

# Ruthenium Amidinato–Carbene Complexes Containing a Ru–Si Bond: Formation and Reversible $\alpha$ -Silyl Group Migration from the Metal to the Carbene Ligand

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**Summary:** Reactions of the coordinatively unsaturated complexes  $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}\{\eta^1\text{-PrNC}(\text{Me})=\text{N}^i\text{Pr}\}]^+\text{X}^-$  with  $\text{Me}_3\text{SiCHN}_2$  resulted in the formation of the amidinato–carbene complexes  $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}\{\text{=CHN}^i\text{PrC}(\text{Me})=\text{N}^i\text{Pr}\}(\text{SiMe}_3)]^+\text{X}^-$ , in which a trimethylsilyl group is bonded to the ruthenium atom. Migration of the silyl group to the carbene ligand occurred on reaction with CO, whereas the reverse reaction was promoted by photochemical dissociation of CO.

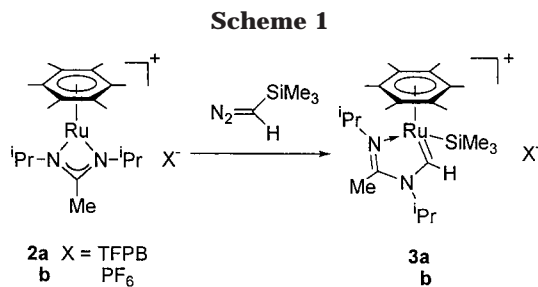
Coordinatively unsaturated transition-metal complexes have received considerable attention in terms of possible intermediates of homogeneous catalysis.<sup>1</sup> In particular, such complexes of ruthenium have been investigated actively in recent years.<sup>2</sup> We recently have prepared novel organoruthenium amidinates,  $(\eta^5\text{-C}_5\text{Me}_5)\text{Ru}(\eta\text{-amidinate})$  (**1**)<sup>3a</sup> and  $[(\eta^6\text{-C}_6\text{R}_6)\text{Ru}(\eta\text{-amidinate})]^+\text{X}^-$  (**2**)<sup>3b</sup> which have formally 16 valence electrons and are highly reactive toward coordination of several 2-electron-donor ligands<sup>3a,b</sup> and oxidative addition of allylic substrates.<sup>3c,d</sup> In our further studies of the reactivity of **1** and **2**, we were interested in their reactions with diazoalkanes. The reactions of certain metal complexes with diazoalkanes represent a route to transition metal carbene complexes.<sup>4</sup> Numerous studies have been undertaken of such reactions from

the viewpoints of organic and organometallic chemistry.<sup>5</sup> Reactions of coordinatively unsaturated Ru(II) complexes with diazoalkanes were reported recently:  $[\text{CpRu}(\text{tmeda})]^+\text{TFPB}^-$  (tmeda = tetramethylethylenediamine, TFPB = tetrakis{3,5-bis(trifluoromethyl)phenyl}borate) reacted with trimethylsilyldiazomethane ( $\text{Me}_3\text{SiCHN}_2$ ) to give  $[\text{CpRu}(\text{tmeda})(=\text{CHSiMe}_3)]^+(\text{TFPB})^-$ ,<sup>2g</sup> whereas treatment of  $\text{RuHCl}(\text{CO})(\text{P}^t\text{Bu}_2\text{Me})_2$  with diazomethane itself resulted in the formation of  $\text{Ru}(\text{CH}_3)\text{Cl}(\text{CO})(\text{P}^t\text{Bu}_2\text{Me})_2$  via a ruthenium–carbene intermediate,  $\text{Ru}(\text{=CH}_2)\text{HCl}(\text{CO})(\text{P}^t\text{Bu}_2\text{Me})_2$ .<sup>2e</sup> These results prompted us to investigate the reactions of **1** and **2** with  $\text{Me}_3\text{SiCHN}_2$ . Although no reaction took place when **1** was treated with this reagent, the cationic complexes  $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}\{\eta^1\text{-PrNC}(\text{Me})=\text{N}^i\text{Pr}\}]^+\text{X}^-$  (**2a**, X = TFPB; **2b**, X =  $\text{PF}_6$ ) reacted instantly. The products were amidinato–carbene complexes having a trimethylsilyl group on the ruthenium,  $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}\{\text{=CHN}^i\text{PrC}(\text{Me})=\text{N}^i\text{Pr}\}(\text{SiMe}_3)]^+\text{X}^-$  (**3a**, X = TFPB; **3b**, X =  $\text{PF}_6$ ). Furthermore, the trimethylsilyl group of these new carbene complexes migrates readily from the metal center to the carbene ligand by coordination of CO or isocyanide to form **4** or **5**, respectively. The reverse carbon to metal  $\alpha$ -silyl group migration involving elimination of CO occurs upon irradiation of **4**. To our knowledge, this is the first example of the formation of amidinato–carbene complexes by the reaction of organometallic complexes with diazoalkanes<sup>6</sup> and a rare case of experimental proof of the reversible  $\alpha$ -silyl group migration from a metal to a carbene ligand.<sup>7,8</sup>

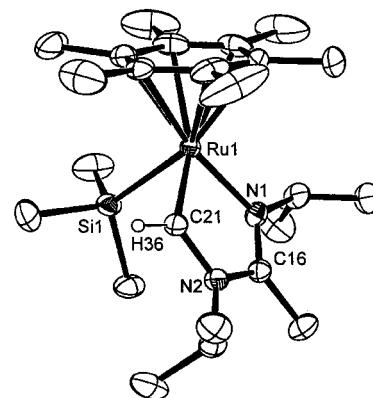
As shown in Scheme 1, the reaction of **2a** or **2b** with  $\text{Me}_3\text{SiCHN}_2$  in  $\text{CH}_2\text{Cl}_2$  at  $-78^\circ\text{C}$  leads to immediate

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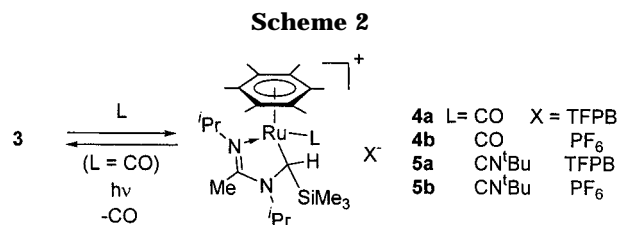
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 (7) Although  $\alpha$ -silyl migration is well investigated in main group organometallic chemistry,<sup>15</sup> it is rarely observed in the organotransition metal chemistry.<sup>8,15</sup> The only example for silyl group migration from a metal to a carbene ligand: Berry, D. H.; Koloski, T. S.; Carroll, P. J. *Organometallics* **1990**, *9*, 2952–2962.  
 (8) Reversible migration reactions of a silyl group from a metal to a silylene ligand: Sharma, H. K.; Pannell, K. H. *Chem. Rev.* **1995**, *95*, 1351–1374.



liberation of N<sub>2</sub> to afford the air- and moisture-stable amidinato-carbene complex containing the Ru–Si(CH<sub>3</sub>)<sub>3</sub> moiety **3a** or **3b**, respectively, in good yield.<sup>9</sup> The structures of **3a** and **3b** were determined by their <sup>1</sup>H and <sup>13</sup>C NMR spectra: existence of the metal-carbene bond is suggested by the <sup>1</sup>H and <sup>13</sup>C resonances appearing at characteristically lower field (for example, **3a** in CD<sub>2</sub>-Cl<sub>2</sub>; δ<sub>H</sub> 10.7 ppm, δ<sub>C</sub> 246 ppm). The <sup>13</sup>C–<sup>1</sup>H coupling constant of the carbene carbon atom was 162 Hz, indicative of the sp<sup>2</sup> character of this carbon atom. The methyl groups of the two <sup>1</sup>Pr groups of the amidinato-carbene ligand are magnetically inequivalent and give four doublets in the <sup>1</sup>H NMR spectrum and four signals in the <sup>13</sup>C NMR spectrum. These spectroscopic features were supported by the X-ray structure determination of **3b**, whose molecular structure is illustrated in Figure 1.<sup>10</sup> There is a trimethylsilyl group (Ru–Si = 2.448(1) Å) and a carbene moiety (Ru–C<sub>carbene</sub> = 1.900(5) Å) bonded to the ruthenium center. The Ru–C bond distance is similar to those of the known amino-carbene complexes of ruthenium.<sup>11</sup> The carbene carbon is bonded with a proton and one nitrogen atom of the amidinate ligand. The other nitrogen atom of the amidinate is coordinated to the ruthenium atom. The resulting five-membered ruthenacycle consisting of the ruthenium atom and the amidinato-carbene ligand is planar. Such a planar structure of an amidinato-carbene-metal unit has been seen in the tungsten complexes [Tp'(CO)<sub>2</sub>W{C(OR)N(R')C(Me)=N(H)}]X-



**Figure 1.** ORTEP drawing of **3b** with thermal ellipsoids drawn at the 30% probability level. All hydrogen atoms except H36 and the counteranion are omitted for clarity. Representative bond distances (Å) and angles (deg) are as follows: Ru1–C21 = 1.900(5), Ru1–N1 = 2.053(4), Ru1–Si1 = 2.4476(15), N1–C16 = 1.292(7), N2–C16 = 1.372(7), N2–C21 = 1.349(6); C21–Ru1–N1 = 76.64(19), Ru1–N1–C16 = 115.5(3), N2–C21–Ru1 = 119.4(4).



ported by Templeton,<sup>6c</sup> in which delocalization of the positive charge provides several possible resonance structures.

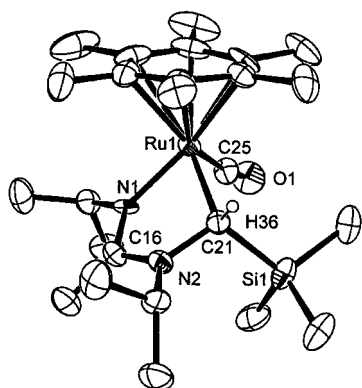
The unprecedented formation of **3** must involve cleavage of the C–SiMe<sub>3</sub> bond in Me<sub>3</sub>SiCHN<sub>2</sub>, which resulted in subsequent Ru–Si and C–N bond formation. As a clue to enable an understanding of the mechanism of these multiple reactions, we have discovered experimentally that silyl group migration from the carbene carbon atom to ruthenium can occur. As shown in Scheme 2, trimethylsilyl group migration from the ruthenium to the carbene ligand was accomplished quantitatively by treatment of **3a** or **3b** with a typical π-acid, σ-donor such as CO or CN<sup>t</sup>Bu to give the complexes **4** and **5**, respectively.<sup>12</sup> No rearrangement occurred when either **3a** or **3b** was treated with phosphines, pyridine, or olefins such as ethyl vinyl ether and acrylonitrile. The migration resulted in a typical higher field shift of the <sup>1</sup>H and <sup>13</sup>C resonances of the CH group bonded with the ruthenium atom; for example, the δ<sub>H</sub> and δ<sub>C</sub> values of **4a** appeared at 3.72 and 56 ppm with J<sub>CH</sub> = 126 Hz due to the sp<sup>3</sup> carbon atom. The <sup>29</sup>Si NMR signal of **4a** appeared at 3.85 ppm, which is higher than

(9) In a typical example for **3**, to a solution of **2** (40 mg, 0.032 mmol) dissolved in CH<sub>2</sub>Cl<sub>2</sub> (ca. 3 mL) was added a hexane solution of Me<sub>3</sub>-SiCHN<sub>2</sub> (10% solution, 0.048 mmol) dropwise at –78 °C. The color of the solution changed immediately from dark blue to red, and the reaction mixture was warmed to room temperature with stirring for 10 min. After removal of the solvent, the resulting crude product was purified by recrystallization from CH<sub>2</sub>Cl<sub>2</sub>/pentane at –35 °C to give **3a** as red crystals (33 mg, 0.024 mmol, 77%). <sup>1</sup>H NMR (600 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ –0.18 (s, Si(CH<sub>3</sub>)<sub>3</sub>), 1.24 (d, J = 7.0 Hz, 3H; CH(CH<sub>3</sub>)<sub>2</sub>), 1.31 (d, J = 5.1 Hz, 3H; CH(CH<sub>3</sub>)<sub>2</sub>), 1.35 (d, J = 6.6 Hz, 3H; CH(CH<sub>3</sub>)<sub>2</sub>), 1.38 (d, J = 6.8 Hz, 3H; CH(CH<sub>3</sub>)<sub>2</sub>), 2.20 (s, 18H; C<sub>6</sub>Me<sub>6</sub>), 2.45 (s, 3H; CCH<sub>3</sub>), 4.06 (sep, J = 6.8 Hz, 1H; CH(CH<sub>3</sub>)<sub>2</sub>), 4.37 (sep, J = 6.7 Hz, 1H; CH(CH<sub>3</sub>)<sub>2</sub>), 7.56 (s, 4H; p-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>), 7.72 (t, J = 2.2 Hz, 8H; o-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>), 10.7 (s, 1H; Ru=CH). Other data are given in the Supporting Information.

(10) Crystal data for **3b**: C<sub>24</sub>H<sub>45</sub>F<sub>6</sub>N<sub>2</sub>PRu; M<sub>r</sub> = 635.75, monoclinic, a = 18.580(3) Å, b = 20.311(3) Å, c = 16.596(3) Å, β = 110.411(3), U = 5868.6(17) Å<sup>3</sup>, T = 293 K, space group C2/c (No. 15), Z = 8, μ(Mo Kα) = 0.683 mm<sup>–1</sup>, 6225 reflections measured, 6225 unique (R<sub>int</sub> = 0.000), 4542 observed (>2σ), final residuals R1 = 0.0601, wR2 = 0.1581 (I > 2σ(I)); R1 = 0.0869, wR2 = 0.1782 (all data).

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(12) In a typical example for **4**: in a Schlenk tube, a CH<sub>2</sub>Cl<sub>2</sub> solution (ca. 3 mL) of **3a** (54 mg, 0.040 mmol) was stirred under a CO atmosphere at room temperature for 2 h. The color of the solution changed from red to yellow. After removal of the solvent, the product **3a** was obtained as a yellow solid (54 mg, 0.039 mmol, 98%). <sup>1</sup>H NMR (600 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ 0.09 (s, Si(CH<sub>3</sub>)<sub>3</sub>), 1.16 (d, J = 6.8 Hz, 3H; CH(CH<sub>3</sub>)<sub>2</sub>), 1.23 (d, J = 7.1 Hz, 3H; CH(CH<sub>3</sub>)<sub>2</sub>), 1.33 (d, J = 7.1 Hz, 3H; CH(CH<sub>3</sub>)<sub>2</sub>), 1.43 (d, J = 7.1 Hz, 3H; CH(CH<sub>3</sub>)<sub>2</sub>), 2.07 (s, 3H; CCH<sub>3</sub>), 2.15 (s, 18H; C<sub>6</sub>Me<sub>6</sub>), 3.48 (sep, J = 7.0 Hz, 1H; CH(CH<sub>3</sub>)<sub>2</sub>), 3.52 (sep, J = 7.1 Hz, 1H; CH(CH<sub>3</sub>)<sub>2</sub>), 3.72 (s, 1H; Ru–CH), 7.56 (s, 4H; p-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>), 7.72 (t, J = 2.2 Hz, 8H; o-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>). IR (KBr): ν̄ 1963 cm<sup>–1</sup> (CO). Other data are given in the Supporting Information.



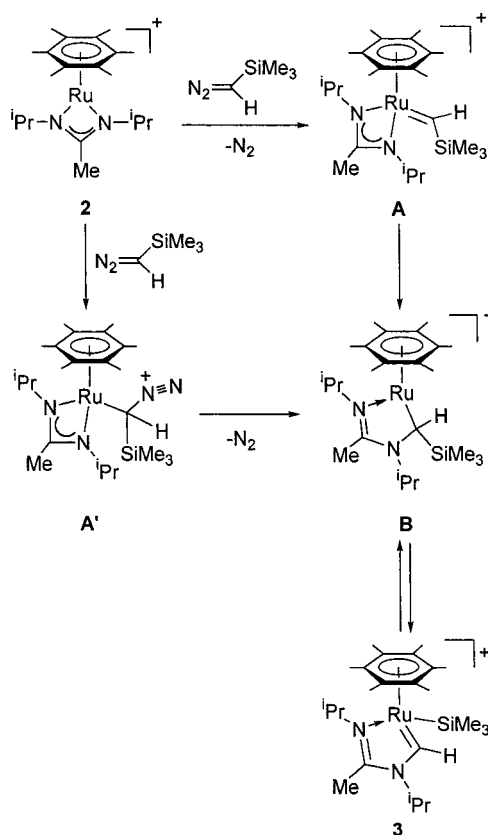
**Figure 2.** ORTEP drawing of **4b** with thermal ellipsoids drawn at the 30% probability level. All hydrogen atoms except H36 and the counteranion are omitted for clarity. Representative bond distances (Å) and angles (deg) are as follows: Ru1–C21 = 2.097(11), Ru1–N1 = 1.960(8), Ru1–C25 = 1.836(9), N1–C16 = 1.294(13), N2–C16 = 1.339(13), N2–C21 = 1.497(13); C21–Ru1–N1 = 75.0(4), Ru1–N1–C16 = 125.0(8), N2–C21–Ru1 = 107.1(6), Ru1–C21–Si1 = 119.7(5).

that of **3a** by 20 ppm (**3a**; 24.61 ppm). The existence of a coordinated CO is suggested by the IR and  $^{13}\text{C}$  NMR spectra ( $\nu_{\text{CO}}$  1963  $\text{cm}^{-1}$ ;  $\delta_{\text{CO}}$  203 ppm). These spectral changes on going from **3a** to **4a** correspond to the  $\alpha$ -silyl migration from [(amidinato)(H)C=RuSiMe<sub>3</sub>] to [(amidinato)(H)(Me<sub>3</sub>Si)CRuCO]. The crystal structure of **4b** is consistent with the NMR data as shown in Figure 2.<sup>13</sup> There is a trimethylsilyl group bonded to the  $\alpha$ -carbon on the ruthenium atom. The Ru–C distance of 2.097 (11) Å is in the range of typical Ru–C single bonds. The  $\alpha$ -carbon is trisubstituted, and pyramidalization of the  $\alpha$ -carbon resulted in loss of the planarity of the ruthenacycle that had been present in **3**. The complexes **4** and **5** were formed by  $\alpha$ -trimethylsilyl group migration from the ruthenium atom to the carbene ligand. Interestingly, the reverse migration from the carbon atom to the ruthenium could be effected by photochemical dissociation of the CO ligand in **4a**, which photoirradiation of **4a** (500 W Xe lamp, room temperature, 5 h) gave rise to regenerated **3a** in 73% yield.

As described above, the reaction of cationic, coordinatively unsaturated ruthenium complexes **2** with Me<sub>3</sub>SiCHN<sub>2</sub> gave the amidinato–carbene silyl complexes **3**, having a Ru–Si bond. A possible mechanism of the conversion of **2** to **3** is illustrated in Scheme 3. The initial step of the reaction may be formation of the ruthenium–carbene intermediate **A** with concomitant liberation of N<sub>2</sub>. Subsequent migration of an amidinate nitrogen atom in **A** from the ruthenium center to the carbon atom to form **B** follows. Such a ruthenium–carbene formation was reported by Kirchner.<sup>2f</sup> Attempted detection of this silylcarbene intermediate by NMR spectroscopy at low temperature failed because the reaction was too rapid.<sup>14</sup> In this sense, a reaction pathway via **A'** cannot be excluded at present.

(13) Crystal data for **4b**: C<sub>25</sub>H<sub>45</sub>F<sub>6</sub>N<sub>2</sub>OPRuSi;  $M_r$  = 663.76, orthorhombic,  $a$  = 22.250(4) Å,  $b$  = 9.234(3) Å,  $c$  = 15.137(3) Å,  $U$  = 3110.1(12) Å<sup>3</sup>,  $T$  = 293 K, space group *Pna*2<sub>1</sub> (No. 33),  $Z$  = 4,  $\mu(\text{Mo K}\alpha)$  = 0.650 mm<sup>-1</sup>, 4682 reflections measured, 4682 unique ( $R_{\text{int}}$  = 0.000), 2155 observed ( $>2\sigma$ ), final residuals  $R_1$  = 0.0498,  $wR_2$  = 0.1263 ( $I > 2\sigma(I)$ );  $R_1$  = 0.1777,  $wR_2$  = 0.1730 (all data).

Scheme 3



The carbon-to-ruthenium trimethylsilyl group migration from the coordinatively unsaturated intermediate **B** leads to formation of **3**. As described above, this pathway is supported by the following experimental evidence: (1) existence of the metal fragment **B** was demonstrated by isolation of the CO and isocyanide adducts **4** and **5** and (2) the observation that **B** could be photochemically generated from **4**; this led to formation of **3**. Experimental evidence for reversible  $\alpha$ -trimethylsilyl group migration between the ruthenium atom and the carbene ligand presented in this paper is quite unique in the chemistry of silyl group rearrangements.<sup>7,8,15,16</sup> We are currently investigating detailed mechanisms of the formation of **3** and the reversible  $\alpha$ -silyl migration.

**Supporting Information Available:** Text giving experimental details and analytical data for new complexes and tables of X-ray structural data, including data collection parameters, positional and thermal parameters, and bond lengths and angles for **3b** and **4b**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(14) Experiments to detect intermediates in the reaction of **2a** with Me<sub>3</sub>SiCHN<sub>2</sub> were carried out as follows: a CD<sub>2</sub>Cl<sub>2</sub> solution (ca. 0.4 mL) of **2a** (10.8 mg, 8.5  $\mu\text{mol}$ ) was treated with a hexane solution of Me<sub>3</sub>SiCHN<sub>2</sub> (12  $\mu\text{mol}$ ) at  $-78^\circ\text{C}$ , and the mixture was immediately ( $\sim 5$  min) subjected to  $^1\text{H}$  NMR measurement at  $-80^\circ\text{C}$ . Only **3a** was observed as the organometallic product.

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