Preparation and characterization of titanocene silyl hydrides [Cp$_2$Ti(μ-HSiH$_2$)]$_2$ and [Cp$_2$Ti(μ-HSiH$_2$)(μ-H)TiCp$_2$]

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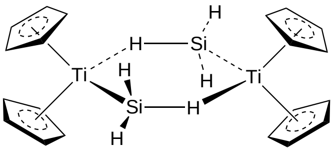
The structure of a complex previously assigned as [Cp$_2$Ti(μ-SiH$_2$)]$_2$ is shown to be [Cp$_2$Ti(μ-H–SiH$_2$)]$_2$.

Titanocene(IV) complexes containing a Ti–Si bond are extemely rare. To our knowledge, only three examples have been reported with convincing structural characterization.[1–3] We have previously reported the titanocene(III) hydrosilyl complexes [Cp$_2$Ti(μ-HSiHPh)]$_2$ **1** and [Cp$_2$Ti(μ-HSiHPh)(μ-H)TiCp$_2$] **2**, which are derived from intermediates in the polymerization of phenylsilane catalyzed by dimethyltitanocene (DMT).[4] The individual steps involved in the latter reaction are very complex and the mechanisms are still poorly understood.[5] Our experience in determining the structures of **1** and **2** sensitized us to the ease with which hydrogen atoms can be missed in the X-ray structures of such compounds. This in turn led us to consider the structure of [Cp$_2$Ti(μ-SiH$_2$)]$_2$ **3**, reported two decades ago by Hencken and Weiss.[3]

Our interest in this question was rekindled recently by the isolation of the complex [Cp$_2$Ti(μ-HSiH$_2$)]$_2$ **4**, from the reaction of dimethyltitanocene (DMT) with trialkoxysilanes. In this reaction, the DMT catalyses the extremely rapid redistribution of (RO)$_3$SiH, according to eqn. (1).[6] The SiH$_4$ produced then reacts further to give the titanocene(III) silyl complex.

$$4\ (\mathrm{RO})_3\mathrm{SiH} \rightarrow \mathrm{SiH_4} + 3\ (\mathrm{RO})_4\mathrm{Si} \qquad (1)$$

The reaction of DMT with excess, chlorine-free,† (MeO)$_3$SiH or (EtO)$_3$SiH in dry hexane under argon gives **4** in good yield as air- and moisture-sensitive dark blue crystals.‡ Solutions of **4** in benzene, or toluene, under an argon atmosphere at room temperature are stable for several hours, decomposing slowly to a new compound [Cp$_2$Ti(μ-HSiH$_2$)(μ-H)TiCp$_2$] **5**.§ This decompostition was evident from changes in the ^{1}H NMR spectrum of the solution and from a color change from greenish blue to dark yellowish green. Essentially the same result was obtained by the direct reaction of SiH$_4$ with Cp$_2$TiMe$_2$.



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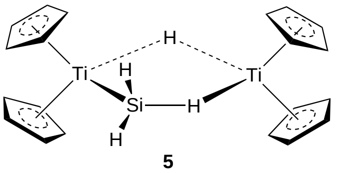

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Complex **4** was readily characterized by comparison of its ^{1}H NMR spectrum to that of the known complex **1**.[4] At both room temperature and low temperature, the ^{1}H NMR spectrum of **4** in [^{2}H$_8$]toluene shows a single resonance at δ 4.58 for all four Cp rings, owing to a plane of symmetry containing the two titanium atoms, two silicon atoms and two hydrides in the six-membered ring, and a C_2 axis perpendicular to and through the center of the six-membered ring. The bridging hydride resonance appears as a triplet at δ −10.07, owing to coupling with the terminal SiH$_2$ protons. A doublet at δ 4.69 is assigned to the terminal SiH$_2$ protons. Similarly, **5** was characterized by comparison of its ^{1}H NMR spectrum to that of **2**.[4] At ambient temperature, **5** gives a broad single resonance at δ 5.50 due to the four Cp ligands. However, upon lowering the temperature to −20 °C the resonance splits into two equal intensity peaks, and a high-field hydride resonance appears at δ −13.22 assignable to the Si–H–Ti proton.[4] The coalescence temperature for the Cp resonances is at *ca.* 0 °C. A second high-field hydride was observed at δ −19.32 at −60 °C assignable to the Ti–H–Ti proton.[4] Integration of this spectrum indicates the formula [Cp$_2$Ti(μ-HSiH$_2$)(μ-H)TiCp$_2$].

^{1}H NMR measurements on the product prepared by reaction of [Cp$_2$TiCl$_2$] with SiH$_3$K, carefully following the published procedure,[3] gave the same ^{1}H NMR specrum as **4**, indicating that the product of this reaction is not the SiH$_2$-bridged titanocene(IV) dimer **3**, originally proposed, but the titanocene(III) silyl dimer **4**. This result is consistent with the reported single crystal X-ray structure analysis.[3] The reported R value was high (*ca.* 9%) and disordering of the Si–H bridges would make detection of the third hydrogen unlikely.¶

We are continuing attempts to make higher quality crystals of **4** and **5** for X-ray diffraction to unequivocally assign their solid state structures. Further investigation of the chemistry of **4** and **5** is also under way.

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Footnotes and References

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† Most commercial samples of alkoxysilanes are adulterated with chlorosilanes to inhibit SiH$_4$ formation.

‡ ^{1}H NMR (200 MHz) data for **4** in [^{2}H$_8$]toluene: δ 4.69 [d, 4 H, ^2J(HH) 5.4 Hz, SiH$_2$], 4.58 (s, 20 H, Cp), −10.07 [t, 2 H, ^2J(HH) 5.4 Hz, SiHTi].

§ ^{1}H NMR (270 MHz) data for **5** in [^{2}H$_8$]toluene at 20 °C: δ 5.80 (br, 2 H, SiH$_2$), 5.50 (s, br, 20 H, Cp); at −20 °C, δ 5.65 (br, 1 H, SiH), 5.58 (s, br, 10 H, Cp), 5.41 (br, 1 H, SiH), 5.36 (s, br, 10 H, Cp), −13.22 (m, 1 H, SiHTi); at −60 °C, δ 5.64 (br, 1 H, SiH), 5.56 (s, br, 10 H, Cp), 5.38 (br, 1 H, SiH), 5.29 (s, 10 H, Cp) −13.3 (m, 1 H, SiHTi), −19.32 (m, 1 H, TiHTi).

¶ A problem with the reported structure is the extreme shortness of the Ti–Si bond (*ca.* 2.1 Å) compared to other values (ref. 2 and 4; *ca.* 2.5–2.7 Å) and the anomalously high temperature factor for the Si. Both of these problems disappear if it is assumed that the bridging group is OH, or O. The fact that the reported elemental analysis corresponds well to a product with an SiH$_2$ (or SiH$_3$) bridge, together with our NMR observations showing the presence of the SIH$_3$ bridged dimers in solution, suggests that the authors may have been unlucky in choosing a crystal of oxidized material.

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