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Synthesis and Structure of *rac*-Bis{[1,2-bis(tetrahydroindenyl)ethane](μ-hydrido)titanium(III)}: An Antiferromagnetic Ti(III) Hydride Dimer

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The hydrides of titanocene are of special importance in catalysis,[1,2] but they are elusive because of their high chemical reactivity and/or their thermal instability. In a pioneering work in this field, Bercaw and Brintzinger[3] prepared and thoroughly investigated a titanocene(III) hydride, **1**, which they postulated to be the dimer, but its structure has never been confirmed by X-ray studies. The analogue, (μ-η^5,η^5-fulvalene)(di-μ-hydrido)-bis(η^5-cyclopentadienyl)titanium(III) (**2**), was identified and structurally characterized by indirect methods at the same time,[4] but its structure was only very recently confirmed by X-ray crystallography.[5]

We report here the preparation, crystal structure, and some EPR spectral properties of *rac*-{[C_2H_4(η^5-tetrahydroindenyl)$_2$]-Ti^{III}(μ-H)}$_2$ (**3**). This compound has relevance to a number of aspects of titanocene chemistry. It is a rare example of a simple, stable titanium hydride species, the first structurally characterized titanocene(III) hydride derivative that does not have a supporting organic bridge, the first structurally characterized chiral titanium hydride, and the first structurally characterized dimer of (BTHIE)Ti^{III}, where BTHIE is 1,2-bis(tetrahydroindenyl)ethane.

3 is produced in good yield as dark green crystals when *rac*-(BTHIE)dimethyltitanium(IV) (**4**) is reacted with an organosilane in toluene/hexane solution. The X-ray crystal structure shows the unit cell to contain two pairs of the racemic *R,R* and *S,S* molecules. An ORTEP diagram of the *S,S* molecule is shown in Figure 1, together with some important bond lengths and angles. The most notable feature of the structure is the considerable rotation of the two planes formed by each pair of the centroids of the C_5 rings and Ti with respect to each other. In most [Cp_2TiX]$_2$ compounds this dihedral angle is 0,[6] while in **3** it is 53°. This feature is presumably a reflection of the steric demands of the tetrahydroindenyl ligands. However, the Cen−Ti−Cen′ angle is in the normal range for bridged titanocene(III) dimers,[7] and it is evident that deformation of the Cen−Ti−Ti−Cen dihedral angle occurs more easily than that of the Cen−Ti−Cen′ angle. The main effect of these nonbonding interactions on the bond parameters of the Ti_2H_2 unit in **3** (see caption to Figure 1), relative to those observed in **2** (Ti−H$_{av}$ = 1.73 Å; Ti−Ti = 2.989 Å; H−Ti−H = 57°; Ti−H−Ti = 120°) and in the mixed valence complex (η^5-tetramethylcyclopentadienyl)titanium(III)-μ-(η^3,η^4-dimethyldimethylenecyclopentadienyl)bis(μ-hydrido)(η^5-tetramethylcyclopentadienyl)titanium(II) (**5**) (Ti−H$_{av}$ = 1.78 Å; Ti−Ti = 2.732 Å; H−Ti−H = 70°; Ti−H−Ti = 98°),[8] is the complete flattening of the ring and elongation of the Ti−H bonds. In both **2** and **5**, the organic bridge compresses the two Ti atoms to give short Ti−Ti distances, shorter Ti−H bonds, and simultaneously induces folding about the H···H axis.

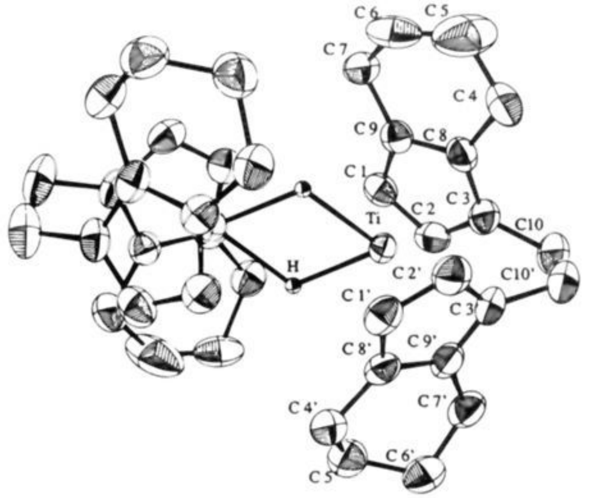

Figure 1. ORTEP diagram of **3**, showing 50% thermal elipsoids. Some relevant bond distances (Å) and angles (deg) are as follows: Ti−Ti, 3.2288(13); Ti−H, 1.90(3); Ti−C(1), 2.392(4); Ti−C(2), 2.367(4); Ti−C(3), 2.404(4); Ti−C(8), 2.417(4); Ti−C(9), 2.446(4); Ti−Cen, 2.0848(6); Ti−Cen′, 2.0832(6); H−Ti−H, 66.0(12); Ti−H−Ti, 113.9(14); Cen−Ti−Cen′, 127.63(3); Cen−Ti−Ti−Cen, 53.06(18).

In frozen toluene or toluene/methyltetrahydrofuran solution, **3** exhibits a six-line EPR spectrum characteristic of a triplet state due to a Ti(III)−Ti(III) exchange interaction, with a *g*-tensor of rhombic symmetry: $g_z = 1.9972$; $g_y = 1.9786$; $g_x = 1.9604$; $D = -0.0433$ cm^{-1}; $E = -0.008\ 16$ cm^{-1}, Figure 2. A sharp line due to the forbidden midfield transition ($\Delta M_s = 2$) is also observed at $g_{eff} = 4.0020$. Hyperfine interaction with the bridging hydrogens is not resolved because this is smaller in magnitude than the inhomogeneous line width of the $\Delta M_s = \pm 1$ transitions of the triplet state. The intense central signal, which is the only signal observed at room temperature, is attributable to a $S = {}^1/_2$ species. Such a signal is commonly present in the EPR spectra of Ti(III) dimers exhibiting a triplet state and is likely due to an impurity or to a paramagnetic monomer.[7]

It is interesting to note that the frozen solution spectrum of **3** is very closely similar to that of [$Cp_2Ti(OCH_3)$]$_2$ (**6**), with the *g* and zero-field splitting (ZFS) parameters differing only slightly ($g_x = 2.001$; $g_y = 1.980$; $g_z = 1.964$; $D = -0.0446$; $E = -0.0069$).[7b] This is not unusual because of the similar geometry. Also, calculation of the Ti−Ti separation from the dipolar component of the ZFS parameter of **3** gives a distance

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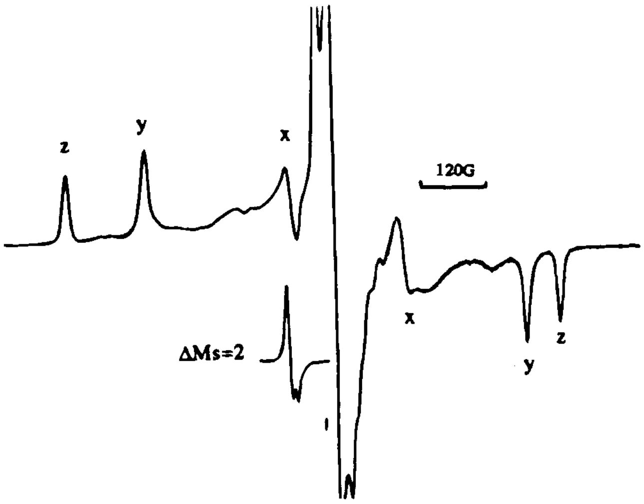

Figure 2. EPR spectrum of **3** in toluene/methyltetrahydrofuran measured in a sealed tube at 130 K.

of 3.39 Å, in good agreement with the value 3.228 Å measured on the solid by X-ray diffraction. The small discrepancy is probably due to the pseudodipolar component of the ZFS. The same calculation performed on **6** also gives a satisfactory result (3.38 Å calculated versus 3.35 Å measured by X-ray diffraction). The present data further confirm the validity and usefulness of this approximation in the calculation of metal–metal distances from ZFS parameters.

The parameters reported here for the triplet state of **3** in frozen solution are also remarkably close to the parameters formerly attributed by us to the compound $Cp_2Ti(\mu\text{-}H)(\mu\text{-}SiH_2Ph)TiCp_2$ (**7**).[2e] Given what is now known about the interconversion of silyl, hydridosilyl, and hydrido species in these systems,[9] the triplet attributed to **7** could be due to contamination with **1**, which is either in equilibrium with **7** or produced by its spontaneous decomposition. The dark blue color of the reaction products of **4** with silane alone are most likely the analogues of silyltitanocene complexes reported earlier.[2e] These silyl species have been shown to give rise to Ti(III)–H complexes,[9] and it may be concluded that the isolation of **3** is the consequence of its being the least soluble component of the reaction product mixture.

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Supplementary Material Available: Experimental procedures and characterization data for **3** and tables of crystal data collection and refinement parameters, bond distances and angles, anisotropic displacement parameters, and hydrogen atom coordinates; unit cell structure of **3** (8 pages); listing of observed and calculated structure factors (11 pages). The 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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