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Synthesis and Structure of Bis(phenyltetramethylcyclopentadienyl)titanium(III) Hydride: The First Monomeric Bis(cyclopentadienyl)titanium(III) Hydride

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Summary: The first structurally characterized monomeric bis(cyclopentadienyl)titanium(III) hydride, $(C_5PhMe_4)_2TiH$ (**4**), was synthesized by hydrogenolysis of $(C_5PhMe_4)_2TiMe$ (**5**). Hydride **4** was found to be a monomeric bent sandwich by X-ray diffraction methods, and the pentamethylcyclopentadienyl analogue $(C_5Me_5)_2TiH$ (**3**) is concluded to possess a similar molecular structure by comparison between the spectroscopic and reactivity data for **3** and **4**.

Titanocene hydrides are intriguing compounds, often postulated as intermediates in catalytic reactions.^{1,2} They also have relevance in olefin polymerization as the products of chain-terminating *b*-hydride transfer reactions.³ Furthermore "titanocene" was proposed to be a dimeric fulvalene-bridged titanium complex with bridging hydrides $[m\text{-}h^5\text{-}h^5\text{-}C_{10}H_8][(\eta^5\text{-}C_5H_5)Ti(m\text{-}H)]_2$ (**1**),⁴ which was recently confirmed by an X-ray structure determination.⁵ Bercaw and Brintzinger were the first to isolate a titanocene(III) hydride, $[(C_5H_5)_2TiH]_2$ (**2**), despite its marginal stability.⁶ This structure was, however, never confirmed by X-ray crystallography.

During an investigation of $(C_5Me_5)_2TiR$ (*R* = alkyl, aryl) compounds at our laboratory,^{21,7} $(C_5Me_5)_2TiH$ (**3**) was synthesized by hydrogenolysis of $(C_5Me_5)_2TiR$,⁸

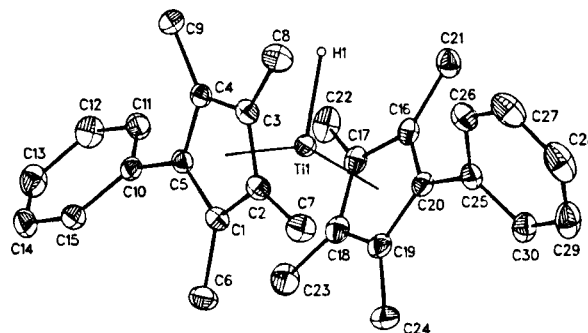


Figure 1. ORTEP drawing of $(C_5PhMe_4)_2TiH$ (**4**) with 50% probability ellipsoids. Hydrogens bonded to carbon are omitted for clarity.

extensively characterized, and, in contrast with **2**, formulated as a monomeric titanocene(III) hydride. X-ray crystal structure determinations were hampered by poor crystal quality. An ordinary bent-sandwich geometry, in analogy with $(C_5Me_5)_2TiR$, seems most likely for **3**, but a fulvene-dihydride structure $((C_5Me_5)(\eta^6\text{-}C_5Me_4CH_2)TiH_2)$ cannot be ruled out.⁹ To lower the symmetry of the ligand environment, 1-phenyl-2,3,4,5-tetramethylcyclopentadienyl¹⁰ was employed, resulting in the synthesis and X-ray structure determination of bis(1-phenyl-2,3,4,5-tetramethylcyclopentadienyl)titanium(III) hydride. $(C_5PhMe_4)_2TiH$ (**4**) is the first structurally characterized monomeric bis(cyclopentadienyl)titanium(III) hydride.

A red-brown solution of **4** is formed quantitatively within minutes after exposing a green pentane solution of $(C_5PhMe_4)_2TiMe$ (**5**) to 1 atm of H_2 at room temperature.¹¹ Beautiful red-brown crystals of **4** separate after cooling to $-20^\circ C$. A single-crystal X-ray diffraction

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(9) When **3** is reacted with 1 atm of D_2 at room temperature, not only the deuteride $(C_5Me_5)_2TiD$ is formed but H/D scrambling into the methyl groups of the Cp^* rings also occurs.^{8a} This facile deuteration of the Cp^* rings distinguishes **3** from analogous $(C_5Me_5)_2MH$ compounds (*M* = Sc, Y, Lu), where the metal deuteride can be prepared without simultaneous H/D scrambling of the Cp^* protons. (a) Thompson, M. E.; Bercaw, J. E. *Pure Appl. Chem.* **1984**, *56*, 1-11. (b) Den Haan, K. H.; Wielstra, Y.; Teuben, J. H. *Organometallics* **1987**, *6*, 2053-2060. (c) Booy, M.; Deelman, B.-J.; Duchateau, R.; Postma, D. S.; Meetsma, A.; Teuben, J. H. *Organometallics* **1993**, *12*, 3531-3540. (d) Watson, P. L. *J. Chem. Soc., Chem. Commun.* **1983**, 276-277.

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analysis determined the molecular structure shown in Figure 1.^{12a}

4 is a monomeric bent sandwich, in which the C₅-PhMe₄ ligands behave as regular cyclopentadienyl ligands.^{12b} The phenyl rings are pointing away from each other, and their planes are at angles of 49.61(9) and 53.66(9)° with the respective Cp planes. The Cp_{centroid}-Ti-Cp_{centroid} angle is very large (150.84°), which apparently is allowed by the fact that the hydride is very small. The Ti-H distance (1.768(15) Å) is comparable to other monomeric ((C₅Me₅)(C₅Me₄-CH₂(C₅H₃MeN))TiH)¹³ (Ti-H = 1.70(4) Å), CpTi(CO)₂-(dmpe)H¹⁴ (1.75(7) Å), CpTi(dmpe)₂H¹⁵ (1.96(6) Å) and dimeric titanium hydrides (**1**⁵ (Ti-H_{av} = 1.73 Å), [**m**-C₅H(CH₃)₂(CH₂)₂[(C₅HMe₄)Ti(**m**-H)]₂ (1.81 Å), *rac*-[(C₂H₄(**h**⁶-tetrahydroindenyl)₂Ti(**m**-H)]₂ (1.90 Å)).

The position of the hydride ligand with respect to the plane defined by Ti and both centers of gravity of the

cyclopentadienyl rings deserves special attention. On the basis of extended Hückel calculations, Lauher and Hoffmann predicted that the Ti-H axis will be about 35° outside this plane in a d¹ Cp₂TiH complex.¹⁸ In a recent paper however, Bercaw and Goddard performed ab initio calculations on Cl₂TiH and concluded that the hydride will reside in the plane through Ti and both ring centroids.¹⁹ In **4** the hydride is found only 2.8(5)° outside the plane, supporting the theoretical considerations of Bercaw and Goddard.

We assume that the pentamethyl analogue **3** has a molecular structure identical to **4**, because of the close resemblance in spectroscopic and experimental data.^{8a} Both **3** and **4** are d¹ 15 electron paramagnetic complexes. The ¹H-NMR spectrum of **4** only shows resonances of the C₅PhMe₄ ligands, which are considerably narrower than for the corresponding methyl compound **5**. No hydride resonance could be detected for either **3** or **4**.²⁰ In the IR spectrum a band at 1505 cm⁻¹ is assigned to *n*(Ti-H), which shifts to 1092 cm⁻¹ after deuteration of **4** via reaction with 1 atm D₂. Simultaneously, H/D scrambling of the methyl and the *o*-phenyl protons of the C₅PhMe₄ ligands is observed. The UV/vis spectrum of **4** shows an absorption at 480 nm, comparable to an absorption at 483 nm for **3**, resulting in a red-brown color for both compounds.²¹ The ESR spectrum of a pentane solution of **4** shows a singlet (*g* = 1.976) with hyperfine coupling to Ti isotopes (*a*(Ti) = 8.9 G) at both room temperature and -100 °C.²² No coupling with the hydride nuclear spin is observed. In contrast with **4**, the ESR spectrum of a pentane solution of **3** only shows a poorly resolved doublet (*g* = 1.973, *a*(H) = 10 G) at room temperature. Below -100 °C a singlet (*g* = 1.976) is observed. Thermolysis of **3** yields the fulvene complex (C₅Me₅)Ti(**h**⁶-C₅Me₄CH₂).^{21,7b} On thermolysis of **4**, only the methyl protons of the C₅PhMe₄ ligand are activated, producing a mixture of two isomers ((C₅PhMe₄)Ti(C₅-1-CH₂-2-Ph-3,4,5-Me₃) and (C₅PhMe₄)Ti(C₅-1-CH₂-3-Ph-2,4,5-Me₃)). No products due to activation of the phenyl protons of the C₅PhMe₄ ligand were observed. A convenient way to characterize paramagnetic Ti(III) complexes consists of oxidation with PbCl₂ to the corresponding diamagnetic Ti(IV) chloride compounds.²³ As expected, oxidation of **4** with PbCl₂ yields (C₅-PhMe₄)₂Ti(H)Cl, while **3** gives (C₅Me₅)₂Ti(H)Cl. Both **3** and **4** catalyze the hydrogenation of 1-hexene to hexane and the dimerization of phenylacetylene.

It was reported that **3** is not capable of ethene polymerization.^{7b} Instead, only one insertion of ethene

(11) Experimental details are as follows: **General comments.** All manipulations of air-sensitive compounds were carried out under N₂, using standard Schlenk-line and glovebox techniques. 1-Phenyl-2,3,4,5-tetramethylcyclopentadiene was prepared according to published procedures.^{10a} A small portion of all new paramagnetic Ti(III) compounds was oxidized with PbCl₂²³ to the corresponding diamagnetic Ti(IV) compounds for facile characterization by ¹H NMR. **Synthesis of (C₅PhMe₄)₂TiCl.** A 3.59 g amount of TiCl₃·3THF (9.70 mmol) was added to a suspension of 4.06 g of LiC₅PhMe₄ (20.0 mmol) in 150 mL of THF and stirred at RT (room temperature) for 10 min. The dark green solution was heated under reflux for 48 h, yielding a blue-green solution. The solvent was evaporated, and the residue was extracted with toluene. After concentration and cooling to -80 °C, a dark blue crystalline solid was obtained. Yield: 3.29 g (71%). ¹H NMR (C₆D₆): **d** -4.6 (s, 12H, C₅PhMe₂Me₂, WHM = 1320 Hz), 2.0 (m, 2H, *p*-Ph), 5.21 (s, 4H, *o*-Ph, 100 Hz), 7.89 (s, 4H, *m*-Ph, 115 Hz), 12.0 (s, 12H, C₅PhMe₂Me₂, 4430 Hz). Oxidation with PbCl₂ yielded purple-red (C₅-PhMe₄)₂TiCl₂.^{10b} ¹H NMR (CDCl₃): **d** 1.89, 2.05 (s, 12H, C₅PhMe₂Me₂), 7.4 (m, 10H, C₅PhMe₄). **Synthesis of (C₅PhMe₄)₂TiMe (**5**).** A 4.5 mL amount of 1.33 M MeLi in ether (5.99 mmol) was added to a solution of 2.70 g of (C₅PhMe₄)₂TiCl (5.66 mmol) in 75 mL of THF at -30 °C. The reaction mixture was allowed to warm to RT under stirring, yielding a green solution. The solvent was evaporated, and the residue was extracted with toluene. After evaporation of toluene the green product was dissolved in pentane and cooled to -80 °C. Dark green crystals (1.80 g (70%)) were isolated. ¹H NMR (C₆D₆): **d** -20.5 (s, 3H, Ti-Me, WHM = 3390 Hz), 1.0 (m, 4H, *o*-Ph), 1.9 (s, 12H, C₅PhMe₂Me₂, 500 Hz), 6.16 (s, 2H, *p*-Ph, 64 Hz), 8.11 (s, 4H, *m*-Ph, 100 Hz), 20.0 (s, 12H, C₅PhMe₂Me₂, 4525 Hz). Oxidation with PbCl₂ yielded brown-orange (C₅PhMe₄)₂Ti(Me)Cl. ¹H NMR (C₆D₆): **d** 0.60 (s, 3H, Ti-Me), 1.66, 1.83, 1.87, 1.93 (s, 6H, C₅PhMeMe₃), 7.0 (m, 10H, C₅PhMe₄). **Synthesis of (C₅PhMe₄)₂TiH (**4**).** A dark green solution of 1.83 g of **5** (4.01 mmol) in 175 mL of pentane was exposed to 1 atm of H₂, and within 2 min the solution turned brown-red. After cooling of the solution to -80 °C, brown-red crystals were isolated. Yield: 1.47 g (83%). ¹H NMR (C₆D₆): **d** 2.0 (s, 4H, *o*-Ph, WHM = 300 Hz), 4.87 (s, 2H, *p*-Ph, 26 Hz), 6.33 (s, 12H, C₅PhMe₂Me₂, 190 Hz), 7.80 (s, 4H, *m*-Ph, 34 Hz), 25.2 (s, 12H, C₅PhMe₂Me₂, 465 Hz). IR (cm⁻¹): 2955 (s), 2857 (s), 2726 (w), 1599 (m), 1505 (s), 1466 (s), 1377 (s), 1179 (w), 1074 (m), 1026 (m), 916 (m), 760 (s), 704 (s), 588 (m), 455 (m). UV/vis (THF): *I*_{max} = 480 nm (*ε* = 78 L·mol⁻¹·cm⁻¹), 575 (sh). ESR (pentane) (RT and -100 °C): singlet (*g* = 1.976, *a*(Ti) = 8.9 G, peak to peak width 3.5 G). Magnetic susceptibility (corrected for diamagnetism): *μ*_{eff} = 1.79 *μ*_B. Anal. Calcd for C₃₀H₃₅Ti: C, 81.25; H, 7.96; Ti, 10.80. Found: C, 81.11; H, 7.99; Ti, 10.72. Oxidation with PbCl₂ yielded orange-brown (C₅PhMe₄)₂Ti(H)Cl: ¹H NMR (C₆D₆): **d** 1.87, 1.89, 1.95, 1.98 (s, 6H, C₅PhMeMe₃), 5.16 (s, 1H, Ti-H), 7.1 (m, 10H, Ph).

(12) (a) Crystal data for **4**: C₃₀H₃₅Ti, triclinic, space group *P* $\bar{1}$ with *a* = 9.097(1) Å, *b* = 12.102(1) Å, *c* = 12.317(1) Å, *α* = 76.646(4)°, *β* = 72.618(4)°, *γ* = 69.643(4)°, *V* = 1201.0(2) Å³, *d*_{calc} = 1.226 g cm⁻³, and *Z* = 2. Data were collected on an Enraf-Nonius CAD-4F diffractometer at 130 K with Mo K α (*I* = 0.710 73 Å). The structure was solved by Patterson methods. Difference Fourier synthesis resulted in the location of all hydrogen atoms, which positions were included in the refinement. *R*_F = 0.033 with *wR* = 0.041 for 4633 unique reflections with *I* ≥ 2.5 σ (*I*) and 422 parameters. (b) Ti-Cen(1), 2.0298(8) Å; C-C_{av}(1), 1.4244 Å; ring slippage(1), 0.035 Å; Ti-Cen(2), 2.0305(8) Å; C-C_{av}(2), 1.4230 Å; ring slippage(2), 0.070 Å.

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(20) This may be explained by either a very broad hydride resonance or by a fast H/D exchange with the solvent.

(21) Upon oxidation with air to Ti(IV) species, these absorption bands disappear.

(22) Any trace of N₂ needs to be rigorously removed, otherwise on cooling to -100 °C a doublet (*g* = 1.992, *a*(H) = 11.9 G) appears in the ESR spectrum of **4** at the expense of the intensity of the singlet at *g* = 1.976, due to formation of a dinitrogen adduct, (C₅PhMe₄)₂Ti(H)N₂. Because of the lower symmetry of this adduct, mixing occurs between the orbital in which the unpaired electron resides and the Ti-H bonding orbital, resulting in the observation of a doublet.

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occurred, producing $(C_5Me_5)_2TiEt$ for which compound a *b*-H agostic interaction was anticipated on the basis of IR spectroscopy. Similarly, **4** reacts with only 1 equiv of ethene, but the IR spectrum of the paramagnetic d^1 product does not show any *b*-H agostic interaction. The structure and reactivity of this complex is being studied at the moment.

The phenyltetramethylcyclopentadienyl ligand proves to be a very useful ligand for the investigation of titanocene chemistry, resulting in formation of well-crystallizable products. The molecular structure of the first monomeric bis(cyclopentadienyl)titanium(III) hydride, $(C_5PhMe_4)_2TiH$, was determined to be a bent sandwich. Since the spectroscopic and experimental data of $(C_5PhMe_4)_2TiH$ and Cp^*_2TiH are very similar,

Cp^*_2TiH is assumed to have a bent-sandwich geometry as well. We are currently exploring the chemistry of (phenyltetramethylcyclopentadienyl)titanium compounds further.

Supporting Information Available: Text giving details of the structure determination of **4** and tables of crystal data, thermal displacement parameters, atomic coordinates, bond lengths, and bond angles (17 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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