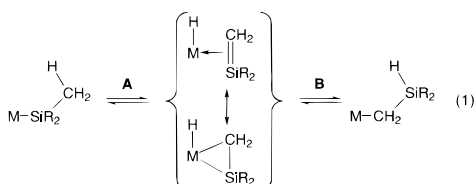# Formation and Interconversion of Ruthenium–Silene and 16-Electron Ruthenium Silyl Complexes

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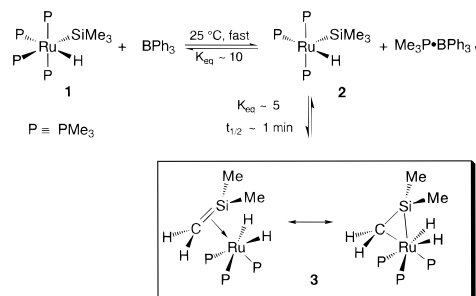
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The formation of new carbon–element bonds by the catalytic activation and functionalization of aliphatic C–H bonds is a particularly attractive process, because relatively simple starting materials are required, and only small amounts of byproducts are generated. Unfortunately, homogeneous catalyst systems that both break aliphatic C–H bonds and form new bonds to carbon remain extremely rare.[1] We have previously reported ruthenium and rhodium catalysts for the synthesis of carbosilanes by the dehydrogenative coupling of alkylsilanes, an efficient C–H functionalization process.[2–5] The key C–H activation step was proposed to involve intramolecular cleavage of a C–H bond by β-hydrogen elimination from a silyl ligand (eq 1, path A), based on studies of selective isotope exchange in osmium and ruthenium silyl complexes[6,7] and on the known related process, β-hydrogen elimination from silylmethyl ligands (eq 1, path B).[8–15] This latter process

has been observed spectroscopically[10,11] and exploited by Tilley and co-workers to prepare stable silene complexes.[12–15] β-Hydrogen elimination from a silyl ligand (path A) has also been invoked to explain the decomposition of iridium SiR_2CH_3[16,17] and platinum SiR_2OH[18] complexes, although the evidence is circumstantial. However, the reverse of path A has been directly observed during

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Scheme 1

the transformation of silene hydride complexes into metal silyls.[10–15] We now report the first direct observation of the intramolecular activation of aliphatic C–H bonds in a 16e– metal silyl complex and thermodynamic and kinetic studies of the transformation.

Addition of triphenylborane as a phosphine sponge to a cyclohexane solution of $(PMe_3)_4Ru(H)SiMe_3$ (**1**) leads to precipitation of $Ph_3B\cdot PMe_3$ and formation of the 16e– complex $(PMe_3)_3Ru(H)SiMe_3$ (**2**) within seconds at room temperature. This unsaturated complex undergoes subsequent β-hydrogen elimination (intramolecular CH activation) to produce the metal silene (or metallacycle) complex $(PMe_3)_3Ru(CH_2=SiMe_2)(H)_2$ (**3**) (Scheme 1). The intramolecular CH activation is reversible, and equilibrium between **2** and **3** is established within ca. 15 min at room temperature. The silene complex **3** is slightly more stable (K_{eq} = [**3**]/[**2**] = 4.4, 30 °C, methylcyclohexane-d_9, in vacuo) and is increasingly favored at lower temperatures. Thermodynamic parameters $\Delta H = -2.7 \pm 0.3$ kcal·mol^{-1} and $\Delta S = -6 \pm 1$ cal·mol^{-1}·K^{-1} were determined from the temperature dependence of K_{eq} between −10.5 and 31.2 °C.

Interestingly, very similar 16e– silyl complexes of ruthenium and osmium have been isolated by Roper[19–21] and Caulton[22–24] although evidence for β-hydrogen elimination from the silyl was not reported. It is likely that the presence of carbonyl and/or chloride ligands imparts additional stability to these unsaturated silyl species relative to the analogous silene complexes.

Although attempts to separate **2** and **3** by crystallization were not successful (vide infra); the mixture is stable indefinitely as a solid and for days in solution in the absence of air, water, and borane contaminants. Both compounds were characterized by multinuclear NMR.[25] The features associated with the silene complex **3** are especially characteristic. The complex exhibits mirror symmetry that renders the pairs of nuclei in the C*H*$_2$, Ru*H*$_2$, Si*Me*$_2$, and two of the three *PMe*$_3$ fragments chemically equivalent. Two sets of phosphine ligands are observed in a 2:1 ratio (^{31}P{^{1}H}: δ 0.37 (d, J_{PP} = 22.5 Hz, 2P), −1.41 (t, J_{PP} = 22.5 Hz, 1P)), and all three phosphines are quasi-cis to the SiMe$_2$ (^{29}Si NMR: δ −12.93, (~dt, J_{PSi} = 4.4 and 2.2 Hz, *Si*Me$_2$)). The values for $^2J_{PSi}$ are similar to that found in the seven-coordinate complex $(PMe_3)_3Ru(H)_3(SiMe_3)$ ($^2J_{PSi}$ = 7.6 Hz)[26] but are much smaller

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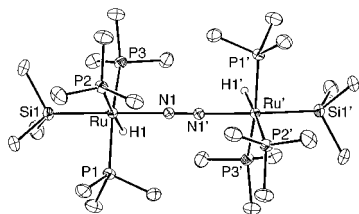(26) Procopio, L. J. Ph.D. Thesis, University of Pennsylvania, 1991.

Figure 1. ORTEP drawing of [(PMe$_3$)$_3$(H)(SiR$_3$)Ru]$_2$(μ-N$_2$) (**4**) (30% thermal ellipsoids). Hydrogen atoms other than the Ru−H are omitted for clarity. Selected bond distances and angles: N−N, 1.104(8) Å; Ru−N, 2.073(4) Å; Ru−H, 1.65(7) Å; Ru−Si, 2.406(2) Å; Ru−N−N, 172.3-(2)°; H−Ru−N, 83(3)°; N−Ru−Si, 173.6(1)°.

than that in the six-coordinate starting complex **1** ($^2J_{PSi}$(trans) = 97.6 Hz, $^2J_{PSi}$(cis) = 26.0 and 17.8 Hz).[26] The protons of the methylene group are chemically equivalent (^{1}H NMR: δ −0.84 (m)), and the methylene carbon is coupled to one trans and two cis phosphines (^{13}C NMR: δ −20.75 (dt, J_{PC} = 21.7 and 6.5 Hz)). Similarly, a single resonance is observed for the two ruthenium hydrides which exhibit a non-first-order pattern (^{1}H NMR: δ −10.6 (m, J_{PH} = 45.6 and 20.5 Hz)). The ^{13}C and ^{29}Si chemical shifts for the silene entity are comparable to those reported by Tilley for isolated ruthenium− and iridium−silene complexes.[12,13,15]

The unsaturated silyl complex **2** also exhibits two sets of phosphine ligands in a 2:1 ratio (in vacuo); ^{31}P{^{1}H}: δ 5.58 (d, J_{PP} = 22.7 Hz, 2P), −3.31 (t, J_{PP} = 22.9 Hz, 1P)), arranged with one phosphine trans and two cis to the hydride (^{1}H NMR: δ −5.94 (~dt, J_{PH} = 34 and 17 Hz, Ru*H*)). All three phosphines are cis to the SiMe$_3$ ligand (^{29}Si NMR: δ 0.62 (br, all J_{PSi} are small and unresolved)). The empty coordination site is trans to the SiMe$_3$ ligand, in accord with the strong trans effect of the silyl, and consistent with the lability of the *trans*-PMe$_3$ in the parent tetrakis(phosphine) complex (**1**) toward substitution with PMe$_3$-d_9 and CO.

Unsaturated complex **2** forms a weak adduct with dinitrogen, [(PMe$_3$)$_3$(H)(SiMe$_3$)Ru]$_2$(μ-N$_2$) (**4**), which has been isolated and fully characterized.[25,27] Evidence for **4** in solution under 1 atm of N$_2$ includes a decrease in the equilibrium concentration of the silene complex **3**[25] and the appearance of new resonances in place of those for **2** in the ^{1}H, ^{13}C, and ^{31}P NMR. The shift is especially pronounced for the Ru−H multiplet (from δ −5.94 to −8.10 in the ^{1}H NMR) and the phosphine resonances (from δ 5.58 and −3.31 to −2.82 and −11.61 in the ^{31}P NMR). The IR spectrum of **4** in pentane solution exhibits bands attributable to Ru−H (1835 cm^{-1}) and N≡N stretches (2150 cm^{-1}). The spectrum in the solid state is similar.

The geometry of **4** and the weak ligation of the N$_2$ ligand is confirmed by the single-crystal X-ray diffraction study of a crystal grown from an equilibrium mixture of **4** and **3** under N$_2$ (Figure 1).[25,28] The structure consists of two P$_3$Ru(H)(SiMe$_3$) centers connected by an essentially linear dinitrogen bridge (Ru−N−N = 172.3(2)°). At each metal, the nitrogen and silyl ligands are trans, and all three phosphines are cis to the silyl. The N−N distance (1.104(8) Å) is on the shorter side of those found in end-on bridging dinitrogen complexes (1.110(3)−1.34(1) Å)[29] and is very close to the value of 1.110 Å in the Ru(II) complex [RuCl$_2$-{C$_5$H$_3$N-2,6-(CH$_2$NMe$_2$)$_2$}]$_2$(μ-N$_2$).[30] Similarly, the Ru−N bond in **4** (2.073(4) Å) is significantly longer than that in any reported ruthenium or osmium complex containing a bridging dinitrogen

Figure 2. Plot of ln([**3**]/[**3**$_0$]) vs time for the reaction of **3** with PMe$_3$ at various temperatures.

ligand (1.873(9)−1.968(9) Å).[30−33] The structure of **4** consists of the same geometrical arrangement of phosphine, hydride, and silyl ligands as proposed for **2**, with the nitrogen bridge occupying the vacant coordination site trans to the silyl. The weak binding of the nitrogen ligand in **4** suggested by the structural parameters is supported by the fact that **2** can be regenerated in solution by simply evacuating the nitrogen atmosphere.

Equilibrium mixtures of **2** and **3** react with donor ligands to yield the known 18e$^-$ complexes *mer*-(L)(PMe$_3$)$_3$Ru(H)SiMe$_3$ (L = P(CD$_3$)$_3$, ^{13}CO), as shown in eq 2.[25,34] Significantly, although
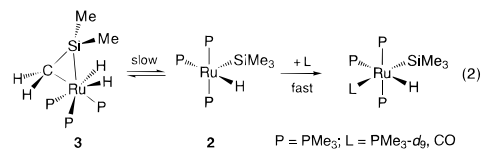
2 reacts immediately, silene complex **3** disappears more slowly (e.g., $t_{1/2}$ = 194 s at 30 °C in the presence of PMe$_3$), and **2** is not detected during the slower reaction of **3**; i.e., equilibrium is not reestablished between **2** and **3**.

The disappearance of **3** in the presence of excess PMe$_3$ was followed by ^{1}H NMR spectroscopy. The rate law is first order in [**3**] and independent of [PMe$_3$] over a 20-fold concentration range (Figure 2). Activation parameters were determined from the temperature dependence of the rate between 31.5 and −5.1 °C ($\Delta H^\ddagger$ = 19.1 ± 0.6 kcal·mol^{-1}, $\Delta S^\ddagger$ = −7 ± 2 cal·mol^{-1}·K^{-1}). These results are all consistent with a unimolecular rate-limiting-step: hydride to silene migration, followed by fast trapping of **2** by phosphine. Thus, an associative reaction of **3** with PMe$_3$ can be effectively excluded.

In conclusion, the metalation of a silyl ligand (β-H elimination) to produce a silametallacycle (silene complex) has been directly observed for the first time, and both the stability relative to the unsaturated metal complex and the kinetics of the reverse process, C−H reductive elimination, have been assessed. This fundamental transformation of a silyl ligand is the best model to date for the catalytic dehydrogenation of alkyl silanes to carbosilanes.

Supporting Information Available: Detail of the synthetic procedures, kinetic measurements, and X-ray structure determination (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(27) Anal. Calcd for C$_{24}$H$_{74}$N$_2$P$_6$Ru$_2$Si$_2$: C, 34.52; H, 8.93; N, 3.35. Found: C, 34.64; H, 8.76; N, 3.06.

(28) Colorless crystals, orthorhombic C222$_1$(No. 20), Z = 4, a = 13.6792-(6) Å, b = 14.7758(7) Å, c = 20.9824(12) Å, V = 4241.0(4) Å^3, D$_{calc}$ = 1.308 g/cm^3. Refinement converged to R$_1$ = 0.0480 and wR$_2$ = 0.1069 for 4542 reflections for which F > 4σ(F) and R$_1$ = 0.0512, wR$_2$ = 0.1090 and GOF = 1.108 for all 4800 unique, nonzero reflections and 181 variables.

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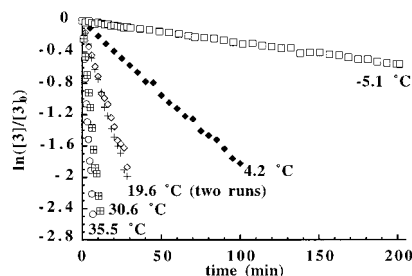
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(34) Although the carbonyl is trans to the silyl in the kinetic product of the reaction with carbon monoxide, isomerization to the thermodynamically more stable *fac* isomer occurs with a half-life of ca. 35 min at 25 °C.[26]