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Intramolecular Aromatic C−H Bond Activation by a Silylene Ligand in a Methoxy-Bridged Bis(silylene)−Ruthenium Complex

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Summary: When a solution of $Cp(Ph_3P)Ru\{SiMe_2\cdots O(Me)\cdots SiMe_2\}$ *(**1**;* $Cp = \eta^5\text{-}C_5H_5$*) and a two-electron-donating ligand L was heated at 130 °C, a C−H bond of a phenyl group was activated by the Ru=Si double bond, and the complexes* $CpLRuSiMe_2(o\text{-}C_6H_4PPh_2)$ *(**2a**, L =* PPh_3*; **2b**, L =* PMe_3*; **2c**, L =* PEt_3*; **2d**, L =* $P(OMe)_3$*; **2e**, L =* ^tBuNC*) were obtained. Heating **1** in the absence of a ligand at 130 °C gave* $CpRuSiMe_2(o\text{-}C_6H_4PPh_2)(H)(SiMe_2OMe)$ *(**3**).*

The reactivity of the metal−silicon double bond of transition-metal−silylene complexes has attracted much attention. In this decade, a number of donor-stabilized[1−5] and donor-free[6] silylene complexes have been synthesized and their reactivities examined. The electrophilicity of the silylene ligand has been demonstrated in several reactions, including the addition of polar molecules such as water,[4d,7] alcohols,[1g,2e,7−10] ketones,[2e,10] etc. and the intermolecular migration of substituents.[11] We now report the first C−H bond activation by an unsaturated metal−silicon bond, probably through aromatic electrophilic substitution induced by the electron-deficient silylene ligand.

A benzene-d_6 solution of the methoxy-bridged bis(silylene)−ruthenium complex $Cp(Ph_3P)Ru\{SiMe_2\cdots O(Me)\cdots SiMe_2\}$ (**1**; $Cp = \eta^5\text{-}C_5H_5$)[1e] and an excess of PPh_3 in a thick-walled NMR tube was heated at 130 °C. After 60 h, the ^1H NMR signals of complex **1** had almost disappeared and those of $HSiMe_2OMe$[12] and the novel complex **2a** newly had appeared instead. The same reaction was performed on a larger scale, and **2a** was isolated as air-stable yellow crystals in 34% yield (eq 1).[13] Analogous reactions of **1** with PMe_3, PEt_3, $P(OMe)_3$, and CN^tBu gave $CpLRuSiMe_2(o\text{-}C_6H_4PPh_2)$ (**2b**, L = PMe_3, 75%; **2c**, L = PEt_3, 54%; **2d**, L = $P(OMe)_3$, 72%; **2e**, L = CN^tBu, 39%).

In the ^1H NMR spectrum of complex **2a**, two singlets assigned to two nonequivalent Si−Me groups were observed at 0.54 and 0.94 ppm, and the signals in the aromatic region were more complicated than those of **1**. In the ^{13}C NMR spectrum for **2a**, 18 signals were observed in the region of aromatic carbons. The ^{31}P NMR spectrum showed mutually coupled doublets at

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(12) $HSiMe_2OMe$ was characterized by comparing its ^1H, ^{13}C, and ^{29}Si NMR spectra with those of the authentic sample prepared by the reaction of $HSiMe_2Cl$ and MeOH in the presence of $(H_2N)_2CO$.

(13) Preparation of **2a**: toluene (2 mL) was transferred to a Pyrex tube (10 mm o.d.) containing complex **1** (49.2 mg, 85.3 μmol) and PPh_3 (23.4 mg, 89.5 μmol) by the trap-to-trap technique in a vacuum line, and the tube was flame-sealed under high vacuum. After the mixture was heated for 60 h at 130 °C, the tube was opened in a glovebox and the solution was poured into a Schlenk tube. On removal of the solvent in vacuo, an orange residue was obtained. Crystallization from toluene−pentane gave **2a** (21.5 mg, 28.8 μmol) as yellow crystals (yield 34%); mp 250 °C dec. Spectral data for **2a**: ^1H NMR (300 MHz, C_6D_6) δ 0.54 (s, 3H, SiMe), 0.94 (s, 3H, SiMe), 4.58 (s, 5H, Cp), 6.71−7.88 (m, 29H, Ar); ^{13}C NMR (75.5 MHz, C_6D_6) δ 9.0 (d, $^2J_{C-P} = 4.5$ Hz, SiMe), 11.6 (d, $^2J_{C-P} = 1.0$ Hz, SiMe), 83.7 (d, $^2J_{C-P} = 1.8$ Hz, Cp), 126.9 (d, $J_{C-P} = 5.8$ Hz, Ar), 127.1 (br, Ar), 127.1 (d, $J_{C-P} = 14.1$ Hz, Ar), 127.5 (d, $J_{C-P} = 12.5$ Hz, Ar), 127.5 (br, Ar), 127.8 (d, $J_{C-P} = 17.0$ Hz, Ar), 128.7 (d, $J_{C-P} = 2.2$ Hz, Ar), 130.9 (d, $J_{C-P} = 4.4$ Hz, Ar), 131.8 (d, $J_{C-P} = 10.6$ Hz, Ar), 132.2 (d, $J_{C-P} = 23.4$ Hz, Ar), 132.9 (br, Ar), 133.0 (d, $J_{C-P} = 10.0$ Hz, Ar), 134.0 (br, Ar), 135.3 (br, Ar), 138.3 (dd, $J_{C-P} = 3.6, 36.6$ Hz, Ar), 145.9 (dd, $J_{C-P} = 1.6, 26.6$ Hz, Ar), 146.5 (dd, $J_{C-P} = 1.7, 40.0$ Hz, Ar), 162.4 (dd, $J_{C-P} = 1.3, 53.5$ Hz, Ar); ^{29}Si NMR (59.6 MHz, C_6D_6) δ 41.4 (dd, $^2J_{Si-P} = 22.3, 24.5$ Hz); ^{31}P NMR (122 MHz, C_6D_6) δ 60.5 (d, $^2J_{P-P} = 29.5$ Hz, PPh_3), 83.4 (d, $^2J_{P-P} = 29.5$ Hz, chelating P); IR (KBr pellet) 1477, 1430 (aromatic C−C stretch), 1086 (in-plane aromatic C−H bend), 785, 741, 721 (out-of-plane aromatic C−H bend) cm^{-1}; MS (FAB, *m*-nitrobenzyl alcohol, Xe) *m/z* 741 (15, M^+), 691 (16, $[Cp(Ph_3P)_2Ru]^+$), 626 (8.2, $[(Ph_3P)_2Ru]^+$), 486 (48, $M^+ - PPh_3$), 429 (100, $[Cp(Ph_3P)Ru]^+$). Anal. Calcd for $C_{43}H_{40}P_2RuSi$: C, 69.05; H, 5.40. Found: C, 69.22; H, 5.47.

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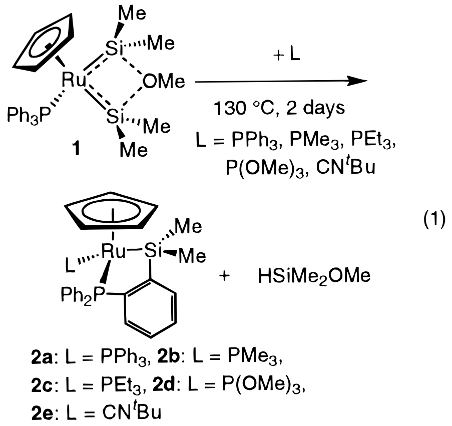
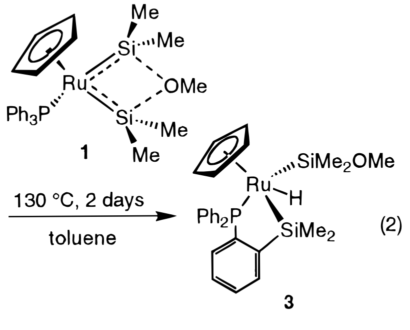


60.5 and 83.4 ppm (d, $^2J_{P-P} = 29.5$ Hz), the latter of which can be assigned to the phosphorus atom in the chelate ring on the basis of the general tendency of downfield shift for the signals of phosphorus in 5-membered chelate phosphines.[14] In the ^{29}Si NMR spectrum, only one signal was observed at 41.4 ppm as a doublet of doublets ($^2J_{Si-P} = 22.3$, 24.5 Hz).

The structure of **2b** was unequivocally determined by X-ray crystallography.[15] The crystal contains the two independent molecules A and B, but there is no essential difference except their chirality. The ORTEP view of molecule A is shown in Figure 1. The Ru−Si bond lengths are 2.352(3) Å in molecule A and 2.354(3) Å in molecule B. They are longer than those of bis(silylene) complex **1** (2.290(5)−2.348(5) Å, average 2.326 Å)[1f] but are relatively short among the values reported for Ru−Si single-bond lengths (2.338−2.507 Å).[16] This shortening of the Ru-Si bonds in **2b** may be attributable to the enhanced back-donation to the silyl group from the electron-rich metal center due to the presence of two phosphorus donors.

When a toluene solution of **1** is heated in the absence of a ligand at 130 °C, complex **3**, a structural isomer of **1** that is stable in the solid state, was isolated as a pale brown powder in 78% yield (eq 2).[17] In the ^{31}P NMR spectrum of **3**, one singlet due to the phosphorus in the chelate ring was observed at 78.5 ppm, which is at slightly higher field than those of complexes **2a**−**e** (83.4−85.1 ppm). In the ^{1}H NMR spectrum, a doublet assigned to a hydrido ligand was observed at −12.68 ppm ($^2J_{H-P} = 6.6$ Hz) and also a singlet of a methoxy



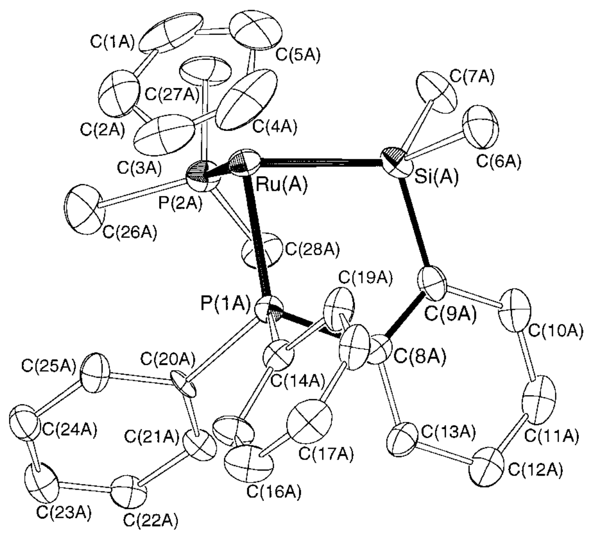


Figure 1. ORTEP diagram of Cp(Me$_3$P)RuSiMe$_2$(*o*-C$_6$H$_4$-PPh$_2$) (**2b**; molecule A). Selected bond lengths (Å) and angles (deg): Ru(A)−Si(A) = 2.352(3), Ru(A)−P(1A) = 2.238(3), Ru(A)−P(2A) = 2.271(3), P(1A)−C(8A) = 1.846(9), C(8A)−C(9A) = 1.388(13), Si(A)−C(9A) = 1.908(11); P(1A)−Ru(A)−P(2A) = 93.70(10), P(1A)−Ru(A)−Si(A) = 82.87(10), P(2A)−Ru(A)−Si(A) = 89.79(10), Ru(A)−Si(A)−C(9A) = 108.1(3), Si(A)−C(9A)−C(8A) = 116.6(7), P(1A)−C(8A)−C(9A) = 115.2(7), Ru(A)−P(1A)−C(8A) = 114.5(7).

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(15) Crystal data for **2b**: formula C$_{28}$H$_{34}$P$_2$RuSi, monoclinic, space group *C*2 (variant of No. 5), $a = 29.227(11)$ Å, $b = 9.799(2)$ Å, $c = 23.877(10)$ Å, $\beta = 127.73(3)°$, $V = 5409(3)$ Å^3, $Z = 8$, $d_{calcd} = 1.38$ g cm^{-3}. X-ray diffraction data were collected at room temperature on a Rigaku AFC-6A diffractometer with graphite-monochromated Mo Kα radiation. Reflections (8334) with 3.52° < 2θ < 60.00° were collected by the ω-scan technique. The structure was solved by heavy-atom methods (SHELXS 86) and refined with full-matrix least squares using individual anisotropic thermal parameters for non-hydrogen atoms. The final *R* factor was 0.060 ($R_w = 0.131$) for 8334 reflections with $|F_o| > 2\sigma(F_o)$.

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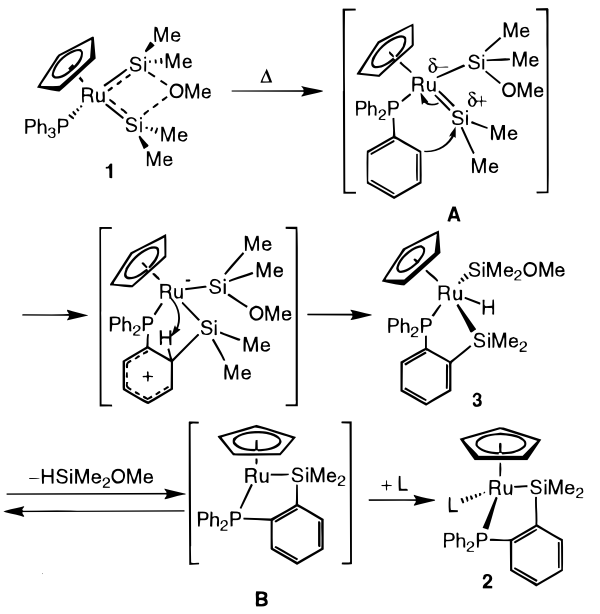
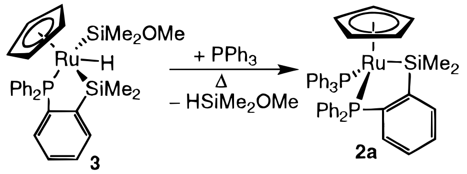
(17) Preparation of **3**: Toluene (1.2 mL) was transferred to a Pyrex tube (10 mm o.d.) containing complex **1** (113 mg, 196 μmol) by the trap-to-trap technique in a vacuum line and the tube was flame-sealed under high vacuum. After the mixture was heated for 47 h at 130 °C, the tube was opened in a glovebox and the solution was poured into a Schlenk tube. After removal of the solvent in vacuo, the brown, oily residue was washed three times with pentane (0.5 mL × 3) at −60 °C and dried under vacuum to afford **3** as a pale brown powder (88 mg, 153 μmol, yield 78%); mp 145 °C dec. Further purification was performed by recrystallization from toluene−pentane. Spectral data for **3**: ^{1}H NMR (300 MHz, C$_6$D$_6$) δ −12.68 (d, $^2J_{H-P} = 6.6$ Hz, 1H, RuH), 0.10 (s, 3H, SiMe), 0.18 (s, 3H, SiMe), 0.58 (s, 3H, SiMe), 0.97 (s, 3H, SiMe), 3.05 (s, 3H, SiOMe), 4.72 (s, 5H, Cp), 6.86−7.88 (m, 14H, Ar); ^{13}C NMR (75.5 MHz, C$_6$D$_6$) δ 9.8 (d, $^2J_{C-P} = 1.3$ Hz, chelating SiMe), 9.9 (s, chelating SiMe), 10.3 (Si*Me$_2$*OMe), 49.6 (SiMe$_2$O*Me*), 85.1 (d, $^2J_{C-P} = 1.9$ Hz, Cp), 127.5 (d, $J_{C-P} = 6.5$ Hz, Ar), 127.7 (d, $J_{C-P} = 28.7$ Hz, Ar), 127.7 (d, $J_{C-P} = 9.8$ Hz, Ar), 128.1 (d, $J_{C-P} = 5.9$ Hz, Ar), 128.5 (d, $J_{C-P} = 2.1$ Hz, Ar), 129.2 (dd, $J_{C-P} = 16.0$ Hz, 2.2 Hz, Ar), 130.2 (d, $J_{C-P} = 4.6$ Hz, Ar), 132.0 (d, $J_{C-P} = 22.6$ Hz, Ar), 132.4 (d, $J_{C-P} = 10.7$ Hz, Ar), 134.3 (d, $J_{C-P} = 10.5$ Hz, Ar), 138.6 (d, $J_{C-P} = 43.1$ Hz, Ar), 144.2 (d, $J_{C-P} = 41.8$ Hz, Ar), 146.2 (d, $J_{C-P} = 54.9$ Hz, Ar), 156.8 (d, $J_{C-P} = 50.0$ Hz, Ar); ^{29}Si NMR δ (59.6 MHz, C$_6$D$_6$) δ 35.2 (d, $^2J_{Si-P} = 13.4$ Hz, chelating Si), 54.0 (d, $^2J_{Si-P} = 12.4$ Hz, SiMe$_2$OMe); ^{31}P NMR δ (122 MHz, C$_6$D$_6$) 78.5 (s); IR (KBr pellet) 2081 (Ru−H), 1479, 1433, 1232 (Si−Me), 1182, 1097 (Si−O−Me) cm^{-1}; MS (FAB, *m*-nitrobenzyl alcohol matrix, Xe) *m*/*z* 576 (2.7, M$^+$), 561 (6.4, M$^+$ − Me), 546 (5.6, M$^+$ − 2Me), 503 (8.3, M$^+$ − SiMe$_2$ − Me), 487 (100, M$^+$ − HSiMe$_2$OMe), 472 (23, M$^+$ − HSiMe$_2$OMe − Me) 429 (3.9, [Cp(Ph$_3$P)Ru]$^+$). Anal. Calcd for C$_{28}$H$_{35}$O$_1$PRuSi$_2$: C, 58.40; H, 6.14. Found: C, 58.65; H, 6.33.

Scheme 1



group at 3.05 ppm. The ^{29}Si NMR spectrum showed two doublets at 35.2 ($^2J_{\mathrm{Si-P}} = 13.4$ Hz) and 54.0 ($^2J_{\mathrm{Si-P}} = 12.4$ Hz) ppm, which demonstrate the existence of two silyl ligands. Their Si−P coupling constants are very similar to each other and also to that of *trans*-Cp(Ph$_3$P)RuH(SiMe$_2$OMe)$_2$ ($^2J_{\mathrm{Si-P}} = 11.6$ Hz).[7] This situation is in contrast to that of Cp(Ph$_3$P)RuH(SiMe$_2$OSiMe$_2$), which has very different $^2J_{\mathrm{Si-P}}$ values (7.0 and 19.0 Hz).[7] These observations suggest that **3** adopts the *trans* geometry.

When a benzene-d_6 solution of complex **3** and PPh$_3$ was heated in an NMR tube at 120 °C, **3** was consumed within 3 days and complex **2a** and HSiMe$_2$OMe were formed quantitatively (eq 3). This result strongly suggests that **3** is an intermediate in the formation of complexes **2a**−**e**.



(3)

A possible mechanism for formation of **2a**−**e** from **1** and L is shown in Scheme 1. The four-membered chelate ring in **1** opens at high temperature to generate intermediate **A**, and the electron-deficient silicon atom of the base-free silylene ligand electrophilically attacks the ortho carbon of a phenyl group in the PPh$_3$ ligands. The proton on the ortho position subsequently migrates to the electronegative ruthenium center to give **3**. In the presence of a two-electron donor L, intermediate **B**, which is generated reversibly by reductive elimination of HSiMe$_2$OMe from **3**, traps L to afford **2**.

This is the first example of C−H bond activation by a silylene complex.

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Supporting Information Available: Text and tables giving synthetic procedures and characterization data for new compounds and details of the X-ray structure determination of **2b** (16 pages). Ordering information is given on any current masthead page.

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