

Reversible C–Si Bond Cleavage in the Methylene/Silyl Complex $\text{Cp}^*_2\text{Ru}_2(\mu\text{-CH}_2)(\mu\text{-Cl})(\text{SiMe}_3)$

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The scission of C–H and C–C bonds by transition metal complexes is an area of great current interest.^{1–6} Occasionally, C–H and C–C bond cleavage processes are chemically reversible, and in particular, examples of reversible β -hydrogen elimination reactions,^{7–9} reversible α -hydrogen eliminations,^{9–15} and reversible β -alkyl elimination reactions^{16–21} are known. In contrast, there are very few examples of the activation of carbon–silicon bonds by transition metal complexes, and most of these are irreversible processes.^{22–28} We now describe an example of a facile, reversible C–Si bond cleavage process that is fast on the NMR time scale; this reaction involves the elimination of an α -silyl group from a CH_2SiMe_3 ligand to give an isolable methylene/silyl product. We also describe the reactivity of this unusual methylene/silyl species toward Lewis bases and protonic acids.

Treatment of the (pentamethylcyclopentadienyl)ruthenium complex $[\text{Cp}^*\text{RuCl}]_4$ ^{29–32} with 1 equiv of $\text{Mg}(\text{CH}_2\text{SiMe}_3)_2$ in

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(6) Perhaps the most common reversible C–C bond activation reactions promoted by transition metals are alkene and alkyne metathesis reactions, and the decarbonylation of metal acyls.

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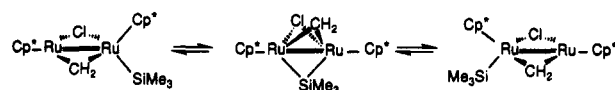
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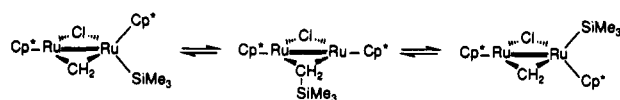
diethyl ether gives a dark red product of stoichiometry “ $\text{Cp}^*_2\text{-Ru}_2(\text{CH}_2\text{SiMe}_3)\text{Cl}$ ” after crystallization from pentane. However, the presence of two downfield singlets at δ 10.77 and 10.01 in the low-temperature ^1H NMR spectrum and the presence of a triplet ($^1J_{\text{C-H}} = 138$ Hz) at δ 170 in the ^{13}C NMR spectrum suggest that the product is not a (trimethylsilyl)methyl complex as expected, but instead contains a bridging methylene group^{33,34} owing to scission of the α -C–Si bond of the CH_2SiMe_3 ligand. The formulation of the product as the methylene/silyl complex $\text{Cp}^*_2\text{-Ru}_2(\mu\text{-CH}_2)(\mu\text{-Cl})(\text{SiMe}_3)$, **1**,³⁵ has been confirmed by a single-crystal X-ray structure determination (Scheme 1). Electron counting and the relatively short Ru–Ru distance of 2.527(1) Å suggest that **1** contains a metal–metal double bond.

Interestingly, the variable temperature ^1H and ^{13}C NMR spectra of **1** reveal that it undergoes two fluxional processes. In the lower energy process, the two Cp^* ring carbon resonances present in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum at -80 °C broaden and coalesce at -50 °C. It is important to note that this low-temperature dynamic process does not exchange the two diastereotopic methylene protons. Analysis of the Cp^* ^{13}C NMR line shapes as a function of temperature yields the activation parameters $\Delta H^\ddagger = 8.9 \pm 0.1$ kcal mol⁻¹ and $\Delta S^\ddagger = 0 \pm 3$ cal mol⁻¹ K⁻¹. The only reasonable mechanism that could exchange the Cp^* groups but not the CH_2 protons is the rapid, reversible migration of the trimethylsilyl group from one ruthenium center to the other via a symmetric $\text{Ru}(\mu\text{-SiMe}_3)\text{Ru}$ intermediate:



This conclusion is supported by other evidence (see below). We are not aware of any well-established precedents for the migration of silyl groups between metal centers.⁴³

Equally interesting is the higher energy dynamic process, in which the two methylene proton resonances, which are sharp in the ^1H NMR spectrum below 0 °C, broaden as the temperature is raised and coalesce at 50 °C. Activation parameters of $\Delta H^\ddagger = 12.0 \pm 0.1$ kcal mol⁻¹ and $\Delta S^\ddagger = -7 \pm 3$ cal mol⁻¹ K⁻¹ can be calculated for this process. Several mechanisms can be written that would effect exchange of the diastereotopic methylene protons; among these are mechanisms that involve rotation of a terminal $\text{Ru}=\text{CH}_2$ group,³⁶ rotation about an unbridged metal–metal bond,³⁷ or formation of a square-planar ruthenium center. However, a control experiment (see below) strongly indicates that the correct mechanism involves reversible migration of the trimethylsilyl group to the methylene carbon to re-form the C–Si bond.



This process does in fact make the two methylene protons equivalent and is the reverse of the pathway by which (presumably)

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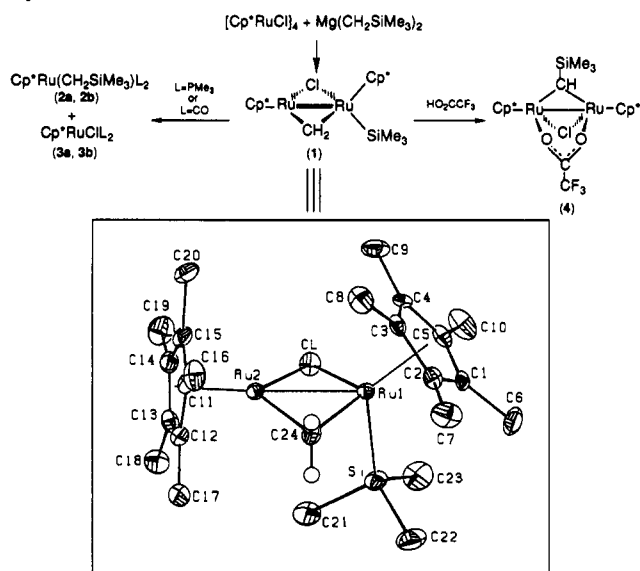
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(35) **1**: ^1H NMR (d_6 -toluene, 300 MHz, -80 °C) δ 10.77 (s, CH_2), 10.01 (s, CH_2), 1.49 (br s, C_5Me_5), 0.64 (s, SiMe_3); $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 75 MHz, -80 °C) δ 170.0 (t, $^1J_{\text{C-H}} = 138$ Hz, CH_2), 94.6 (s, C_5Me_5), 81.6 (s, C_5Me_5), 10.2 (q, $^1J_{\text{C-H}} = 127$ Hz, C_5Me_5), 6.8 (q, $^1J_{\text{C-H}} = 127$ Hz, SiMe_3).

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Scheme I. Synthesis, Crystal Structure, and Reactivity of $\text{Cp}^*\text{Ru}_2(\mu\text{-CH}_2)(\mu\text{-Cl})(\text{SiMe}_3)$, **1^a**


^a Selected bond distances (Å) and angles (deg) for **1**: Ru(1)–Ru(2) 2.527(1), Ru(1)–Si 2.387(2), Ru(1)–C(24) 2.030(8), Ru(2)–C(24) 2.066(9), Ru(1)–Cn(1) 1.896(8), Ru(2)–Cn(2) 1.795(9), Ru(1)–C(24)–Ru(2) 76.2(3), Ru(2)–Ru(1)–Si 96.02(7), Ru(2)–Ru(1)–Cn(1) 137.2(2), Ru(1)–Ru(2)–Cn(2) 168.1(3), Si–Ru(1)–Cn(1) 126.2(3), where “Cn” stands for the centroid of the corresponding Cp* ring.

the methylene/silyl complex is generated from the reactants. This is the first example of a C–Si bond cleavage/re-formation process in an organotransition metal complex that is chemically reversible on the NMR time scale.^{25,38}

One of the most convincing pieces of evidence that *both* the low- and high-energy dynamic processes involve movement of the SiMe₃ group comes from a study of the structurally related cation $[\text{Cp}^*\text{Ru}_2(\mu\text{-CH}_2)(\mu\text{-Cl})(\text{PMe}_3)^+]$, whose preparation is described below. This cation is identical with **1** except that the SiMe₃ group has been replaced by a PMe₃ ligand; despite the structural and electronic similarity, this molecule shows no evidence of fluxional processes even at 160 °C. This result strongly suggests that the SiMe₃ group must be *directly* involved in the dynamic processes that **1** exhibits.

The reactivity of **1** provides further evidence that the C–Si bond can be re-formed. Treatment of **1** with 4 equiv of PMe₃ in diethyl ether gives the known²⁹ mononuclear Ru^{II} products Cp*Ru(CH₂SiMe₃)(PMe₃)₂, **2a**, and Cp*RuCl(PMe₃)₂, **3a**, in quantitative yield. Sealed NMR tube studies show that this reaction *instantaneously* goes to completion to give **2a** and **3a** even at –80 °C. Re-formation of the C–Si bond is also achieved

(38) Rapid reversible C–Si bond cleavage/re-formation processes have been observed in silyl-substituted cyclopentadienes and related indenenes. See: Ashe, A. J. *J. Am. Chem. Soc.* **1970**, *92*, 1233–1235. Abel, E. W.; Dunster, M. O.; Waters, A. J. *Organomet. Chem.* **1973**, *49*, 287–321. Ustynyuk, Y. U.; Kisin, A. V.; Pribytkova, I. M.; Zenkin, A. A.; Antonova, N. D. *J. Organomet. Chem.* **1972**, *42*, 47–63.

by carbonylation; treatment of **1** with 2 atm of CO gives the carbonyl complexes Cp*Ru(CH₂SiMe₃)(CO)₂, **2b**, and Cp*RuCl(CO)₂, **3b**.³⁹

Protonation of **1** with HO₂CCF₃ at room temperature also gives a product in which the C–Si bond has re-formed, Cp*₂Ru₂(μ-CHSiMe₃)(μ-O₂CCF₃)(μ-Cl), **4**.⁴⁰ If the reaction is performed with DO₂CCF₃, no deuterium is present in the μ-CHSiMe₃ group of the product, as shown by ¹H and ¹³C NMR spectroscopy. This result suggests that protonation occurs by direct attack at the metal center, since protonation at the alkylidene carbon should leave some deuterium in the μ-CHSiMe₃ group of the product. Migration of the silyl group to the methylene carbon could occur either before or after reductive elimination of HD.

Curiously, protonation of **1** at low temperatures, –78 °C, with HO₂CCF₃ gives a different product, Cp*₂Ru₂(μ-CH₂)(μ-Cl)(μ-O₂CCF₃), **5**;⁴¹ under these conditions the SiMe₃ group is lost and appears in the reaction mixture as the silyl ester Me₃SiO₂CCF₃. Treatment of **5** with trimethylphosphine gives the cation $[\text{Cp}^*\text{Ru}_2(\mu\text{-CH}_2)(\mu\text{-Cl})(\text{PMe}_3)^+][\text{O}_2\text{CCF}_3^-]$, **6**,⁴² which is structurally analogous to **1** but which is completely nonfluxional.

In conclusion, we have discovered the first example of rapid reversible C–Si bond cleavage promoted by a transition metal complex. Further investigations of the chemical behavior of this system are underway.

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Supplementary Material Available: Tables of crystal data, atomic coordinates, anisotropic thermal parameters, and full bond distances and angles for **1** (9 pages); listing of final observed and calculated structure factors for **1** (19 pages). Ordering information is given on any current masthead page.

(39) Compounds **2a**, **2b**, **3a**, and **3b** have been characterized by NMR spectroscopy and infrared spectroscopy. All compounds reported gave satisfactory elemental analyses.

(40) **4**: ¹H NMR (CD₂Cl₂, 500 MHz, 25 °C) δ 13.45 (s, CHSiMe₃), 1.60 (s, C₅Me₅), 0.03 (s, CHSiMe₃); ¹³C NMR (CD₂Cl₂, 125 MHz, 25 °C) δ 195.3 (d, ¹J_{C-H} = 120 Hz, CHSiMe₃), 164.5 (q, ²J_{C-F} = 37 Hz, CO₂CF₃), 113.0 (q, ¹J_{C-F} = 288 Hz, CO₂CF₃), 87.5 (s, C₅Me₅), 10.9 (q, ¹J_{C-H} = 127 Hz, C₅Me₅), 5.0 (q, ¹J_{C-H} = 118 Hz, CHSiMe₃).

(41) **5**: ¹H NMR (CD₂Cl₂, 300 MHz, 25 °C) δ 11.22 (d, ²J_{H-H} = 0.8 Hz, CH₂), 9.55 (d, ²J_{H-H} = 0.8 Hz, CH₂), 1.62 (s, C₅Me₅); ¹³C NMR (CD₂Cl₂, 75 MHz, 25 °C) δ 177.3 (CH₂), 87.2 (s, C₅Me₅), 10.3 (q, ¹J_{C-H} = 126.6 Hz, C₅Me₅).

(42) **6**: ¹H NMR (CD₂Cl₂, 300 MHz, 25 °C) δ 10.88 (t, ²J_{H-H} = 3.5 Hz, ³J_{P-H} = 3.5 Hz, CH₂), 9.83 (dd, ²J_{H-H} = 3.5 Hz, ³J_{P-H} = 18.5 Hz, CH₂), 1.65 (d, ⁴J_{P-H} = 1.5 Hz, C₅Me₅), 1.64 (s, C₅Me₅), 1.17 (d, ²J_{P-H} = 9.5 Hz, PMe₃); ¹³C{¹H} NMR (CD₂Cl₂, 75 MHz, 25 °C) δ 176.0 (CH₂), 98.2 (d, ²J_{C-P} = 2.4 Hz, C₅Me₅), 85.2 (s, C₅Me₅), 18.3 (d, ²J_{P-H} = 30.8 Hz, PMe₃), 11.1 (s, C₅Me₅), 10.0 (s, C₅Me₅); ³¹P{¹H} NMR (CD₂Cl₂, 121 MHz) δ 5.4 (s).

(43) **Note Added in Proof:** An example of the irreversible migration of a silyl group between metal centers has recently appeared: Braunstein, P.; Knorr, M.; Hirle, B.; Reinhard, G.; Schubert, U. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1583–1585.