SYNTHESIS AND STRUCTURE OF BIS(PHENYL-TETRAMETHYL-CYCLOPENTADIENYL)TITANIUM(III) HYDRIDE - THE FIRST MONOMERIC BIS(CYCLOPENTADIENYL)TITANIUM(III) HYDRIDE

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Synthesis and Structure of Bis(phenyltetramethylylcyclopentadienyl)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, (C₅-PhMe₅)₃TiH (4), was synthesized by hydrolysis of (C₅PhMe₅)₂TiMe (5). Hydride 4 was found to be a monomeric bent sandwich by X-ray diffraction methods, and the pentamethylcyclopentadienyl analogue (C₅Me₅)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. They also have relevance in olefin polymerization as the reactivity data for the first structurally characterized monomeric bis(cyclopentadienyl)titanium(III) hydride. (C₅Me₅)₃TiH (3) was synthesized by hydrolysis of (C₅Me₅)₂TiR. ⁸

During an investigation of (C₅Me₅)₂TiR (R = alkyl, aryl) compounds at our laboratory, (C₅Me₅)₃TiH (3) was synthesized by hydrolysis of (C₅Me₅)₂TiR. ⁸

Figure 1. ORTEP drawing of (C₅PhMe₅)₃TiH (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 (C₅Me₅)₂TiR, seems most likely for 3, but a fulvene-dihydride structure ((C₅Me₅)₃TiH) cannot be ruled out. ⁹ To lower the symmetry of the ligand environment, 1-phenyl-2,3,4,5-tetramethylylcyclopentadienyl ¹⁰ was employed, resulting in the synthesis and X-ray structure determination of bis(1-phenyl-2,3,4,5-tetramethylylcyclopentadienyl)titanium(III) hydride. (C₅PhMe₅)₃TiH (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 (C₅PhMe₅)₂TiMe (5) to 1 atm of H₂ at room temperature. ¹¹ Beautiful red-brown crystals of 4 separate after cooling to -20 °C. A single-crystal X-ray diffraction

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(11) Experimental details are as follows: General comments. All manipulations of air-sensitive compounds were carried out under N(2) using standard Schlenk-line and glovebox techniques. 1-Phenyl-2,3,4,5-tetramethylcyclopentadiene was prepared according to published procedures. (12) Paramagnetic complexes were oxidized with PbCl(2) to the corresponding diamagnetic Ti(V) compounds for facile characterization by 'H NMR. Synthesis of (C(5)Me(5))TiCl(5) (Si(5)Me(4)) was carried out by adding to a suspension of 4.06 g of LiC(5)Me(5), which was prepared according to published procedures. (13) A small portion of all new paramagnetic Ti(III) compounds was oxidized with PbCl(2), resulting in a red-brown color for both compounds. (14) The ESR spectrum of a pentane solution of 4 shows a singlet (g = 1.976) with hyperfine coupling to Ti isotope(s) (a(Ti) = 8.9 G) at both room temperature and -100 °C. 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 (C(5)Me(5))Ti[eta(5)-C(5)Me(5)C(5)H(5)]. On thermolysis of 4, only the methyl protons of the C(5)Me(5) ligand are activated, producing a mixture of two isomers ((C(5)Me(5))Ti(C(5)-1-CH(2)-2-Ph-3,4,5-Me(3)) and (C(5)Me(5))Ti(C(5)-1-CH(2)-2-3,4,5-Me(3))). No products due to activation of the phenyl protons of the C(5)Me(4) ligand were observed. A convenient way to characterize paramagnetic Ti(III) complexes consists of oxidation with PbCl(2) to the corresponding diamagnetic Ti(IV) chloride compounds. As expected, oxidation of 4 with PbCl(2) yields (C(5)Me(5))Ti(H)Cl, while 3 gives (C(5)Me(5))Ti(H)Cl. Both 3 and 4 catalyze the hydrogenation of 1-oxene to hexane and the dimerization of phenylacetylene.

It was reported that 3 is not capable of ethene polymerization. Instead, only one insertion of ethene

occurred, producing (C₅Me₅)$_2$TiEt for which compound a β-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 d¹ product does not show any β-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, (C₅PhMe₄)$_2$TiH, was determined to be a bent sandwich. Since the spectroscopic and experimental data of (C₅PhMe₄)$_2$TiH 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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