Preparation and X-ray Structure of $Cp_2Ti(Ph_2SiH_2)(PMe_3)$

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Received August 1, 1994

Transition metal silyl hydride complexes have been proposed as intermediates in the catalytic hydrosilylation of olefins[1] and the polymerization of organosilanes.[2,4,6] Several of these complexes have been prepared and studied in detail.[3] Harrod and co-workers have isolated and characterized several dinuclear[4] and mononuclear[5] titanocene complexes from the reaction of dimethyltitanocene and phenylsilane (Figure 1). The compound $Cp_2Ti(\mu\text{-}Si(H)_2Ph)(\mu\text{-}H)TiCp_2$, **2**, is of particular interest and can be viewed as being composed of a titanocene hydrido silyl complex and titanocene. It has been suggested that the titanocene silyl hydride monomer is an active participant in silane polymerization.[6]

The bonding in transition metal silyl hydride complexes has classically been described by either of two limiting structures, **A** or **C** (Figure 2). However, there are many complexes that cannot be accurately described by either **A** or **C** and are thus best represented by an intermediate structure such as **B**.[3a] We have previously reported the synthesis of some group 4 silyl hyrdride complexes, $Cp_2M(H)(SiR_3)(PMe_3)$, M = Zr, Hf.[7] The physical data for these complexes indicate that they are true metal silyl hydride complexes (structure **A**). In this communication we report the preparation and characterization of a novel titanocene complex, $Cp_2Ti(Ph_2SiH_2)(PMe_3)$, which, in our view, has a hybrid structure like **B**.

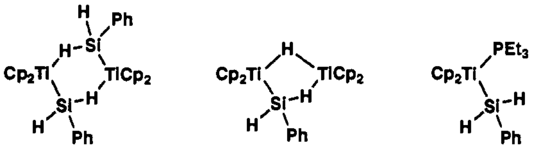


Figure 1. Representative titanium silyl hydride complexes.

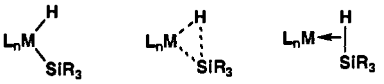
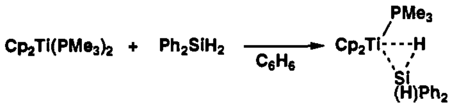


Figure 2. Bonding in transition metal silyl hydride complexes.

Treatment of a benzene solution of $Cp_2Ti(PMe_3)_2$[8] with diphenylsilane followed by addition of cold hexanes caused precipitation of an air and moisture sensitive yellow solid identified as $Cp_2Ti(Ph_2SiH_2)(PMe_3)$, **4** (eq 1). Compound **4** was obtained in 63% isolated yield after washing with hexane. Complex **4** is unstable in solution and decomposes to the dinuclear species $\{(\mu\text{-}(\eta^1{:}\eta^5\text{-}C_5H_4))(Cp)Ti(PMe_3)\}_2$[9] and Ph_2SiH_2. However, in the presence of excess Ph_2SiH_2, benzene solutions of **4** are stable for several days.



$$Cp_2Ti(PMe_3)_2 + Ph_2SiH_2 \xrightarrow[C_6H_6]{} Cp_2Ti(PMe_3)(H)(Si(H)Ph_2)$$

4

eq. 1

The ^1H NMR spectrum (300 MHz, C_6D_6) of **4** at room temperature exhibits a broad resonance at 6.36 ppm assigned to the silicon hydride and a broad doublet at –3.93 ppm assigned to the titanium hydride. At –55 °C in THF-d_8 (500 MHz) these resonances are completely resolved; the Si–H resonance is located at 6.03 ppm as a doublet of doublets (J_{HH} = 11 Hz, J_{HP} = 4 Hz) while the Ti–H signal is observed at –4.14 ppm, also as a doublet of doublets (J_{HH} = 11 Hz, J_{HP} = 68 Hz). The Ti–H resonance is 3.87 ppm upfield of that for the corresponding zirconium complex,[7] reflecting the more electron rich character of the metal in **4**. In comparison, the Ti–H resonance for the recently reported titanium(IV) hydride, $(^tBu_3SiO)_2(^tBu_3SiNH)TiH$, is at 8.62 ppm.[10]

The ^{29}Si NMR spectrum of complex **4** (99 MHz, THF-d_8, –50 °C) shows a doublet of doublets indicating coupling of the silicon of two hydrogens[11] (J_{SiH1} = 28 Hz, J_{SiH2} = 161 Hz). The large silicon–hydrogen coupling constant of 161 Hz is consistent with those found in normal silanes (150–200 Hz)[3a] while the smaller value of 28 Hz is slightly larger than values typically observed for silyl–hydride complexes in which there is no interaction between Si and H ($J_{SiH} < 20$ Hz).[3a] This suggests the possibility of a three-center interaction between the titanium hydride, the titanium, and the silicon atom. Consistent with this hypothesis is the large H–H coupling constant of 11 Hz. For the corresponding zirconium analog, $Cp_2Zr(H)(SiPh_2H)(PMe_3)$,[1d,7] in which a three-center interaction is not present, the H–H coupling constant is 3 Hz. The IR spectrum displays a weak Ti–H stretch at 1508 cm^{-1} (ν(Ti–D) = 1042 cm^{-1}). This value is slightly lower than that reported for the only other known titanocene(IV) hydride, $Cp_2{}^*TiH_2$ (ν(Ti–H) = 1560 cm^{-1})[12] and slightly higher than the value reported for the titanocene(III) hydride $[Cp^*\{C_5Me_4CH_2(C_5H_3N)\}TiH]$ (ν(Ti–H) = 1475 cm^{-1}).[13] The IR stretch for $(^tBu_3SiO)_2(^tBu_3SiNH)TiH$ is observed at 1645 cm^{-1}.[10]

The silane moiety in complex **4** is only weakly bound and is readily displaced by dinitrogen according to eq 2, leading to

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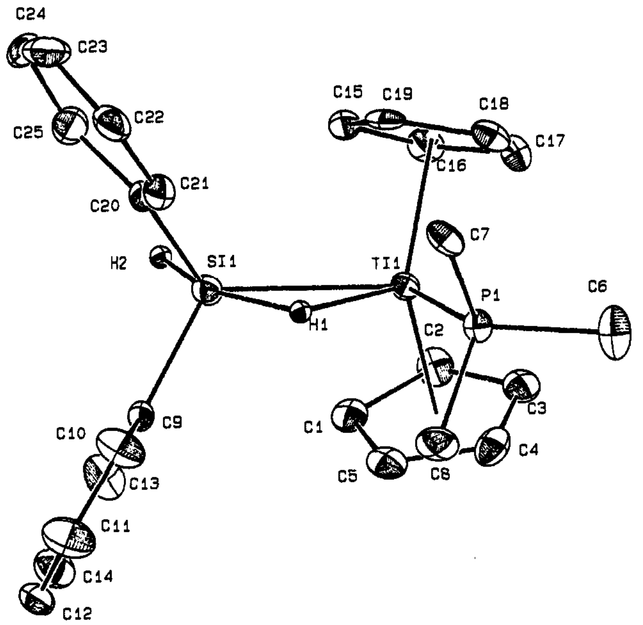
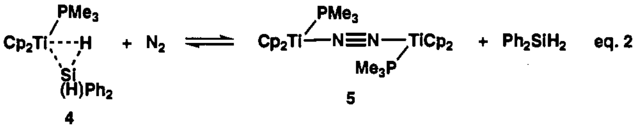


Figure 3. ORTEP drawing of $Cp_2Ti(Ph_2SiH_2)(PMe_3)$, **4**.

Table 1. Some Selected Bond Distances and Angles for $Cp_2Ti(Ph_2SiH_2)(PMe_3)$, **4**

bond distances, Å		bond angles, deg	
Ti–H_1	1.81(5)	Si–Ti–H_1	44(2)
Ti–Si	2.597(2)	Si–Ti–H_2	112(2)
Ti–P	2.550(2)	Si–Ti–P	111.78(7)
Si–H_1	1.69(5)	H_1–Si–H_2	156(2)
Si–H_2	1.56(5)	C_{20}–Si–H_1	92(2)
		C_{20}–Si–H_2	100(2)
		C_9–Si–H_1	94(2)
		C_9–Si–H_2	103(2)
		C_9–Si–C_{20}	105.4(3)
		Ti–Si–C_9	118.2(2)

formation of the previously reported dinitrogen complex **5**.[14] Under vacuum, nitrogen can be removed to regenerate **4**.



In order to achieve a more complete bonding picture, complex **4** was examined by X-ray crystallography. Importantly, the hydrogen atoms were located and anisotropically refined. The ORTEP drawing of complex **4** is shown in Figure 3, and selected bond distances and angles are listed in Table 1.

The Ti–H bond of 1.81 Å is 0.11 Å longer than that of a terminal Ti(III)–H bond in $[Cp^*\{C_5Me_4CH_2(C_5H_3N)\}TiH]$ (Ti–H = 1.70 Å)[13] but well within the normal range of 1.66–1.97 Å found for bridging titanium hydrides.[4,15] The Ti–P distance (2.550 Å) is in good agreement with that of the dinitrogen complex **5** (2.539 Å)[14] and 0.1 Å shorter than that of complex **3** (Figure 1, Ti–P = 2.651 Å)[5a] (the longer bond in this complex may be due to greater steric crowding of the more bulky PEt_3 ligand). The Ti–Si distance of 2.597 Å is similar to that of other titanocene silyl derivatives, which are typically between 2.60 and 2.63 Å.[4,5]

A most interesting feature of the structure is the geometry of the silicon atom. This geometry is best described as a distorted trigonal bipyramid with the two hydrogen atoms occupying the apical positions and Ti, C_{20}, and C_9 defining the equatorial plane. The silicon atom is displaced from the equatorial plane toward H_2 with C_{20}–Si–H_2 and C_9–Si–H_2 being 100° and 103°, respectively. The Si–H_2 distance of 1.56 Å is 0.09 Å longer than the terminal Si–H distance in the related complex **2** (Figure 1, Si–H = 1.47 Å),[4] likely due to the trans influence of the H_1 ligand. The Si–H_1 distance of 1.69 Å is substantially (15%) longer than the typical Si–H distance (1.47 Å) but still short enough for an interaction with the silicon atom.[3a]

The Si–Ti–H_1 angle of 44° is 10° smaller than that of the related zirconium complex $Cp_2Zr(H)(SiPh_3)(PMe_3)$[7] while the Si–Ti–P angle of 111.78° is roughly the same as that found in $Cp_2Zr(H)(SiPh_3)(PMe_3)$ (Si–Zr–P = 112.68°). The similarity of the Si–M–P angle in these two complexes indicates that the smaller Si–Ti–H_1 angle is not due to steric crowding resulting from the smaller size of the titanium atom. The smaller Si–Ti–H_1 angle thus reflects a bonding interaction between silicon and H_1.

Since complexes similar to **4** have been implicated in the catalytic polymerization of organosilanes,[6] we investigated the use of complex **4** as a catalyst for this reaction. When a solution of **4** is treated with excess Ph_2SiH_2, no reaction is observed. However, in the presence of norbornene, complex **4** catalytically and quantitatively converts Ph_2SiH_2 to the dimer, $[Ph_2Si(H)]_2$. This reaction is complete within 1 h at 45 °C, and no induction period is observed. Furthermore, no olefin hydrosilylation[1d,6] is observed.

In summary, we have prepared and characterized the first adduct of $Cp_2Ti(PMe_3)$ and diphenylsilane. Both the spectroscopic and structural data suggest that there is a three-center interaction between the silicon, the titanium, and the hydride ligand. The bonding in complex **4** is best described by the intermediate structure B (Figure 2). While not totally unambiguous, the low Si–H_1 coupling constant as well as the structural data (short Ti–Si distance and long Si–H_1 distance) indicate that **4** has more character of a metal silyl hydride complex (structure A) than of a metal silane complex (structure C).

Acknowledgment. This work was supported, in part, by the Office of Naval Research, the National Science Foundation, the National Institutes of Health, W. R. Grace, and the donors of the Petroleum Research Fund, administered by the American Chemical Society, to whom we are grateful. E.S. thanks the Ford Foundation for a fellowship. P.P. acknowledges the Spanish Ministry of Education and Science for a fellowship. C.A.W. acknowledges support as an ACS Organic Division Predoctoral Fellow (sponsored by the Monsanto Company). S.L.B. acknowledges additional support as an Alfred P. Sloan Foundation Fellow and a Camille & Henry Dreyfus Foundation Teacher Scholar.

Supplementary Material Available: Detailed experimental procedures for the preparation and spectroscopic characterization of complex **4**, along with tables of bound distances, bond angles, and final positional and thermal parameters for **4** (31 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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