Synthesis and structural characterization of $Cp_2Ti(SiH_3)(PMe_3)$

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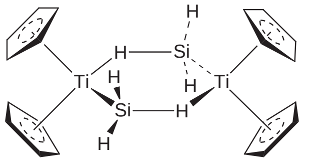
The title compound, the first example of a structurally fully characterized, unsubstituted silyl complex of a group 4 element, has been synthesized and showed unusual thermal stability compared to its analog $Cp_2Ti(SiH_2Me)(PMe_3)$.

Very few reports of reactions of SiH_4 with transition metal compounds have appeared, presumably because of the hazards associated with its use.[1]‡ There are also very few examples of structurally well characterised transition metal complexes with SiH_3 ligands.[2] We recently reported the synthesis of compounds **1** and **2** by reaction of SiH_4 with Cp_2TiMe_2.[3] This reaction can be carried out either with SiH_4 from a cylinder, or with SiH_4 generated *in situ* by catalytic redistribution of $SiH(EtO)_3$. The latter reaction is a convenient procedure for the safe generation of small amounts of SiH_4.[3] Although the structures of **1** and **2** were confidently assigned on the basis of their NMR spectra, we have not been able to obtain either of them in the form of crystals suitable for structure determination by X-ray diffraction. We now report the preparation and structure determination of the related phosphine complex, $Cp_2Ti(SiH_3)(PMe_3)$ **3**, an analog of the organosilyl complexes reported earlier,[4,5] and the first structurally fully characterized, unsubstituted silyl complex of a group 4 metal.



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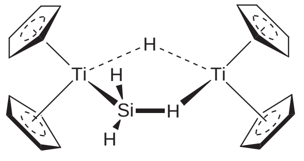

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Reaction of Cp_2TiMe_2 with SiH_4 in the presence of PMe_3 in diethyl ether–toluene solution proceeds smoothly to give **3** in 76% yield as square purple plates. Solutions of **3** in toluene or benzene are relatively thermally stable and so could be fully characterized both in solution and in solid state. The structure of **3**, together with some bond parameters, is shown in Fig. 1.§ Of the bond parameters, only the Ti–Si bond length falls outside the range previously determined for $Cp_2Ti(SiHRR')(PMe_3)$ complexes (R = H, R′ = Ph **4**; R = Ph, R′ = Ph **5** or Me **6**).[4] The relevant values are: 2.594(2) **3**, 2.650(1) **4**, 2.652(1) **5** and 2.646(2) Å **6**, indicative of a stronger Ti–Si bond in **3**. The Ti–Si bond distance in **3** is essentially identical to those observed in the phenylsilyl analogue of **1** and in $(Bu^tCH_2)_3TiSi(SiMe_3)_3$.¶ The perspective of **3** shown in Fig. 1 is chosen to show the perfect *gauche* arrangements of the SiH_3 and PMe_3 ligands with respect to the Cp_2Ti unit and the mirror plane symmetry of the molecule. These features are not exhibited by the other organosilyl complexes where the local symmetry of the silyl ligand is lower than C_{3v}.

The spectroscopic data are consistent with the structure revealed by the X-ray analysis. The ^1H NMR spectrum of **1** is consistent with it being a paramagnetic species since only broad resonances were observed and no resonance was observed in the $^{31}P\{^1H\}$ spectrum. Solutions of **3** in toluene give the characteristic EPR spectrum shown in Fig. 2. The doublet of quartets (g = 1.9956) is accounted for by the coupling of the single unpaired electron of Ti^{III} to a single ^{31}P nucleus (a_P = 28.6 G) and to the three Si–H protons (a_H = 4.3 G). Satellites due to coupling to the Ti isotopes [I = 7/2, ^{49}Ti (5.5%); I = 5/2, ^{47}Ti (7.75%)] with a_{Ti} = 7.8 G are also observable. The values for a_P and a_{Ti} are in, or very close to, the ranges observed for **4**, **5** and **6** (28.8–29.9 G and 7.7 to 8.7 G respectively), as is the g value (1.9944–1.9976).[4,5] The value for a_H is somewhat larger than the values for the organosilyl complexes (2.6–3.2 G) which may be a result of the slightly shorter Ti–Si bond in **3**.[4,5]

Solutions of **3** in toluene are stable for several days at room temperature in an argon atmosphere. This stability is unusual and unexpected, given the fact that the compound is a primary silane.[4–6] The closest analog $Cp_2Ti(SiH_2Me)(PMe_3)$ **7**, synthesized from the reaction of Cp_2TiMe_2 and SiH_3Me, generated *in situ* by catalytic redistribution of $SiHMe(EtO)_2$,[3] in the presence of PMe_3 in hexane solution, was stable only for several hours and decomposed to the titanocene(III) hydride **8** and the titanocene(III) silyl compound **9**, as shown in Scheme 1.‖ Similar dehydrocoupling reactions were also observed for other analogous $Cp_2Ti(SiHRR')(PMe_3)$ compounds.[5] We attribute the greater stability of **3** to stronger Ti–Si and Ti–P bonds and a resulting high formation constant for the phosphine complex.

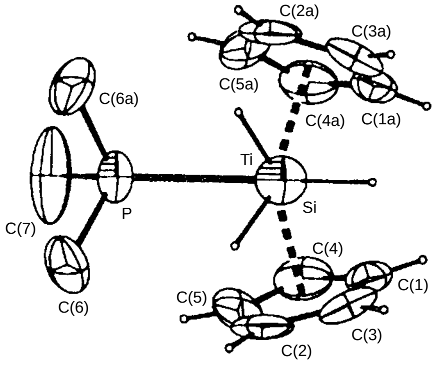


Fig. 1 A view of the structure of **3** down the Si–Ti bond (30% probability ellipsoids). Selected bond lengths (Å) and bond angles (°): Ti–P 2.559(2), Ti–Si 2.594(2), Si–H(av.) 1.53(7); P–Ti–Si 83.91(6), Cp(cent)–Ti = 2.031(3), Cp(cent)–Ti–Cp(cent) 134.2(4).

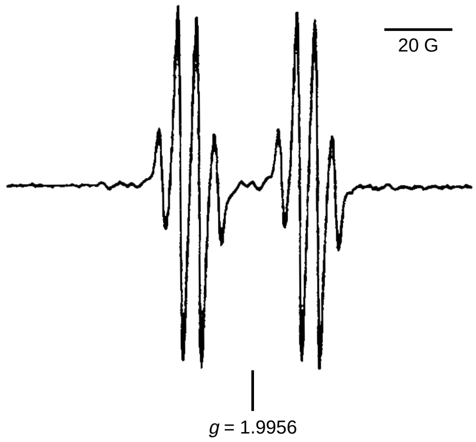
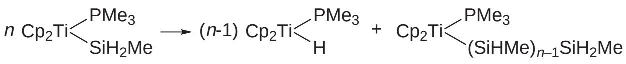


Fig. 2 EPR spectrum of **3** in toluene at room temperature



7 **8** **9**

Scheme 1

The consequent suppression of phosphine dissociation to give the coordinatively unsaturated intermediate necessary for reaction of the titanium with Si–H bonds prevents the hydrogen transfer reaction depicted in Scheme 1. In the absence of PMe_3, Cp_2TiMe_2 catalyses the rapid dehydrocoupling of SiH_4 to an insoluble, pyrophoric polymer.

Studies of reactions of SiH_4 with other group 4 compounds are in progress.

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Notes and References

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‡ SiH_4 spontaneously explodes and burns immediately on exposure to air.

§ *Crystal data*: **3**: $C_{13}H_{22}PSiTi$, M = 285.26, orthorhombic, space group *Pcmn*, a = 8.661(4), b = 12.516(4), c = 14.330(4) Å, V = 1553(1) Å^3, Z = 4, Z' = $\frac{1}{2}$, D_c = 1.220 g cm^{-1}, $F(000)$ = 604, crystal size: 0.78 × 0.60 × 0.26 mm. Data were collected at 220 K on a Enraf-Nonius CAD4 diffractometer using Cu-Kα radiation (λ = 1.540 56 Å) in the ω–2θ scan mode. A total of 22400 reflections were measured in the range $5.96° < \theta < 69.83°$ giving 1553 unique reflections, of which 1500 with $I > 2\sigma(I)$ were considered observed. Analytical absorption correction (μ = 62.37 cm^{-1}; range 0.03–0.29). The structure was solved by direct method using SHELXS96 and refined by full-matrix least squares on F^2. Hydrogens on Si were located on the difference map and refined successfully. R = 0.062 [for $I > 2\sigma(I)$] and wR_2 = 0.1703 (for all data). CCDC 182/828.

¶ Ti–Si bond distances in $[Cp_2Ti(\mu\text{-}HSiHPh)]_2$ and in $(Bu^tCH_2)_3Ti\text{-}Si(SiMe_3)_3$ are 2.594(2) Å (average) and 2.594(7) Å respectively.[6]

‖ *EPR data in toluene*: **7**: g = 1.9941, a_{Ti} = 7.0 G, a_P = 28.97 G, a_H = 3.35 G. **8**: g = 1.9929, a_{Ti} = 6.8 G, a_P = 28.2 G, a_H = 10.6 G. **9**: g = 1.9933, a_P = 28.74 G, a_H = 3.37 G. Bercaw and Brintzinger also reported the generation of a titanocene hydride phosphine compound $Cp_2TiH(PPh_3)$ which gave a similar EPR spectrum to **8**.[7]

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