

## Carbonylation Chemistry of the Tantalum Silyl Hydride Cp\*(2,6-<sup>i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>N=)Ta[Si(SiMe<sub>3</sub>)<sub>3</sub>]H: The Unexpected Formation of a Ta(V) Carbonyl Complex and the Complete Reduction of CO

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Studies on the dehydropolymerization of silanes, as catalyzed by early transition metal complexes, have focused on the possible intermediacy of d<sup>0</sup> metal silyl hydrides L<sub>m</sub>M(SiR<sub>3</sub>)H.<sup>1</sup> Isolated compounds of this type are quite rare<sup>2–4</sup> and represent an intriguing class of chemical species, since they contain two reactive σ-bonds. We have therefore concentrated efforts on the synthesis and study of such compounds, and have found that whereas the hafnium complex CpCp\*Hf[Si(SiMe<sub>3</sub>)<sub>3</sub>]H (Cp\* = η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>) is isolable,<sup>4</sup> the silyl hydride (ArN=)Mo[Si(SiMe<sub>3</sub>)<sub>3</sub>]H (Ar = 2,6-<sup>i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) appears to be highly unstable with respect to elimination of HSiMe<sub>3</sub>.<sup>5</sup> More recently, we have achieved the synthesis and isolation of the 16-electron silyl hydride complex Cp\*(ArN=)Ta[Si(SiMe<sub>3</sub>)<sub>3</sub>]H (**1**).<sup>6</sup> Here we report the surprising carbonylation chemistry of **1**, which leads initially to the formally d<sup>0</sup> carbonyl complex Cp\*(ArN=)Ta(CO)[Si(SiMe<sub>3</sub>)<sub>3</sub>]H (**2**).

A pentane solution of **1** reacted rapidly with carbon monoxide (1 atm, -40 °C) to produce the adduct **2**, obtained as orange crystals from cold pentane in 72% yield (Scheme 1). The infrared spectrum of **2** displays a strong carbonyl absorption at 1986 cm<sup>-1</sup> and a weak band at 1793 cm<sup>-1</sup> assigned to the Ta–H bond. Upon isotopic substitution, these bands shift to ν<sub>CO</sub> = 1942 cm<sup>-1</sup> (for **2**-<sup>13</sup>C) and ν<sub>TaD</sub> = 1263 cm<sup>-1</sup> (for **2**-d). In the <sup>1</sup>H NMR spectrum, the hydride resonance for **2** appears at 8.11 ppm, which is considerably upfield with respect to the hydride signal of **1** (δ = 21.49 ppm). In contrast to the latter resonance for **1**, the hydride resonance for **2** exhibits well-resolved satellites from coupling to <sup>29</sup>Si (J<sub>SiH</sub> = 28.5 Hz). In the <sup>13</sup>C NMR spectrum, the carbonyl resonance is found at 245.7 ppm (J<sub>CH</sub> = 2.5 Hz for **2**-<sup>13</sup>C), and the <sup>29</sup>Si NMR spectrum contains a doublet (J<sub>SiH</sub> = 28.5 Hz) for the Ta–Si(SiMe<sub>3</sub>)<sub>3</sub> resonance at -102.7 ppm (compare the singlet at -22.9 ppm observed for **1**). The above data is inconsistent with the η<sup>2</sup>-silaacyl structure originally expected for **2**, given the reactivity of other d<sup>0</sup> metal silyl complexes<sup>7</sup> and the fact that xylyl isonitrile inserts cleanly into the Ta–Si bond of **1** to produce a stable η<sup>2</sup>-silaamine complex.<sup>6</sup>

The X-ray crystal structure of **2** revealed the molecular geometry illustrated in Scheme 1, with the silyl ligand positioned cis to the carbonyl and hydride ligands. The hydride ligand was not observed, but its approximate position is evident from the otherwise empty coordination site between Si(1) and N(1). The Ta–Si distance is considerably longer than in **1** (2.809(2) vs 2.689(1) Å), and the Ta–C(carbonyl) distance of 2.101(7) Å is longer than analogous distances found in Ta(III) carbonyl complexes such as Cp<sub>2</sub>Ta(CO)(SiH<sup>t</sup>Bu<sub>2</sub>)<sup>8</sup> (2.009(5) Å) and Cp<sub>2</sub>Ta(CO)H<sup>9</sup> (2.034(7) Å).

The formation of a d<sup>0</sup> metal carbonyl complex would seem surprising, although a few examples now exist.<sup>10,11</sup> Two possible bonding schemes could account for the stability of **2**. For a d<sup>0</sup> Ta(V) center, donation from a ligand-based orbital into the π\* orbital of the CO ligand could lead to a stable complex.<sup>11</sup> Alternatively, significant interaction between the silyl and hydride ligands could result in a silane σ-complex<sup>12,13</sup> of d<sup>2</sup> Ta(III) and d → π\* back-bonding to the CO ligand. The observed J<sub>Si(Ta)H</sub> coupling constant of 28.5 Hz is intermediate between ranges expected for predominant η<sup>2</sup>-silane character (50–80 Hz) and classical silyl hydrides (≤20 Hz),<sup>12a</sup> but is virtually identical to the corresponding value of 28 Hz reported for Cp<sub>2</sub>Ti(H)(SiHPh<sub>2</sub>)(PMe<sub>3</sub>), which was shown to have considerable η<sup>2</sup>-silane character.<sup>3b</sup> However, the small difference in ν(TaH) infrared stretching frequencies for **1** and **2** (1785 and 1793 cm<sup>-1</sup>, respectively) indicates the presence of a normal, terminal Ta–H bond in **2**. In addition, the bond angles about Si(1) in **2** are similar to those in related Ta–Si(SiMe<sub>3</sub>)<sub>3</sub> complexes<sup>6</sup> and reveal none of the distortions that would be expected for a significant H···Si(1) interaction.

The infrared ν<sub>CO</sub> stretching frequency for **2**, 1986 cm<sup>-1</sup>, indicates donation of electron density into the π\* orbital of the CO ligand, as this value is much lower than that observed for the cationic Ta(V) carbonyl complex Cp<sub>2</sub>Ta(CO)H<sub>2</sub><sup>+</sup> (2112 cm<sup>-1</sup>)<sup>14</sup> and is close to values reported for related d<sup>1</sup> metal carbonyl species.<sup>15</sup> The possibility that electron density from the Ta–Si bond donates into the carbonyl π\* orbital is suggested by the unusually acute Si–Ta–C(carbonyl) angle of 67.6(2)°, which results in a Si(1)···C(11) interatomic distance of only 2.79 Å. This situation is therefore analogous to that described for the Zr(IV) silanimine carbonyl complex Cp<sub>2</sub>Zr(η<sup>2</sup>-Me<sub>2</sub>Si=N<sup>t</sup>Bu)(CO)

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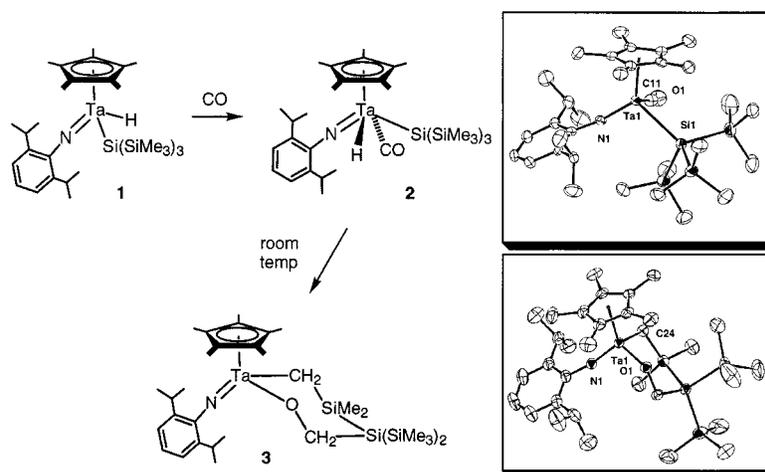
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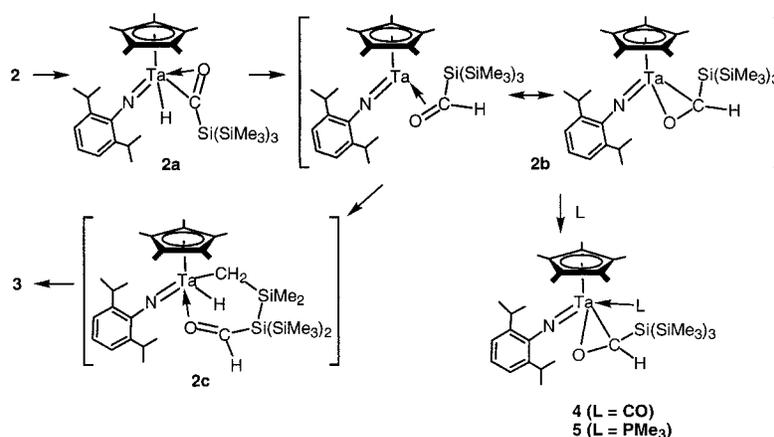
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(7) Typical values for η<sup>2</sup>-silaacyl complexes: ν<sub>CO</sub> = ca. 1500 cm<sup>-1</sup>; δ(<sup>13</sup>COSi) = ca. 390 ppm. For example, see: (a) Tilley, T. D. *J. Am. Chem. Soc.* **1985**, *107*, 4084. (b) Campion, B. K.; Falk, J.; Tilley, T. D. *J. Am. Chem. Soc.* **1987**, *109*, 2049. (c) Elsner, F. H.; Tilley, T. D.; Rheingold, A. L.; Geib, S. J. *J. Organomet. Chem.* **1988**, *358*, 169. (d) Arnold, J.; Tilley, T. D.; Rheingold, A. L.; Geib, S. J.; Arif, A. M. *J. Am. Chem. Soc.* **1989**, *111*, 149. (e) Campion, B. K.; Heyn, R. H.; Tilley, T. D. *J. Am. Chem. Soc.* **1990**, *112*, 2011.

## Scheme 1



## Scheme 2



( $\nu_{\text{CO}} = 1797 \text{ cm}^{-1}$ ), which exhibits a  $\text{Si}\cdots\text{C}(\text{carbonyl})$  distance of only 2.35 Å.<sup>11b</sup> This interaction in the latter complex leads to a significant  $^2J_{\text{SiC}}$  coupling constant of 24 Hz, which is somewhat larger than that observed for **2**-<sup>13</sup>C (15 Hz).

On standing at room temperature, pentane solutions of **2** quantitatively transform within 24 h to a new compound **3**, as indicated by a color change to light yellow (Scheme 1). Complex **3**, isolated in 96% yield, was identified as a six-membered tantalacycle with the former carbonyl and silyl ligands incorporated into the ring. The molecular structure features a chairlike geometry for the metallacycle, with all bonding parameters in the expected ranges (Scheme 1). Transformation of the deuteride **2-d** to **3-d** occurs with selective incorporation of deuterium into the axial position of the methylene group derived from the carbonyl ligand (from NOE experiments). A possible mechanism for the formation of **3** is given in Scheme 2 (intermediates were not observed by monitoring the reaction at  $-40 \text{ }^\circ\text{C}$ ).

Evidence in support of part of the mechanism of Scheme 2 was obtained by trapping of the silylaldehyde intermediate **2b**. In the presence of an excess of CO (1 atm), the decomposition of **2** led to only a small amount of **3**, and the red adduct  $\text{Cp}^*(\text{ArN}=\text{Ta}(\text{CO})\{\eta^2\text{-OCH}[\text{Si}(\text{SiMe}_3)_3]\})$  (**4**) was isolated in 58% yield. On the basis of NMR data for the silylaldehyde ligand ( $\delta(\text{CHSi}) = 2.15 \text{ ppm}$ ,  $^2J_{\text{Si,H}} = 9.2 \text{ Hz}$ ;  $\delta(^{13}\text{CHSi}) = 77.3 \text{ ppm}$ ), **4** is best described as having metallacycle character. Furthermore, the high value of  $2006 \text{ cm}^{-1}$  for the CO infrared stretching frequency ( $1964 \text{ cm}^{-1}$  for **4**-<sup>13</sup>C<sub>2</sub>) appears to reflect the presence of a Ta(V) (rather than a Ta(III)) center. Similarly, the adduct  $\text{Cp}^*(\text{ArN}=\text{Ta}(\text{PMe}_3)\{\eta^2\text{-OCH}[\text{Si}(\text{SiMe}_3)_3]\})$  (**5**) formed as the main product (61%, by NMR spectroscopy) when the decomposition occurred in the presence of 1 equiv of PMe<sub>3</sub>. Hydrolyses of **4** and **5** produced

the alcohol  $\text{HOCH}_2\text{Si}(\text{SiMe}_3)_3$ <sup>16</sup> as the main product (>90%, by NMR spectroscopy and GC–mass spectrometry).

The results described here represent new and unexpected transformations in the carbonylation chemistry of d<sup>0</sup> metal silyl derivatives, which typically react rapidly with CO to give silacyl insertion products (including, for example  $\text{Cp}^*\text{Cl}_3\text{TaSiMe}_3$ <sup>7d</sup>). The silyl hydride **1** reacts differently in that it initially forms a stable carbonyl complex, which is best described as a Ta(V) complex which gains stability via a back-bonding interaction involving donation of electron density from the Ta–Si  $\sigma$ -bond to the  $\pi^*$  orbital of the carbonyl. Under relatively mild conditions, this species undergoes a series of migrations to produce **3**, which contains a completely reduced C–O bond. The latter result suggests new possibilities for the use of carbon monoxide as a synthon in hydrosilation chemistry, and these are currently under investigation.

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**Supporting Information Available:** Detailed experimental procedures for the preparation and spectroscopic characterization of complexes **1**–**5**, tables of crystal, data collection, and refinement parameters, atomic coordinates, bond distances, bond angles, and anisotropic displacement parameters for **2** and **3** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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