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# 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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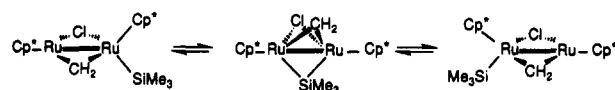
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The scission of C–H and C–C bonds by transition metal complexes is an area of great current interest.<sup>1–6</sup> Occasionally, C–H and C–C bond cleavage processes are chemically reversible, and in particular, examples of reversible  $\beta$ -hydrogen elimination reactions,<sup>7–9</sup> reversible  $\alpha$ -hydrogen eliminations,<sup>9–15</sup> and reversible  $\beta$ -alkyl elimination reactions<sup>16–21</sup> 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.<sup>22–28</sup> 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  $\alpha$ -silyl group from a  $\text{CH}_2\text{SiMe}_3$  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  $[\text{Cp}^*\text{RuCl}]_4$ <sup>29–32</sup> with 1 equiv of  $\text{Mg}(\text{CH}_2\text{SiMe}_3)_2$  in

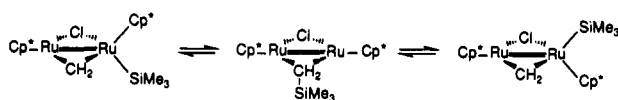
diethyl ether gives a dark red product of stoichiometry " $\text{Cp}^*_2\text{Ru}_2(\text{CH}_2\text{SiMe}_3)\text{Cl}$ " after crystallization from pentane. However, the presence of two downfield singlets at  $\delta$  10.77 and 10.01 in the low-temperature  $^1\text{H}$  NMR spectrum and the presence of a triplet ( $J_{\text{C-H}} = 138$  Hz) at  $\delta$  170 in the  $^{13}\text{C}$  NMR spectrum suggest that the product is not a (trimethylsilyl)methyl complex as expected, but instead contains a bridging methylene group<sup>33,34</sup> owing to scission of the  $\alpha$ -C–Si bond of the  $\text{CH}_2\text{SiMe}_3$  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**,<sup>35</sup> 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  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of **1** reveal that it undergoes two fluxional processes. In the lower energy process, the two  $\text{Cp}^*$  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  $\text{Cp}^*$   $^{13}\text{C}$  NMR line shapes as a function of temperature yields the activation parameters  $\Delta H^\ddagger = 8.9 \pm 0.1$  kcal mol<sup>-1</sup> and  $\Delta S^\ddagger = 0 \pm 3$  cal mol<sup>-1</sup> K<sup>-1</sup>. The only reasonable mechanism that could exchange the  $\text{Cp}^*$  groups but not the  $\text{CH}_2$  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.<sup>43</sup>

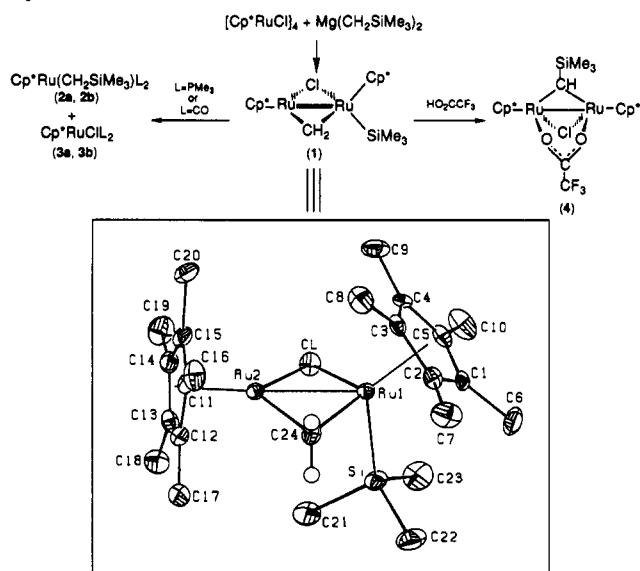
Equally interesting is the higher energy dynamic process, in which the two methylene proton resonances, which are sharp in the  $^1\text{H}$  NMR spectrum below  $0$  °C, broaden as the temperature is raised and coalesce at  $50$  °C. Activation parameters of  $\Delta H^\ddagger = 12.0 \pm 0.1$  kcal mol<sup>-1</sup> and  $\Delta S^\ddagger = -7 \pm 3$  cal mol<sup>-1</sup> K<sup>-1</sup> 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,<sup>36</sup> rotation about an unbridged metal–metal bond,<sup>37</sup> 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**:  $^1\text{H}$  NMR ( $d_6$ -toluene, 300 MHz,  $-80$  °C)  $\delta$  10.77 (s,  $\text{CH}_2$ ), 10.01 (s,  $\text{CH}_2$ ), 1.49 (br s,  $\text{C}_5\text{Me}_5$ ), 0.64 (s,  $\text{SiMe}_3$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 75 MHz,  $-80$  °C)  $\delta$  170.0 (t,  $J_{\text{C-H}} = 138$  Hz,  $\text{CH}_2$ ), 94.6 (s,  $\text{C}_5\text{Me}_5$ ), 81.6 (s,  $\text{C}_5\text{Me}_5$ ), 10.2 (q,  $J_{\text{C-H}} = 127$  Hz,  $\text{C}_5\text{Me}_5$ ), 6.8 (q,  $J_{\text{C-H}} = 127$  Hz,  $\text{SiMe}_3$ ).
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**Scheme I. Synthesis, Crystal Structure, and Reactivity of  $\text{Cp}^*_2\text{Ru}_2(\mu\text{-CH}_2)(\mu\text{-Cl})(\text{SiMe}_3)$ , **1**<sup>a</sup>**


<sup>a</sup> 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  $\text{Cp}^*$  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.<sup>25,38</sup>

One of the most convincing pieces of evidence that *both* the low- and high-energy dynamic processes involve movement of the  $\text{SiMe}_3$  group comes from a study of the structurally related cation  $[\text{Cp}^*_2\text{Ru}_2(\mu\text{-CH}_2)(\mu\text{-Cl})(\text{PMe}_3)]^+$ , whose preparation is described below. This cation is identical with **1** except that the  $\text{SiMe}_3$  group has been replaced by a  $\text{PMe}_3$  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  $\text{SiMe}_3$  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  $\text{PMe}_3$  in diethyl ether gives the known<sup>29</sup> mononuclear  $\text{Ru}^{\text{II}}$  products  $\text{Cp}^*\text{Ru}(\text{CH}_2\text{SiMe}_3)(\text{PMe}_3)_2$ , **2a**, and  $\text{Cp}^*\text{RuCl}(\text{PMe}_3)_2$ , **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

(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  $\text{Cp}^*\text{Ru}(\text{CH}_2\text{SiMe}_3)(\text{CO})_2$ , **2b**, and  $\text{Cp}^*\text{RuCl}(\text{CO})_2$ , **3b**.<sup>39</sup>

Protonation of **1** with  $\text{HO}_2\text{CCF}_3$  at room temperature also gives a product in which the C–Si bond has re-formed,  $\text{Cp}^*_2\text{Ru}_2(\mu\text{-CHSiMe}_3)(\mu\text{-O}_2\text{CCF}_3)(\mu\text{-Cl})$ , **4**.<sup>40</sup> If the reaction is performed with  $\text{DO}_2\text{CCF}_3$ , no deuterium is present in the  $\mu\text{-CHSiMe}_3$  group of the product, as shown by  $^1\text{H}$  and  $^{13}\text{C}$  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  $\text{HO}_2\text{CCF}_3$  gives a different product,  $\text{Cp}^*_2\text{Ru}_2(\mu\text{-CH}_2)(\mu\text{-Cl})(\mu\text{-O}_2\text{CCF}_3)$ , **5**;<sup>41</sup> under these conditions the  $\text{SiMe}_3$  group is lost and appears in the reaction mixture as the silyl ester  $\text{Me}_3\text{SiO}_2\text{CCF}_3$ . Treatment of **5** with trimethylphosphine gives the cation  $[\text{Cp}^*_2\text{Ru}_2(\mu\text{-CH}_2)(\mu\text{-Cl})(\text{PMe}_3)]^+[\text{O}_2\text{CCF}_3]^-$ , **6**,<sup>42</sup> 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.

**Acknowledgment.** We thank the National Science Foundation for support of this research through Grant CHE 89-17586, and W.L. thanks the University of Illinois Department of Chemistry for a fellowship. G.S.G. is the recipient of a Camille and Henry Dreyfus Teacher-Scholar Award (1988–1993) and an A.P. Sloan Foundation Research Award (1988–1993).

**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**:  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 500 MHz, 25 °C)  $\delta$  13.45 (s,  $\text{CHSiMe}_3$ ), 1.60 (s,  $\text{C}_5\text{Me}_5$ ), 0.03 (s,  $\text{CHSiMe}_3$ );  $^{13}\text{C}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 125 MHz, 25 °C)  $\delta$  195.3 (d,  $^1J_{\text{C-H}} = 120$  Hz,  $\text{CHSiMe}_3$ ), 164.5 (q,  $^2J_{\text{C-F}} = 37$  Hz,  $\text{CO}_2\text{CF}_3$ ), 113.0 (q,  $^1J_{\text{C-F}} = 288$  Hz,  $\text{CO}_2\text{CF}_3$ ), 87.5 (s,  $\text{C}_5\text{Me}_5$ ), 10.9 (q,  $^1J_{\text{C-H}} = 127$  Hz,  $\text{C}_5\text{Me}_5$ ), 5.0 (q,  $^1J_{\text{C-H}} = 118$  Hz,  $\text{CHSiMe}_3$ ).

(41) **5**:  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 300 MHz, 25 °C)  $\delta$  11.22 (d,  $^2J_{\text{H-H}} = 0.8$  Hz,  $\text{CH}_2$ ), 9.55 (d,  $^2J_{\text{H-H}} = 0.8$  Hz,  $\text{CH}_2$ ), 1.62 (s,  $\text{C}_5\text{Me}_5$ );  $^{13}\text{C}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 75 MHz, 25 °C)  $\delta$  177.3 ( $\text{CH}_2$ ), 87.2 (s,  $\text{C}_5\text{Me}_5$ ), 10.3 (q,  $^1J_{\text{C-H}} = 126.6$  Hz,  $\text{C}_5\text{Me}_5$ ).

(42) **6**:  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 300 MHz, 25 °C)  $\delta$  10.88 (t,  $^2J_{\text{H-H}} = 3.5$  Hz,  $^3J_{\text{P-H}} = 3.5$  Hz,  $\text{CH}_2$ ), 9.83 (dd,  $^2J_{\text{H-H}} = 3.5$  Hz,  $^3J_{\text{P-H}} = 18.5$  Hz,  $\text{CH}_2$ ), 1.65 (d,  $^4J_{\text{P-H}} = 1.5$  Hz,  $\text{C}_5\text{Me}_5$ ), 1.64 (s,  $\text{C}_5\text{Me}_5$ ), 1.17 (d,  $^2J_{\text{P-H}} = 9.5$  Hz,  $\text{PMe}_3$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 75 MHz, 25 °C)  $\delta$  176.0 ( $\text{CH}_2$ ), 98.2 (d,  $^2J_{\text{C-P}} = 2.4$  Hz,  $\text{C}_5\text{Me}_5$ ), 85.2 (s,  $\text{C}_5\text{Me}_5$ ), 18.3 (d,  $^2J_{\text{P-H}} = 30.8$  Hz,  $\text{PMe}_3$ ), 11.1 (s,  $\text{C}_5\text{Me}_5$ ), 10.0 (s,  $\text{C}_5\text{Me}_5$ );  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 121 MHz)  $\delta$  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.