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Reversible C–Si Bond Cleavage in the Methylene/Silyl Complex $Cp^*_2Ru_2(\mu\text{-}CH_2)(\mu\text{-}Cl)(SiMe_3)$

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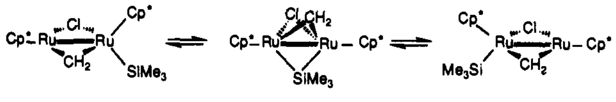
The scission of C–H and C–C bonds by transition metal complexes is an area of great current interest.[1-6] Occasionally, C–H and C–C bond cleavage processes are chemically reversible, and in particular, examples of reversible β-hydrogen elimination reactions,[7-9] reversible α-hydrogen eliminations,[9-15] 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.

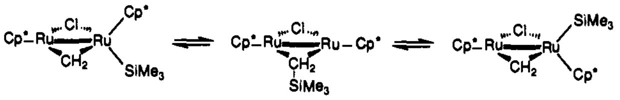
Treatment of the (pentamethylcyclopentadienyl)ruthenium complex $[Cp^*RuCl]_4$[29-32] with 1 equiv of $Mg(CH_2SiMe_3)_2$ in diethyl ether gives a dark red product of stoichiometry "$Cp^*_2Ru_2(CH_2SiMe_3)Cl$" after crystallization from pentane. However, the presence of two downfield singlets at δ 10.77 and 10.01 in the low-temperature ^1H NMR spectrum and the presence of a triplet ($^1J_{C-H}$ = 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 $Cp^*_2Ru_2(\mu\text{-}CH_2)(\mu\text{-}Cl)(SiMe_3)$, **1**,[35] has been confirmed by a single-crystal X-ray structure determination (Scheme I). 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 $^{13}C\{^1H\}$ 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 $Ru(\mu\text{-}SiMe_3)Ru$ 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 diasterotopic methylene protons; among these are mechanisms that involve rotation of a terminal $Ru{=}CH_2$ 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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(35) **1**: ^1H NMR (d_8-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, $SiMe_3$); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 75 MHz, −80 °C) δ 170.0 (t, $^1J_{C-H}$ = 138 Hz, CH_2), 94.6 (s, C_5Me_5), 81.6 (s, C_5Me_5), 10.2 (q, $^1J_{C-H}$ = 127 Hz, C_5Me_5), 6.8 (q, $^1J_{C-H}$ = 127 Hz, $SiMe_3$).

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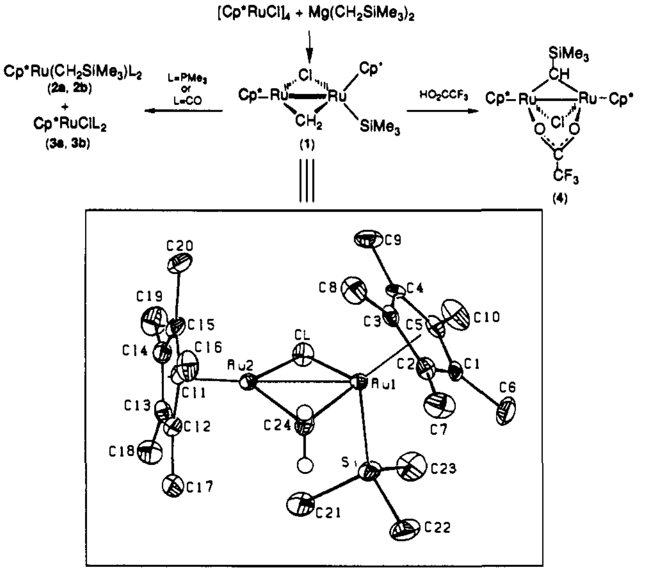
Scheme I. Synthesis, Crystal Structure, and Reactivity of $Cp^*_2Ru_2(\mu\text{-}CH_2)(\mu\text{-}Cl)(SiMe_3)$, **1**[a]



[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 $SiMe_3$ group comes from a study of the structurally related cation $[Cp^*_2Ru_2(\mu\text{-}CH_2)(\mu\text{-}Cl)(PMe_3)^+]$, whose preparation is described below. This cation is identical with **1** except that the $SiMe_3$ group has been replaced by a PMe_3 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 $SiMe_3$ 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 PMe_3 in diethyl ether gives the known[29] mononuclear Ru^{II} products $Cp^*Ru(CH_2SiMe_3)(PMe_3)_2$, **2a**, and $Cp^*RuCl(PMe_3)_2$, **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 by carbonylation; treatment of **1** with 2 atm of CO gives the carbonyl complexes $Cp^*Ru(CH_2SiMe_3)(CO)_2$, **2b**, and $Cp^*RuCl(CO)_2$, **3b**.[39]

Protonation of **1** with HO_2CCF_3 at room temperature also gives a product in which the C–Si bond has re-formed, $Cp^*_2Ru_2(\mu\text{-}CHSiMe_3)(\mu\text{-}O_2CCF_3)(\mu\text{-}Cl)$, **4**.[40] If the reaction is performed with DO_2CCF_3, no deuterium is present in the $\mu\text{-}CHSiMe_3$ group of the product, as shown by ^1H and ^{13}C 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 $\mu\text{-}CHSiMe_3$ 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 HO_2CCF_3 gives a different product, $Cp^*_2Ru_2(\mu\text{-}CH_2)(\mu\text{-}Cl)(\mu\text{-}O_2CCF_3)$, **5**;[41] under these conditions the $SiMe_3$ group is lost and appears in the reaction mixture as the silyl ester $Me_3SiO_2CCF_3$. Treatment of **5** with trimethylphosphine gives the cation $[Cp^*_2Ru_2(\mu\text{-}CH_2)(\mu\text{-}Cl)(PMe_3)^+][O_2CCF_3^-]$, **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.

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(38) Rapid reversible C–Si bond cleavage/re-formation processes have been observed in silyl-substituted cyclopentadienes and related indenes. 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.

(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 (CD_2Cl_2, 500 MHz, 25 °C) δ 13.45 (s, $CHSiMe_3$), 1.60 (s, C_5Me_5), 0.03 (s, $CHSiMe_3$); ^{13}C NMR (CD_2Cl_2, 125 MHz, 25 °C) δ 195.3 (d, $^1J_{CH}$ = 120 Hz, $CHSiMe_3$), 164.5 (q, $^2J_{CF}$ = 37 Hz, CO_2CF_3), 113.0 (q, $^1J_{CF}$ = 288 Hz, CO_2CF_3), 87.5 (s, C_5Me_5), 10.9 (q, $^1J_{CH}$ = 127 Hz, C_5Me_5), 5.0 (q, $^1J_{CH}$ = 118 Hz, $CHSiMe_3$).

(41) **5**: ^1H NMR (CD_2Cl_2, 300 MHz, 25 °C) δ 11.22 (d, $^2J_{HH}$ = 0.8 Hz, CH_2), 9.55 (d, $^2J_{HH}$ = 0.8 Hz, CH_2), 1.62 (s, C_5Me_5); ^{13}C NMR (CD_2Cl_2, 75 MHz, 25 °C) δ 177.3 (CH_2), 87.2 (s, C_5Me_5), 10.3 (q, $^1J_{CH}$ = 126.6 Hz, C_5Me_5).

(42) **6**: ^1H NMR (CD_2Cl_2, 300 MHz, 25 °C) δ 10.88 (t, $^2J_{HH}$ = 3.5 Hz, $^3J_{PH}$ = 3.5 Hz, CH_2), 9.83 (dd, $^2J_{HH}$ = 3.5 Hz, $^3J_{PH}$ = 18.5 Hz, CH_2), 1.65 (d, $^4J_{PH}$ = 1.5 Hz, C_5Me_5), 1.64 (s, C_5Me_5), 1.17 (d, $^2J_{PH}$ = 9.5 Hz, PMe_3); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 75 MHz, 25 °C) δ 176.0 (CH_2), 98.2 (d, $^2J_{CP}$ = 2.4 Hz, C_5Me_5), 85.2 (s, C_5Me_5), 18.3 (d, $^2J_{PH}$ = 30.8 Hz, PMe_3), 11.1 (s, C_5Me_5), 10.0 (s, C_5Me_5); $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 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.