl (11). To a 20 mL scintillation vial containing $HClSiPh_2$ (40.3 μL, 0.206 mmol) and Cp*(PMe_3)Ir(Me)(OTf) (117 mg, 0.206 mmol) was added 5 mL of CH_2Cl_2. The resulting yellow solution was mixed thoroughly for 30 s with a pipet, and gas evolution was observed. This solution was added to solid bis(triphenylphosphoranylidene)ammonium chloride (118.2 mg, 0.2059 mmol) in another vial, and the resulting solution was similarly mixed and then allowed to stand for 15 min. The solvent was removed in vacuo and the residue extracted with 2 × 3 mL of benzene. The benzene was removed in vacuo to give a bright yellow-orange powder, which was recrystallized from CH_2Cl_2/CH_3CN at −35 °C. The yield of recrystallized material was 66.0 mg (0.100 mmol, 49%). ^1H NMR (500 MHz): δ 7.85 (m, 4 H, Si−*Ph*), 7.21 (m, 6 H, Si−*Ph*), 1.54 (d, $J_{P-H} = 2$ Hz, 15 H, C_5Me_5), 1.26 (d, $J_{P-C} = 14$ Hz, 9 H, PMe_3). $^{13}C\{^1H\}$ NMR (126 MHz): δ 146.2 (s, Ar *C*), 145.1 (s, Ar *C*), 135.4 (s, Ar *C*H), 134.7 (Ar *C*H), 128.3 (s, Ar *C*H), 128.1 (s, Ar *C*H), 127.6 (s, Ar *C*H), 127.2 (s, Ar *C*H), 97.8 (d, $J_{P-C} = 3$ Hz, C_5Me_5), 16.9 (d, $J_{P-C} = 39$ Hz, PMe_3), 9.5 (s, C_5Me_5). $^{31}P\{^1H\}$ NMR (162 MHz): δ −38.7. ^{29}Si NMR (INEPT, 99 MHz): δ 6.7. IR: 3046, 2960, 2915, 1426, 1261, 1092, 1029, 955, 803, 705, 515, 485 cm^{-1}. Anal. Calcd for $C_{25}H_{34}PIrSiCl_2$: C, 45.72; H, 5.22. Found: C, 45.64; H, 5.16.

[Cp*(PMe$_3$Ir(η^2-SiPh$_2$(C$_6$H$_4$))(H)][B(C$_6$F$_5$)$_4$] (12). A 20 mL scintillation vial was charged with 2 mL of a CH_2Cl_2 solution of Cp*(PMe_3)Ir(Me)OTf (**1**; 101 mg, 0.179 mmol). To this was added a CH_2Cl_2 solution (2 mL) of $HSiPh_3$ (46.5 mg, 0.179 mmol) at room temperature. Gas evolution was observed immediately after addition. The solution was stirred for 5 min and then cooled in a −35 °C freezer for 5 min. The solution was then added to a 2 mL CH_2Cl_2 solution of $(Et_2O)_2LiB(C_6F_5)_4$ (136 mg, 0.179 mmol) which had also been cooled in a −35 °C freezer for 5 min. The resulting mixture immediately became cloudy. The reaction mixture was returned to the −35 °C freezer for 10 min and was then filtered through a glass fiber filter. The solvent was removed in vacuo, and the resulting light cream colored foam was recrystallized from Et_2O/pentane at −35 °C to afford 166 mg (81%) of **12** as a pale yellow crystalline solid. ^1H NMR (500 MHz): δ 7.81 (br s, 2H, Ar *H*), 7.38 (m, 12H, Ar *H*), 7.18 (s, 2H, Ar *H*), 1.71 (d, $J_{P-H} = 2.0$ Hz, 15H, C_5Me_5), 1.18 (d, $J_{P-H} = 11$ Hz, 9H, PMe_3), −12.7 (d, $J_{P-H} = 20$ Hz, 1H, Ir−*H*). $^{13}C\{^1H\}$ NMR (126 MHz): δ 152.4, (s, Ar *C*), 149.9 (m, B(C_6F_5), 138.0 (m, B(C_6F_5)), 136.0 (m, B(C_6F_5)), 136.4 (s, Ar *C*H), 134.7 (s, Ar *C*H), 134.5 (s, Ar *C*), 134.1 (s, Ar *C*H), 133.1 (s, Ar *C*H), 133.1(s, Ar *C*H), 132.4 (d, $J_{P-C} = 4$ Hz, Ar *C*H), 131.8 (s, Ar *C*H), 131.2 (s, Ar *C*H), 131.2 (s, Ar *C*), 129.6 (s, Ar *C*H), 128.9 (s, Ar *C*), 129.0 (s, Ar *C*H), 128.4 (s, Ar *C*), 126.1 (s, Ar *C*H), 124.0 (m, B(C_6F_5)), 102.9 (d, $J_{C-P} = 2$ Hz, C_5Me_5), 16.4 (d, $J_{C-P} = 43$ Hz, PMe_3), 9.6 (s, C_5Me_5). $^{31}P\{^1H\}$ NMR (162 MHz): δ −35.9 (s). $^{19}F\{^1H\}$ NMR (376 MHz): δ −133 (s), −164 (t, $J_{B-F} = 19$ Hz), −167 (s). $^{29}Si\{^1H\}$ NMR (99 MHz): δ −62.5 (br s). IR: 3050, 3000, 2919, 2084, 1643, 1514, 1465, 1382, 1274, 1085, 979, 856, 703, 511 cm^{-1}. Anal. Calcd for $C_{55}H_{39}F_{20}IrPBSi$: C, 49.23; H, 2.93. Found: C, 49.0; H, 3.32.

[Cp*(PMe$_3$)Ir(η^2-CH$_2$SiMe$_2$)(H)][B(C$_6$F$_5$)$_4$] (13). A 20 mL scintillation vial was charged with 5 mL of a CH_2Cl_2 solution of Cp*(PMe_3)Ir($SiMe_2OTf$)(Me) (**3**; 68.2 mg, 0.109 mmol). The solution was pipetted onto solid $(Et_2O)_2LiB(C_6F_5)_4$ (95.0 mg, 0.109 mmol), and the resulting slurry was mixed with the pipet for 30 s. The slurry was then filtered through a Celite/fiberglass plug, and the filtrate was removed in vacuo. The residue was redissolved in 3 mL of CH_2Cl_2, filtered through fiberglass, and layered with 12 mL of pentane. The vial was stored at −35 °C for 2 days, and pale yellow crystals grew during this time (54.0 mg, 0.004 67 mmol, 43%). The crystals were isolated by decanting the mother liquors, washing with 2 × 1 mL of pentane, and drying in vacuo. ^1H NMR (400 MHz): δ 1.97 (d, $J_{P-H} = 2.0$ Hz, 15H, C_5Me_5), 1.50 (d, $J_{P-H} = 10.8$ Hz, 9H, PMe_3), 0.77 (s, 3H, Si−*Me*), 0.72 (s, 3H, Si−*Me*), 0.46 (d, $J_{H-H} = 14$ Hz, 1H, Ir−C*H*$_2$), 0.06 (dd, $J_{H-H} = 14$ Hz, $J_{P-H} = 19$ Hz, 1H, Ir−C*H*$_2$), −14.8 (d, $J_{P-H} = 20$ Hz, 1H, Ir−*H*). $^{13}C\{^1H\}$ 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)), 99.9 (s, C_5Me_5), 18.4 (d, $J_{P-C} = 41$ Hz, PMe_3), 10.2 (C_5Me_5), −2.7 (s, Si−*Me*), −3.0 (s, Si−*Me*), −16.8 (bs, Ir−*C*H$_2$). ^{31}P NMR (162 MHz); δ −39.5 (s). ^{19}F NMR (376 MHz): δ −133 (s), −164 (t, $J_{B-F} = 19$ Hz), −167 (s). ^{29}Si NMR (99 MHz): δ 2.1 (d, $J_{P-Si} = 13$ Hz). IR: 2991, 2140, 2034, 1642, 1513, 1464, 1384, 1276, 1088, 980, 774, 756 cm^{-1}. Anal. Calcd for $C_{40}H_{33}F_{20}IrBPSi$: C, 41.57; H, 2.88. Found: C, 41.87; H, 2.87.

{Cp*(PMe$_3$)Ir[SiMe$_2$(Et$_2$O)](Me)}[B(C$_6$F$_5$)$_4$] (14). This complex is observed to be in equilibrium with **13** and was not isolated. ^1H NMR (190 K, 500 MHz): δ 4.33 (m, 2H, diastereotopic CH_3CH_2OEt), 4.22 (m, 2H, diastereotopic CH_3CH_2OEt), 1.64 (s, 15H, Cp*), 1.38 (d, $J_{P-H} = 11$ Hz, 9H, PMe_3), 1.30 (vt, $J_{H-H} = 5$ Hz, 6H, $CH_3CH_2OCH_2CH_3$), 0.49 (s, 3H, Si−*Me*), 0.43 (s, 3H, Si−*Me*), −0.06 (d, $J_{P-H} = 5$ Hz, 3H, Ir−*Me*). $^{13}C\{^1H\}$ NMR (190 K, 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)), 95.6 (s, C_5Me_5), 68.0 (s, Si-bound CH_3CH_2OEt), 14.7 (br s, PMe_3 overlapping with CH_3CH_2OEt of free Et_2O), 12.5 (s, Si-bound CH_3CH_2OEt), 8.7 (C_5Me_5), 7.2 (s, Si−*Me*), 6.6 (s, Si−*Me*), −32.0 (d, $J_{P-C} = 8$ Hz, Ir−*Me*). ^{31}P NMR (190 K, 202 MHz): δ −43.7 (br s). ^{19}F NMR (376 MHz): δ −133 (s), −164 (t, $J_{B-F} = 19$ Hz), −167 (s). ^{29}Si NMR INEPT (190 K): δ 10.9.

[Cp*(PMe$_3$)Ir(SiPh$_2$)(H)][B(C$_6$F$_5$)$_4$] (16). To a 20 mL scintillation vial containing 5 mL of a CH_2Cl_2 solution of Cp*(PMe_3)Ir(Me)(OTf) (22.3 mg, 0.0393 mmol) was added H_2SiPh_2 (7.3 μL, 0.0393 mmol) by syringe. Upon mixing with a pipet, the solution became pale yellow and effervescence was observed. After 30 s, this solution was pipetted onto solid $(Et_2O)_2LiB(C_6F_5)_4$ (32.8 mg, 0.0393 mmol), which produced a slightly darker yellow slurry. This slurry was mixed for 30 s with a pipet. The slurry was then filtered through a Celite/fiberglass filter and the filter plug washed with 1 mL of CH_2Cl_2. The solvent was then removed in vacuo to give an off-white foam (46.8 mg, 94%). Because precipitation of $(Et_2O)_xLiOTf$ in the salt metathesis reaction was not an effective means of purification, samples of **16** prepared in this manner were typically contaminated with 0.2−0.5 equiv of lithium etherate salts. Prolonged metathesis reaction times (2 h) had no effect on the product composition, and the presence of these salts had no apparent effect on the reactivity of **16**. ^1H NMR (400 MHz): δ 7.62 (d, $J_{H-H} = 7$ Hz, 4H, Si−Ar), 7.46 (m, 6 H, Si−Ar), 1.84 (d, $J_{P-H} = 2$ Hz, 15 H, C_5Me_5), 1.29 (d, $J_{P-H} = 14$ Hz, 9H, PMe_3), −17.40 (d, $J_{P-H} = 36$ Hz, 1 H, Ir−*H*). $^{13}C\{^1H\}$ NMR (126 MHz): δ 149.9 (m, B(C_6F_5)), 138.6 (s, Ar *C*), 138.0 (m, B(C_6F_5)), 136.0 (m, B(C_6F_5)), 134.3 (s, Ar *C*H), 130.0 (s, Ar *C*H), 128.1 (s, Ar *C*H), 124.0 (m, B(C_6F_5)), 96.9 (s, C_5Me_5), 21.2 (d, $J_{P-C} = 40$ Hz, PMe_3), 9.7 (s, C_5Me_5). $^{31}P\{^1H\}$ NMR (162 MHz): δ −49.3. ^{29}Si NMR (INEPT, 99 MHz): δ 351.1. $^{19}F\{^1H\}$ NMR (376 MHz): δ −133 (s), −164 (t, $J_{B-F} = 19$ Hz), −167 (s). IR: 2984, 2921, 2142 (Ir−H), 1643, 1514, 1467, 1383, 1275, 1089, 980, 756, 703, 661, 502 cm^{-1}. Satisfactory elemental analysis could not be obtained.

Determination of Rate Constants and Isotope Effects. The solutions used for kinetic runs were prepared by pipetting a 0.5 mL CD_2Cl_2 solution of Cp*(PMe_3)Ir(Me)(OTf) onto solid H_2SiMes_2 and transferring this solution to a Wilmad PS-504 NMR tube containing a known amount of 1,3,5-trimethoxybenzene internal standard. The tube was then attached directly to a Kontes high-vacuum stopcock using a Cajon Ultra-

Torr reducing union, flame-sealed under active vacuum, and kept frozen until directly before the kinetic run. The competition kinetic isotope effect using $HSiPh_3$ and $DSiPh_3$ was determined by first charging a Wilmad PS-504 NMR tube with 1.0 and 50 equiv each of $HSiPh_3$ and $DSiPh_3$. The tube was then attached to a Kontes high-vacuum stopcock using a Cajon Ultra-Torr reducing union, and 0.5 mL of CD_2Cl_2 was vacuum-transferred into the tube at −196 °C. The tube was warmed first to 0 °C over 2 min and then to room temperature. The relative amounts of CH_3D and CH_4 were determined by integration of the ^1H NMR spectrum and then statistically correcting the data.

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Supporting Information Available: Tables giving X-ray structural data for complexes **2**, **4**, and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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