

**Synthesis and Characterization of Chelating Bis(silane) Complexes**  
**[RuH<sub>2</sub>{(η<sup>2</sup>-HSiMe<sub>2</sub>)<sub>2</sub>X}(PCy<sub>3</sub>)<sub>2</sub>] (X = C<sub>6</sub>H<sub>4</sub>, O)**  
**Containing Two Ru–(η<sup>2</sup>-Si–H) Bonds**

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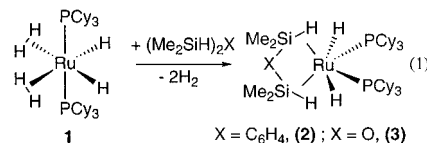
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The η<sup>2</sup>-coordination of σ bonds to transition metals is an intense area of research in coordination chemistry. Furthermore, reactivity studies of the resulting complexes have intensified over the past few years.<sup>1</sup> However, complexes accommodating more than one σ bond are rare: a few bis-agostic compounds are known,<sup>2</sup> and to date only two examples of thermally stable bis(dihydrogen) complexes have been isolated, RuH<sub>2</sub>(H<sub>2</sub>)<sub>2</sub>(PCy<sub>3</sub>)<sub>2</sub> (**1**) and Tp\*<sub>2</sub>RuH(H<sub>2</sub>)<sub>2</sub>.<sup>3</sup> Whereas several transition metal complexes in which a simple silane, HSiR<sub>3</sub>, is η<sup>2</sup>-coordinated to the metal center have been reported,<sup>4</sup> no mononuclear complexes containing two M–(η<sup>2</sup>-Si–H) bonds have been isolated so far. The mononuclear complex [IrH<sub>2</sub>(η<sup>2</sup>-HSiEt<sub>3</sub>)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>][SbF<sub>6</sub>] obtained by addition of 2 equiv of Et<sub>3</sub>SiH to [IrH<sub>2</sub>(THF)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>][SbF<sub>6</sub>] was only characterized in solution by <sup>1</sup>H NMR.<sup>5</sup> Some dinuclear (μ-silyl) complexes {[Cp\*Ru(μ-η<sup>2</sup>-HSiRR')]<sub>2</sub>(μ-H)H}<sup>6,7</sup> have been reported, and, in the case of R = Et, an X-ray structure determination proved the existence of two Ru–(η<sup>2</sup>-H–Si) bonds.<sup>6</sup> The synthesis and the X-ray structure of the diiron complex [(CO)<sub>2</sub>Fe]<sub>2</sub>(μ-η<sup>2</sup>-HSiPh<sub>2</sub>) have been recently reported, and the two agostic Fe–H–Si bonds are characterized by NMR by a J<sub>H–Si</sub> of 23 Hz.<sup>8</sup>

We have previously shown that one dihydrogen ligand from the bis(dihydrogen) complex RuH<sub>2</sub>(H<sub>2</sub>)<sub>2</sub>(PCy<sub>3</sub>)<sub>2</sub> (**1**) is easily substituted by HEPH<sub>3</sub> (E = Si, Ge) leading to the formation of RuH<sub>2</sub>(H<sub>2</sub>)(HEPH<sub>3</sub>)(PCy<sub>3</sub>)<sub>2</sub>.<sup>9</sup> Subsequently, we have demonstrated that **1** is an efficient catalyst precursor for the selective dehydrogenative silylation of ethylene into the vinylsilane CH<sub>2</sub>=CHSiEt<sub>3</sub>.<sup>10</sup> Thus, the extension of this system provides a potential entry into a method for preparing vinylsiloxane compounds which are of great interest for the manufacture of

silicones.<sup>11</sup> We report here the reaction of **1** with the bis(silane) compounds, 1,2-bis(dimethylsilyl)benzene and 1,1,3,3-tetra-methylidisiloxane, which leads to the first two examples of a transition metal bis(silane) complex, where the two H–Si bonds are η<sup>2</sup>-coordinated to the metal.

Addition of (Me<sub>2</sub>SiH)<sub>2</sub>(C<sub>6</sub>H<sub>4</sub>) or (Me<sub>2</sub>SiH)<sub>2</sub>O to **1** suspended in pentane leads to an immediate dissolution and reprecipitation of a white powder, isolated and characterized as [RuH<sub>2</sub>{(η<sup>2</sup>-HSiMe<sub>2</sub>)<sub>2</sub>X}(PCy<sub>3</sub>)<sub>2</sub>] (X = (C<sub>6</sub>H<sub>4</sub>), (**2**); X = O, (**3**)) in ca. 90% yield. These complexes result from the substitution of the two dihydrogen ligands of **1** by the bis(silane) (see eq 1). **2** and **3**



have been characterized by elemental analysis and by multinuclear NMR and IR spectroscopies, and the structure of **2** has been determined by X-ray crystallography.<sup>12,13</sup> The <sup>1</sup>H NMR spectrum of **2** shows at 296 K in the hydride region a triplet at δ –7.74 with J<sub>P–H</sub> = 13 Hz and an AA'XX' multiplet at δ –12.03. These two signals observed in a 1:1 integration ratio are respectively attributed to the two η<sup>2</sup>-bound Si–H protons and the two hydrides. On warming, these two signals coalesce at 355 K, leading to one broad signal at δ –9.9. This exchange is characterized by a 64.5 kJ/mol barrier. T<sub>1</sub> measurements on the hydride resonances give a minimum value of 155 ms at 243 K and 250 MHz (no significant difference is observed for the Si–H and hydride signals). This rules out the presence of any (η<sup>2</sup>-H<sub>2</sub>) ligand in **2**. The <sup>31</sup>P{<sup>1</sup>H} spectrum shows at 296 K a single resonance at δ 51. The <sup>29</sup>Si{<sup>31</sup>P} INEPT <sup>1</sup>H spectrum at 288 K shows a doublet at δ 4.8 with a J<sub>Si–H</sub> value of 63 Hz. This value falls in the upper limit of the known range (20–100 Hz) of J<sub>Si–H</sub> values for (η<sup>2</sup>-Si–H) bonds.<sup>4,8,14–16</sup> The IR spectrum (Nujol mulls) displays one broad Ru–H stretch at 1969 cm<sup>–1</sup> and an Ru–(η<sup>2</sup>-H–Si) band is observed at 1778 cm<sup>–1</sup>.<sup>17</sup> This value together with the J<sub>Si–H</sub> value are in agreement with the coordination of two (η<sup>2</sup>-Si–H) bonds. This is corroborated by an X-ray diffraction study.<sup>13</sup> The molecular structure of **2**

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(12) Complex **2**: (Me<sub>2</sub>SiH)<sub>2</sub>C<sub>6</sub>H<sub>4</sub> (30 μL, 0.14 mmol) was added to a solution of **1** (90 mg, 0.13 mmol) in pentane (6 mL). The mixture was stirred for 10 min, and a white solid precipitated. It was collected by filtration, washed twice with pentane (1.5 mL), and dried under vacuum (yield 90%). Anal. Calcd for RuC<sub>46</sub>H<sub>86</sub>P<sub>2</sub>Si<sub>2</sub>: C, 64.37; H, 10.10. Found: C, 64.43; H, 10.68. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, 296 K): δ –7.74 (t, 2H, Ru–H–Si), –12.03 (AA'XX', 2H, J<sub>H–P</sub> = 25 and 46 Hz, Ru–H), 1.16 (s, 12H, Si–CH<sub>3</sub>), 1.23–2.28 (m, 66H, PCy<sub>3</sub>), 8.03 (m, 2H, C<sub>6</sub>H<sub>4</sub>, J<sub>H–H</sub> = 7.4 and 1.2 Hz) 7.41 (m, 2H, C<sub>6</sub>H<sub>4</sub>, J<sub>H–H</sub> = 7.4 and 1.2 Hz). <sup>29</sup>Si{<sup>31</sup>P} INEPT <sup>1</sup>H nonrefocused (79.5 MHz, C<sub>6</sub>D<sub>6</sub>, 288 K) δ 4.8 (d, J<sub>Si–H</sub> = 63 Hz). <sup>29</sup>Si INEPT <sup>1</sup>H refocused (79.5 MHz, C<sub>6</sub>D<sub>6</sub>) δ 4.8 (t, J<sub>Si–P</sub> = 8.3 Hz). <sup>31</sup>P{<sup>1</sup>H} NMR (161.99 MHz, C<sub>6</sub>D<sub>6</sub>): δ 50.97. IR (Nujol mull): 1778 cm<sup>–1</sup> (ν Ru–H–Si); 1969 cm<sup>–1</sup> (ν Ru–H). Complex **3**: Anal. Calcd for RuC<sub>40</sub>H<sub>82</sub>O<sub>2</sub>P<sub>2</sub>Si<sub>2</sub>: C, 60.12; H, 10.35. Found: C, 59.90; H, 10.38. <sup>1</sup>H NMR (200 MHz, C<sub>6</sub>D<sub>6</sub>, 296 K): δ –9.48 (br, 4H, Ru–H), 1.12 (s, 12H, Si–CH<sub>3</sub>), 1.1–2.25 (m, 66H, PCy<sub>3</sub>). T<sub>1</sub> min = 144 ms (250 MHz, C<sub>7</sub>D<sub>8</sub>, 253 K). <sup>31</sup>P{<sup>1</sup>H} NMR (81.015 MHz, C<sub>6</sub>D<sub>6</sub>): δ 49.94. <sup>29</sup>Si{<sup>31</sup>P} NMR (79.5 MHz) δ –5.7 (d, J<sub>Si–H</sub> = 22 Hz). IR (Nujol mulls): 1699 cm<sup>–1</sup> (ν Ru–H–Si); 2045 and 1969 cm<sup>–1</sup> (ν Ru–H).

(13) Crystal data for **2**: colorless crystal, monoclinic, I2/a, a = 21.033–(4) Å, b = 19.714(2) Å, c = 25.336(5) Å, β = 90.01(2)°, Z = 8, R = 0.0446, GOF = 1.071.

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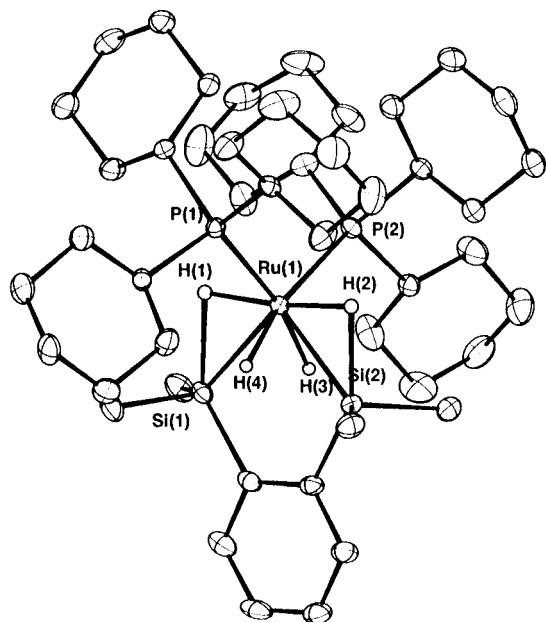
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**Figure 1.** CAMERON view of  $[\text{RuH}_2\{(\eta^2\text{-HSiMe}_2)_2(\text{C}_6\text{H}_4)\}(\text{PCy}_3)_2]$  (**2**). Selected bond lengths ( $\text{\AA}$ ): Ru–P(1), 2.482(1); Ru–P(2), 2.469(1); Ru–Si(1), 2.425(1); Ru–Si(2), 2.429(1); Si(1)–H(1), 1.88(3); Si(2)–H(2), 1.83(3); Ru–H(1), 1.65(3); Ru–H(2), 1.63(3); Ru–H(3), 1.67(3); Ru–H(4), 1.60(3). Selected bond angles (deg): P(1)–Ru–P(2), 109.06(4); P(1)–Ru–H(3), 168.3(11); P(2)–Ru–H(4), 168.6(12); H(1)–Ru–H(2), 171.9(17); Ru–H(1)–Si(1), 86.6(15); Ru–H(2)–Si(2), 88.8(16); Si(1)–Ru–Si(2), 87.65(4); P(1)–Ru–Si(1), 112.17(4); P(1)–Ru–Si(2), 120.17(4); P(2)–Ru–Si(1), 117.65(4); P(2)–Ru–Si(2), 109.23(4).

is shown in Figure 1. The ruthenium atom is in a roughly octahedral environment if the chelating bis(silane) ligand is considered to occupy two coordination sites with the hydrogens being in the axial positions. The chelating bis(silane) plane is nearly coplanar with the ruthenium atom. The phosphines are unusual in being cis, not trans, as normally observed in most of the  $[\text{Ru}](\text{PCy}_3)_2$  complexes. The four hydrogen atoms were located in difference Fourier map, and their coordinates were refined with an equivalent isotropic thermal parameter. As expected the Si(1)–H(1) and Si(2)–H(2) bond lengths (1.88(3) and 1.83(3)  $\text{\AA}$ , respectively) indicate significant Si–H bond lengthening which suggests substantial Ru ( $d\pi$ ) to Si–H ( $\sigma^*$ ) back-donation. The four Ru–H bond lengths are equal within experimental error (1.60(3) to 1.67(3)  $\text{\AA}$ ). The Ru–H–Si angles are close to  $87^\circ$ , and the average Ru–Si bond lengths are 2.427  $\text{\AA}$  in the range observed for ruthenium silyl compounds (2.34–2.51  $\text{\AA}$ ).<sup>18</sup> The bis(silane) ligand is rather strongly bonded to the ruthenium as evidenced by preliminary reactivity studies. For example, no substitution of the bis(silane) ligand could be achieved when bubbling  $\text{H}_2$  or CO to **2**.

The  $^1\text{H}$  NMR spectra of **3** are also temperature dependent (178–296 K,  $\text{C}_7\text{D}_8$ , 250 MHz). But, as opposed to **2**, at 296 K, **3** is fluxional and presents only one broad singlet at  $\delta$  –9.4. A decoalescence is observed at 253 K leading to two broad signals of equal intensity at  $\delta$  –8.5 and –9.9. They appear as two ill-resolved triplets at 213 K with  $J_{\text{P-H}} \sim 13$  and 45 Hz, respectively. The exchange process between the classical

hydrides ( $\delta$  –9.9) and the two  $\eta^2\text{-H-Si}$  ( $\delta$  –8.5) is characterized by a  $\Delta G^\ddagger$  of 47.5 kJ/mol, thus much lower than that for **2**.<sup>19</sup> The fluxionality of **2–3** might involve complexation–decomplexation of the Si–H bonds to the ruthenium center, a process much easier in the case of **3** as evidenced by the substitution reactions (vide infra). The  $^{29}\text{Si}\{^{31}\text{P}\}$  INEPT  $^1\text{H}$  spectrum at 213 K shows a doublet at  $\delta$  –5.7 (79.5 MHz,  $\text{C}_7\text{D}_8$ ) with a  $J_{\text{Si-H}}$  value of 22 Hz. This value falls now in the lower limit of the range of values (20–100 Hz) found for known  $\eta^2$ -silane complexes.<sup>4,8,14–16</sup> The IR spectrum (Nujol mulls) displays two Ru–H stretches at 2045 and 1969  $\text{cm}^{-1}$  indicative of a *cis* dihydride structure, and the existence of the Ru–( $\eta^2$ -H–Si) bonds is confirmed by the presence of a broad band at 1699  $\text{cm}^{-1}$ .<sup>17</sup> This value together with the very small  $J_{\text{Si-H}}$  value are in agreement with the coordination of stretched ( $\eta^2$ -Si–H) bonds. It is of interest to note that  $\text{IrH}_5(\text{PPh}_3)_2$  reacts with  $(^i\text{Pr}_2\text{SiH})_2\text{O}$  to give a classical dihydride bis(silyl) complex  $\text{IrH}_3(\text{disil})(\text{PPh}_3)_2$  (disil =  $(^i\text{Pr}_2\text{Si})_2\text{O}$ ).<sup>20</sup> Classical bis(silyl) complexes  $[(\text{CO})_4\text{Fe}]_2(\eta\text{-R}_2\text{SiOSiR}_2)$  are also obtained by reaction of  $(\text{R}_2\text{HSi})_2\text{O}$  with  $\text{Fe}(\text{CO})_5$ .<sup>8</sup>

Substitution of the ( $\eta^2$ -HSiMe<sub>2</sub>)<sub>2</sub>O ligand in **3** is easily achieved by bubbling  $\text{H}_2$  or CO or by adding  $^i\text{BuNC}$ . In all cases, free disiloxane is recovered (G.C. and  $^1\text{H}$  NMR) and **1**,  $\text{RuH}_2(\text{CO})_2(\text{PCy}_3)_2$ , or  $\text{RuH}_2(^i\text{BuNC})_2(\text{PCy}_3)_2$  are, respectively, isolated in quantitative yield.<sup>21</sup> These reactions confirm that in **3** the disiloxane ligand is weakly bonded to the ruthenium. Thus, the chelate effect of the bis(silane) ligand has allowed the stabilization of **2** and **3**, but steric effects may account for their different reactivity. In particular, the less rigid disiloxane ligand may allow the decoordination of only one ( $\eta^2$ -H–Si) bond, hence favoring substitution reactions.

In summary, we were able to isolate the first mononuclear complexes containing two Ru–( $\eta^2$ -H–Si) bonds. The bis(silane) compounds act as chelating ligands, this chelating effect being responsible for the stabilization of **2** and **3**. Spectroscopic data and preliminary reactivity studies indicate different stretching of the Ru–( $\eta^2$ -H–Si) bonds in **2** and **3**. In addition to catalytic investigations,<sup>22</sup> future efforts will be directed toward synthesizing such species and correlating the stretching of the Ru–( $\eta^2$ -H–Si) bonds to the reactivity of the complexes.

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**Supporting Information Available:** Experimental data for  $\text{RuH}_2(^i\text{BuNC})_2(\text{PCy}_3)_2$  and X-ray diffraction data for **2** (9 pages). See any current masthead page for ordering and Internet access instructions.

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(19) A second decoalescence is achieved when cooling further the temperature. The slow exchange limit is obtained at 178 K, and four broad signals of equal intensity are observed at  $\delta$  –8.1, –8.5, –9.4, and –10.2. The two coalescence temperatures at 198 and 190 K combined with the  $\Delta\nu = 195$  and 94.5 Hz, respectively, for the two types of protons give a  $\Delta G^\ddagger$  of roughly 38 kJ/mol. The  $^{31}\text{P}\{^1\text{H}\}$  spectrum shows at 178 K two very broad signals at  $\delta$  53.2 and 52.7 indicative of an arrested distorted structure.

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