Base-Free Silylene Complexes without π-Donor Stabilization. Molecular Structure of [Cp*(PMe$_3$)$_2$Ru=SiMe$_2$][B(C$_6$F$_5$)$_4$]

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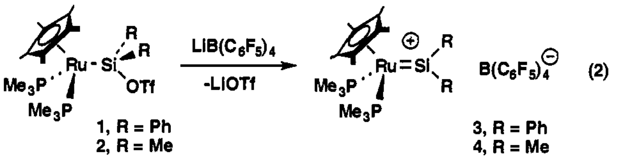
Endeavors to explore and exploit the chemistry of transition-metal silylene complexes, which span nearly three decades,[1] have recently gained momentum with isolation of the first stable examples. These compounds all possess electron-rich metal fragments and are stabilized by π-donation from one or more thiolate substituents to the sp^2 silicon center.[2-4] Ruthenium silylene complexes Cp*(PMe$_3$)$_2$Ru=Si(SR)$_2^+$ (Cp* = η^5-C$_5$Me$_5$; R = Et, Tol-*p*)[2] and the platinum complex [*trans*-(Cy$_3$P)$_2$(H)-Pt=Si(SEt)$_2$]$^+$ [3] have been obtained by an abstraction process outlined in eq 1 (OTf = O$_3$SCF$_3$; M′ = an alkali metal). A

$$\mathrm{MSi(SR)_3 \xrightarrow[-Me_3SiSR]{Me_3SiOTf} MSi(SR)_2OTf \xrightarrow[-M'OTf]{M'BAr_4} M{=}Si(SR)_2{}^+BAr_4{}^-} \quad (1)$$

neutral, transition-metal-substituted silylene complex, Cp*(PMe$_3$)$_2$RuSi[S(Tol-*p*)]Os(CO)$_4$, has also been prepared by a salt-elimination reaction of Cp*(PMe$_3$)$_2$RuSi[S(Tol-*p*)](OTf)$_2$ with Na$_2$Os(CO)$_4$.[4] With the first few silylene complexes finally available, it should be possible to begin mapping out reactivity patterns for this important class of compounds. It would of course be of most interest to examine silylene complexes which might represent likely catalytic intermediates,[1] and these would in general possess alkyl or silyl (rather than heteroatom) substituents at silicon. Here we report the isolation and structural characterization of the first such silylene complexes, using the strategy of eq 1.

The synthesis of the starting triflate Cp*(PMe$_3$)$_2$RuSiPh$_2$OTf (**1**) has been described previously.[5] Using analogous methodology, Cp*(PMe$_3$)$_2$RuSiMe$_2$S(Tol-*p*) was prepared from Cp*(PMe$_3$)$_2$RuCH$_2$SiMe$_3$ and HSiMe$_2$S(Tol-*p*) and then converted to Cp*(PMe$_3$)$_2$RuSiMe$_2$OTf (**2**) by reaction with Me$_3$SiOTf.[6] Following our previously devised pathway to the base-stabilized silylene complex Cp*(PMe$_3$)$_2$RuSiPh$_2$(NCMe)$^+$,[5] we attempted to generate Cp*(PMe$_3$)$_2$Ru=SiPh$_2^+$ in dichloromethane solution via reaction of **1** with NaBPh$_4$. However, only mixtures of decomposition products were observed for this reaction, apparently because the silylene product decomposes faster than it can be formed from the sparingly soluble NaBPh$_4$ reagent.

Reactions of **1** and **2** with the soluble reagent LiB(C$_6$F$_5$)$_4$·OEt$_2$[7] in dichloromethane-d_2 at −30 °C, as monitored by ^{29}Si{^{1}H} NMR spectroscopy, result in rapid and nearly quantitative conversion to the silylene complexes **3** and **4** (eq 2).[6] The formation of **3** and **4** is signaled by characteristic upfield ^{29}Si NMR shifts, at δ 299 (t, J_{SiP} = 32 Hz) and 311 (br), respectively. As expected, **3** and **4** combine with acetonitrile to afford the previously characterized adducts [Cp*(PMe$_3$)$_2$RuSiR$_2$(NCMe)]$^+$ (R = Me,[8] Ph[5]). At room temperature, both silylene complexes are unstable in dichloromethane solution and decompose with half-lives of 3 and 7 h, respectively. However, they are significantly more stable in the solid state. Red-orange crystals of **3** cocrystallize with dichloromethane and desolvate upon isolation to the formula [Cp*(PMe$_3$)$_2$Ru=SiPh$_2$][B(C$_6$F$_5$)$_4$]·0.1CH$_2$Cl$_2$ (by combustion analysis). Problems with crystal desolvation initially hindered isolation of single crystals of **3** and **4**.



(2)

X-ray quality crystals of **4** were finally obtained by addition of a ^{n}Bu$_2$O solution (0.5 mL) of LiB(C$_6$F$_5$)$_4$·OEt$_2$ (0.07 mmol) to a 1,2-dichlorobenzene solution (1 mL) of **2** (0.07 mmol) at 23 °C, followed by slow addition of ^{n}Bu$_2$O (ca. 2.5 mL, over ca. 5 min) until crystals began to form. Further crystallization at room temperature occurred over ca. $^1/_2$ h to afford 0.028 g (38%) of **4**. The molecular structure of the cation in **4**[9] (Figure 1) consists of a dimethylsilylene ligand that is planar at silicon (summation of bond angles = 359(1)°) and coordinated to a Cp*(PMe$_3$)$_2$Ru$^+$ fragment. The Ru–Si distance of 2.238(2) Å is the shortest yet reported, just shorter than the Ru–Si bond lengths in Cp*(PMe$_3$)$_2$RuSi[S(Tol-*p*)]Os(CO)$_4$, 2.286(2) Å,[4] and Cp*(PMe$_3$)$_2$RuSi[S(Tol-*p*)](phen)$^{2+}$, 2.269(5) Å.[10]

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(6) Selected data, Cp*(PMe$_3$)$_2$RuSiMe$_2$S(Tol-*p*): yield 88%. Anal. Calcd for C$_{25}$H$_{46}$P$_2$RuSSi: C, 52.7; H, 8.14. Found: C, 52.8; H, 7.82. ^{1}H NMR (benzene-d_6, 300 MHz, 23 °C): δ 0.63 (s, 6H, SiMe$_2$), 1.22 (vir t, 18 H, PMe$_3$), 1.78 (s, 15 H, Cp*), 2.10 (s, 3 H, C$_6$H$_4$*Me*), 7.00 (d, *J* = 8 Hz, 2 H, C$_6$*H*$_4$Me), 7.68 (d, *J* = 8 Hz, 2 H, C$_6$*H*$_4$Me). ^{31}P{^{1}H} NMR (benzene-d_6, 121.5 MHz, 23 °C): δ 5.37. ^{29}Si{^{1}H} NMR (benzene-d_6, 59.6 MHz, 23 °C): δ 50.19 (t, $^2J_{\mathrm{SiP}}$ = 42 Hz). **2**: yield 95%. Anal. Calcd for C$_{19}$H$_{39}$F$_3$O$_3$P$_2$RuSSi: C, 38.3; H, 6.60. Found: C, 38.3; H, 6.55. ^{1}H NMR (benzene-d_6, 300 MHz, 23 °C): δ 0.68 (s, 6 H, SiMe$_2$), 1.37 (vir t, 18 H, PMe$_3$), 1.77 (t, J_{HP} = 1 Hz, 15 H, Cp*), 2.10 (s, 3 H, C$_6$H$_4$*Me*), 7.00 (d, *J* = 8 Hz, 2 H, C$_6$*H*$_4$Me), 7.68 (d, *J* = 8 Hz, 2 H, C$_6$*H*$_4$Me). ^{31}P{^{1}H} NMR (benzene-d_6, 121.5 MHz, 23 °C): δ 5.50. ^{29}Si{^{1}H} NMR (benzene-d_6, 59.6 MHz, 23 °C): δ 133.29 (t, $^2J_{\mathrm{SiP}}$ = 33 Hz). **3**: yield 22% (not optimized). Anal. Calcd for C$_{52.1}$H$_{43.2}$BCl$_{0.2}$F$_{20}$P$_2$RuSSi: C, 49.7; H, 3.46. Found: C, 49.1; H, 3.42. ^{1}H NMR (dichloromethane-d_2, 300 MHz, −30 °C): δ 1.50 (br, 18 H, PMe$_3$), 1.91 (br, 15 H, Cp*), 7.53 (br, 10 H, SiPh$_2$). ^{31}P{^{1}H} NMR (dichloromethane-d_2, 121.5 MHz, −30 °C): δ 1.67. ^{29}Si{^{1}H} NMR (dichloromethane-d_2, 59.6 MHz, −30 °C): δ 299 (t, J_{SiP} = 32 Hz). **4**: yield 38% (not optimized). Anal. Calcd for C$_{42}$H$_{39}$BF$_{20}$P$_2$RuSSi: C, 44.8; H, 3.49. Found: C, 44.7; H, 3.42. ^{1}H NMR (dichloromethane-d_2, 300 MHz, 0 °C): δ 0.99 (s, 6 H, SiMe$_2$), 1.44 (vir t, 18 H, PMe$_3$), 1.88 (t, J_{HP} = 1 Hz, 15 H, Cp*). ^{31}P{^{1}H} NMR (dichloromethane-d_2, 121.5 MHz, 0 °C): δ 2.29. ^{29}Si{^{1}H} NMR (dichloromethane-d_2, 59.6 MHz, 0 °C): δ 311.4 (br).

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(9) Crystal data for [Cp*(PMe$_3$)$_2$RuSiMe$_2$][B(C$_6$F$_5$)$_4$]: C$_{42}$H$_{39}$BF$_{20}$P$_2$RuSi, monoclinic, $P2_1/n$, a = 13.577(2) Å, b = 22.314(4) Å, c = 15.423(3) Å, β = 94.44(2)°, V = 4658.4(15) Å^3, Z = 4, D_{calcd} = 1.605 g cm^{-3}, T = 240 K, μ(Mo Kα) = 5.42 cm^{-1}. Of 8444 data collected ($2\theta_{\max}$ = 50°, Siemens P4 diffractometer), 8128 were independent and 4112 were observed at $5\sigma(F)$. All non-hydrogen atoms were refined with anisotropic thermal parameters, and hydrogen atoms were treated as idealized contributions. At convergence, $R(F)$ = 5.78% and $R(\mathrm{w}F)$ = 7.46%.

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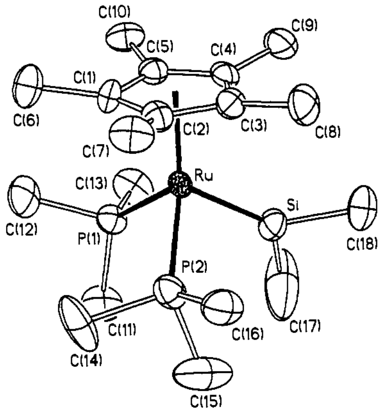

Figure 1. Structure of the cation in **4**. Important bond distances (Å) and angles (deg): Ru–Si 2.238(2), Si-C(17) 1.721(16), Si-C(18) 1.826(12), Ru-P(1) 2.290(3), Ru-P(2) 2.293(3); C(17)-Si-C(18) 99.7(8), Ru-Si-C(17) 133.5(7), Ru-Si-C(18) 125.5(5), P(1)-Ru-P(2) 93.0(1), P(2)-Ru-Si 89.1(1), P(1)-Ru-Si 92.8(1).

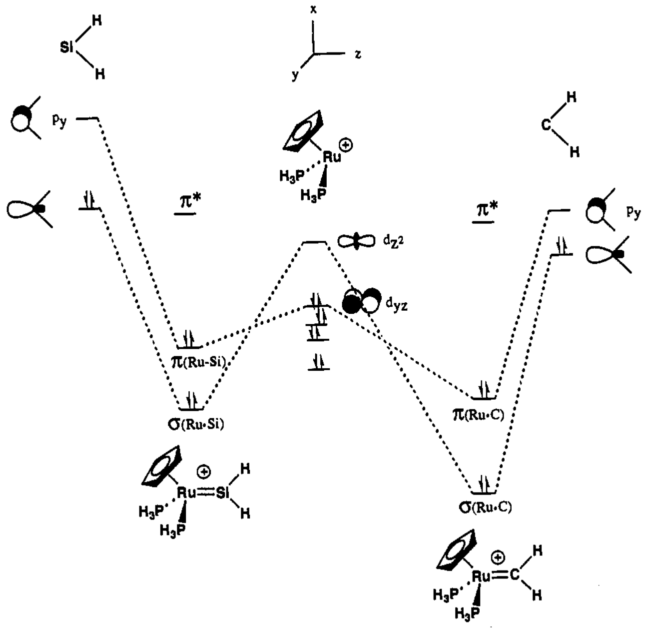

Figure 2. Orbital interaction diagram, based on Fenske–Hall molecular orbital calculations, for $Cp(PH_3)_2Ru{=}CH_2^+$ and $Cp(PH_3)_2Ru{=}SiH_2^+$.

To better understand the bonding in **4**, molecular orbital calculations using Fenske–Hall methods[11] were performed on the model compound $Cp(PH_3)_2Ru{=}SiH_2^+$ and, for comparison, $Cp(PH_3)_2Ru{=}CH_2^+$. Geometrical parameters were based on the structure of **4** and idealized to C_s symmetry, except that a Ru–CH_2 bond distance of 1.85 Å was used.[12] Rotation of the SiH_2 group about the Ru–Si vector produces an energy minimum at 0° (Cp centroid–Ru–Si–H dihedral angle), which rises to a maximum at 90°. The observed dihedral angle of 34° for **4** therefore seems to be determined largely by steric factors. The $Ru{=}CH_2$ and $Ru{=}SiH_2$ bonds are classical σ/π double bonds with the σ component derived from a metal orbital of primarily d_{z^2} character, which accepts electrons from the silylene (or carbene) lone pair. The Ru=Si(C) π-bond may be characterized as a back-bonding interaction involving donation of electron density from a metal orbital of primarily d_{yz} character to a p_y orbital on the ligand, as indicated by the fragment interaction diagram of Figure 2. In general Ru=Si bonding involves poorer overlap, to the extent that the p_y–d_{yz} overlap decreases from 0.20 in the carbene to 0.15 in the silylene. Finally, a Mulliken population analysis clearly indicates that the Si center is more electron deficient than the corresponding carbene carbon. More importantly, it may be noted that in $Cp(PH_3)_2Ru{=}CH_2^+$ the carbene carbon is stabilized by a net gain of electron density from the metal fragment (from –0.14 in free CH_2 to –0.34 for the coordinated carbene), while the silylene silicon is destabilized by losing electron density to the metal (from +0.26 to +0.34), even after the back-donation is considered. This may explain the difficulties encountered in isolating complexes of this type. Bonding to the metal fragment leaves the silylene more electron deficient than in the uncomplexed form, rendering the silicon atom more receptive to attack by nucleophiles or to π-donation from heteroatom substituents. A similar molecular orbital analysis on $[trans\text{-}(PCy_3)_2(H)Pt{=}Si(SEt)_2]^+$ indicated that the silylene ligand is stabilized heavily via π-donation from the sulfur atoms, and not by formation of a π-bond to platinum.[3]

Now that stable transition-metal silylene complexes with a number of different substitution patterns are known, it is clear that such species are viable synthetic targets and reasonable chemical intermediates. Future work will concentrate on defining reactivity patterns for this important class of compounds.

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Supplementary Material Available: Experimental procedures and characterization data for complexes and tables of crystal, data collection, and refinement parameters, bond distances and angles, anisotropic displacement parameters, and hydrogen atom coordinates (14 pages); listing of observed and calculated structure factors (19 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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