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An Observable Silene/Silylene Rearrangement in a Cationic Iridium Complex

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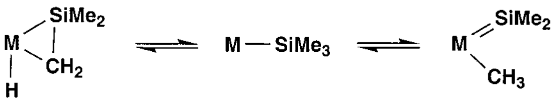
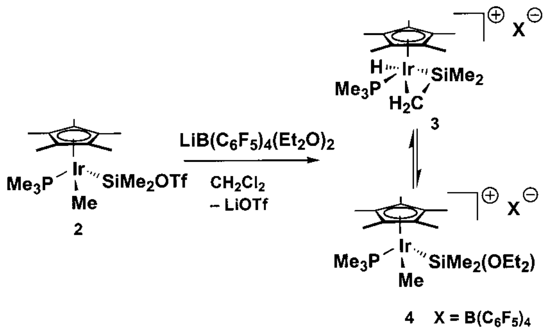
Summary: The iridium complex Cp(PMe*$_3$*)Ir(Me)(SiMe*$_2$*OTf) (***2***) reacts with LiB(C*$_6$*F*$_5$*)*$_4$*(Et*$_2$*O)*$_2$ *to form a mixture of the silene complex [Cp*(PMe*$_3$*)Ir(*η^2*-CH*$_2$*SiMe*$_2$*)(H)][B(C*$_6$*F*$_5$*)*$_4$*] (***3***) and the base-stabilized silylene complex [Cp*(PMe*$_3$*)Ir(Me)(SiMe*$_2$*(Et*$_2$*O))][B(C*$_6$*F*$_5$*)*$_4$*] (***4***). The silene complex* ***3*** *has been crystallographically characterized. Addition of pyridine to this mixture affords Cp*(PMe*$_3$*)Ir(Me)(SiMe*$_2$*(L)][B(C*$_6$*F*$_5$*)*$_4$*] (***5a***, L = pyridine) in good yield, whereas addition of CO or ethylene results in clean formation of Cp*(PMe*$_3$*)Ir(L)(SiMe*$_3$*)][B(C*$_6$*F*$_5$*)*$_4$*] (***8a***, L = CO;* ***8b***, L =* C_2H_4*).*

Numerous catalytic transformations are based on conversions involving organosilanes, since Si−H activation via oxidative addition is a facile process.[1] In general, this process introduces a silyl ligand, which may react further via metal-mediated rearrangements. Thus, a thorough understanding of this rearrangement chemistry is key to the development of new catalytic processes. Despite much research focus, however, these rearrangements are not well understood. Berry and coworkers recently reported the first direct observation of intramolecular activation (or β-hydrogen elimination) of aliphatic C−H bonds in a 16-electron metal silyl to generate a silene complex, showing that a silene ligand can be derived from a silyl complex.[2,3] Likewise, we have shown that observable base-free silylene ligands may be derived from silyl ligands by α-migration.[4] Reactivity studies in the iridium system described here provide evidence for a third type of isomerization, involving silene and silylene ligands (eq 1). Whereas the free silene/silylene interconversion between $SiMe_2$ and $H_2C{=}Si(H)Me$ has been the topic of considerable experimental and theoretical investigation,[1] this is the first report of such a process within the coordination sphere of a transition metal.



(1)

The Ir(III) complex Cp*(PMe$_3$)Ir(Me)OTf (OTf = OSO_2CF_3) (**1**) reacts rapidly with trimethylsilane by Si−H activation followed by rearrangement, giving Cp*(PMe$_3$)Ir(Me)(SiMe$_2$OTf) (**2**) as the final product.[5,6] To determine whether this system can be used to generate an unsolvated silylene complex,[7,8] we have investigated reactions designed to remove the triflate anion from **2**. Treatment of **2** with 1 equiv of LiB(C_6F_5)$_4$(Et$_2$O)$_2$ in CH_2Cl_2 solvent at 25 °C produces an equilibrium mixture of silene complex [Cp*(PMe$_3$)Ir(η^2-CH$_2$SiMe$_2$)(H)][B(C_6F_5)$_4$] (**3**) and [Cp(PMe$_3$)Ir(SiMe$_2$(Et$_2$O))(Me)][B(C_6F_5)$_4$] (**4**), established after 4 h at 25 °C, in a ratio of 2.6:1 favoring silene complex **3**. (eq 2). The salt metathesis is complete within seconds, and monitoring the reaction mixture after 5 min at 25 °C gave no indication of observable reaction intermediates, although the intermediacy of the Ir(III) silyl complex [Cp*(PMe$_3$)Ir(SiMe$_3$)][B(C_6F_5)$_4$] is suspected.



(2)

The room-temperature ^{1}H NMR spectrum (CD_2Cl_2) of complex **3** exhibits the expected resonances, including those for diastereotopic methyl groups at 0.77 and 0.72 ppm, diastereotopic methylene protons at 0.46 and 0.05 ppm for the metalated carbon atom, and an Ir−H resonance at −14.9 ppm. Several of the ^{1}H NMR resonances for **4** are broadened at room temperature, indicating a fluxional process. However, at 190 K the spectrum sharpens, and full spectroscopic characterization of the diethyl ether complex is possible. A variable-temperature ^{1}H NMR spectroscopy experiment also gave support for the **3**:**4** equilibrium, in that the ratio of silene **3** to ether-stabilized silylene complex **4** is approximately 1:1 at 220 K and returns to 2.6:1 upon warming again to 298 K. For entropic reasons, a reduced proportion of silene complex at lower temperature is expected.

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10.1021/om010435a CCC: $20.00

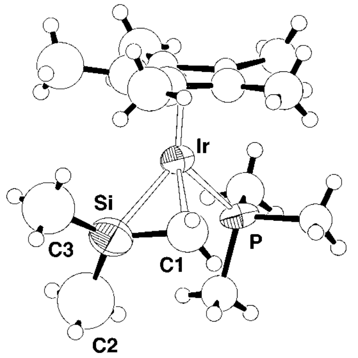
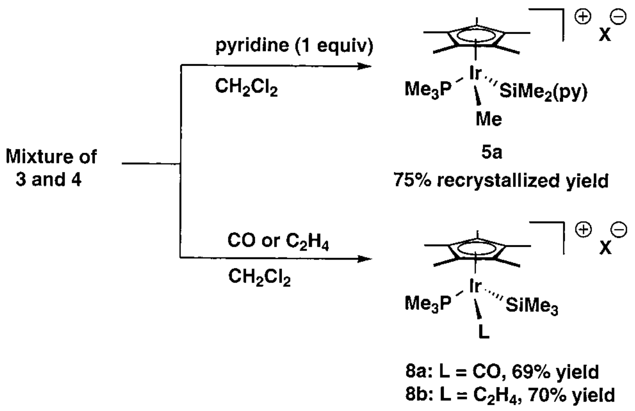


Figure 1. ORTEP diagram of the cationic portion of complex **3** (iridium-bound hydrogen observed by IR and ^{1}H NMR spectroscopy not located; borate counterion not shown for clarity). Selected bond lengths and angles: Ir–P 2.182(8) Å; Ir–C1 2.22(2) Å, Ir–Si 2.439(8) Å; Si–C1 1.84(2) Å; Si–C2 1.84(2) Å; C1–Si–C2 119(1)°; C1–Si–C3 125(1)°; C2–Si–C3 109(1)°.

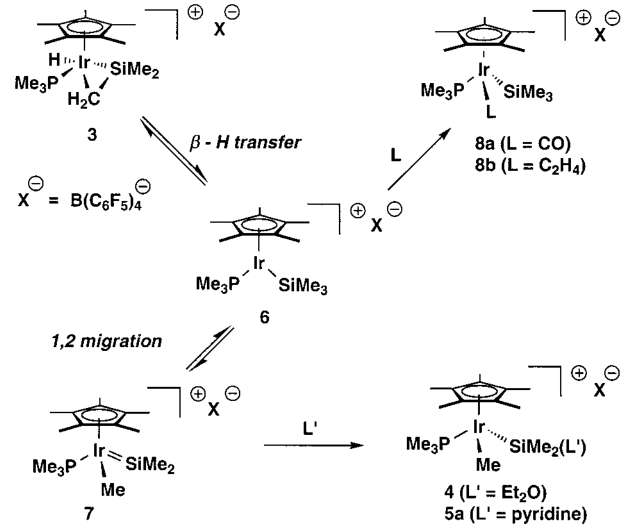
The silene complex **3** can be isolated in 43% yield as an analytically pure off-white solid by crystallization from pentane/CH_2Cl_2. Use of the soluble salt $LiB(C_6F_5)(Et_2O)_2$ appears to be crucial in rapidly accessing the silene complex before appreciable decomposition takes place; salt metathesis with $NaBPh_4$ or $Na(B(3,5\text{-}CF_3)\text{-}C_6H_3)_4$ resulted in decomposition. The C–H coupling constant for the methylene group of **3** was measured to be 147.5 Hz by ^{13}C NMR spectroscopy. This value lies between the values assigned to sp^3 (125.0 Hz for CH_4) and sp^2 (156.2 Hz for C_2H_4) hybridization[9] and indicates partial contributions from two resonance forms involving coordinated silene and metallasilacyclopropane structures.

Crystals of **3** suitable for an X-ray diffraction study were grown from a CH_2Cl_2/pentane mixture. An ORTEP diagram of the cationic portion of the complex can be seen in Figure 1. The sum of the C–Si–C angles around the silicon center is 353°, which again is between the values assigned to sp^3 (329°) and sp^2 (360°) hybridization, indicating partial double bond character between silicon and the metalated carbon atom. The solid-state structure of **3** exhibits Si–C bond lengths that are within experimental error of each other, although structural disorder mandates that the data obtained can reliably be used only to establish atom connectivity (see Supporting Information). Other silene complexes exhibit modestly shortened Si–CH_2 bonds.[10–12]

Scheme 1



Scheme 2



Treatment of a mixture of **3** and **4** with pyridine produced $[Cp^*(PMe_3)Ir(Me)(SiMe_2(py))][B(C_6F_5)_4]$ (**5a**), in 75% isolated yield as a bright yellow crystalline solid (Scheme 1). We propose that equilibration of **3** and **4** and conversion of this mixture to **5a** occur by the pathway illustrated in Scheme 2. Carbon–hydrogen reductive elimination (β-H transfer) results in formation of cationic 16-electron silyl species **6**, which then goes on to form base-free metal–silylene complex **7** by migration of a methyl group from silicon to iridium.[5] Trapping of this species by pyridine leads to isolable complex **5a**; the related complex, $[Cp^*(PMe_3)Ir(Me)(SiMe_2(py))][OTf]$ (**5b**), is prepared in 98% isolated yield by treating the migrated triflato species $Cp^*(PMe_3)Ir(Me)(SiMe_2OTf)$ (**2**) with 1 equiv of pyridine.

In contrast to the reaction with pyridine, treatment of **3** and **4** with carbon monoxide provides the nonmigrated silyl carbonyl complex $[Cp^*PMe_3Ir(SiMe_3)(CO)][B(C_6F_5)_4]$ (**8a**) in 69% recrystallized yield. Again, we postulate the intermediacy of the iridium silyl cation **6**, which is trapped by CO (Scheme 2). We believe this change in selectivity is 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. We find here that ethylene reacts with a mixture of **3** and **4** like CO rather than pyridine, leading to the silyl ethylene complex $[Cp^*PMe_3Ir(SiMe_3)(C_2H_4)][B(C_6F_5)_4]$ (**8b**) in 70% isolated yield as pale yellow crystals. To the best of our knowledge, this is the first reported *cationic* silyl ethylene complex, and it provides circumstantial evidence for the existence of $[Cp^*P(OMe)_3Co(SiEt_3)(\text{olefin})]^+$, a postulated intermediate in catalytic hydrosilylation of olefins by $[Cp^*\text{-}(P(OMe)_3)CoCH_2CH_2\text{-}\mu\text{-}H]^+B[3,5\text{-}(CF_3)_2C_6H_3]_4^-$.[13]

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[11] Campion, B. K.; Heyn, R. H.; Tilley, T. D.; Rheingold, A. L. *J. Am. Chem. Soc.* **1993**, *115*, 5527. In contrast to the reactivity of the ruthenium silene complex described in this paper, we have never observed silicon–hydrogen reductive elimination behavior from silene complex **3** to produce a species such as "$Cp^*(PMe_3)Ir(CH_2SiMe_2H)$".

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The chemistry of metal complexes containing reactive silicon-based fragments appears 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.[14] 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.[15] 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 can be used to control the course of reactions from this equilibrium manifold. We are currently exploring the relevance of these observations in attempts to develop new catalytic transformations.

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Supporting Information Available: Characterization data and crystallographic information (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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