Titanium Hydride Formation through Hydrogen Transfer from 2-Methylpyridine to a Titanium Fulvene Compound; the First Structurally Characterized Terminal Titanium Hydride

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In a study of the thermolysis of compounds of the type [Cp*₂TiR] (Cp* = η⁵-C₅Me₅; R = H or alkyl), we observed stepwise hydrogen abstraction from one of the Cp* ligands.[1]

We are currently focusing our attention on the reactivity of these modified Cp* ligands. In 1 the tetramethylfulvene ligand may be coordinated either as a combined cyclopentadienyl-alkyl ligand, the “tucked-in” mode A,[2] or as a neutral conjugated triene B.[3]

In a series of exploratory studies with a variety of substrates with active protons, e.g., acids and alcohols, 1 reacted as a cyclopentadienyl-alkyl complex with transfer of hydrogen from the substrate to the fulvene ligand, thus restoring the original Cp* ligand.[4]

A completely different and unprecedented reaction took place when 1 was exposed to pyridine derivatives. At -80°C the dark purple 1 reacts quickly with 2-methylpyridine in Et₂O to give a dark green solution, which changes to an intense dark blue on warming to room temperature. Concentration and cooling of the solution to -30°C resulted in the formation of beautiful dark blue crystals of 2.[5]

The molecular structure of 2 (Fig. 1)[6] shows that hydrogen transfer from the 6-position of 2-methylpyridine to titanium, concurrent with C-C bond formation between pyridine and the methylene group of the fulvene ligand, has taken place. In this way a Cp* ligand is functionalized with a pyridine ligand to form a chelating ligand.

<table>
<thead>
<tr>
<th>[Cp*(C₅Me₅CH₂)₂Ti] + C₅H₅MeN</th>
<th>ΔT°</th>
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<tbody>
<tr>
<td>1</td>
<td></td>
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<tr>
<td>[Cp*(C₅Me₅CH₂(C₅H₅MeN))₂TiH</td>
<td>2</td>
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</table>

Compound 2 is the first structurally characterized dicyclopentadienyltitanium hydride with a terminal Ti-H bond. The Ti-H distance (1.70(4) Å) is substantially longer than in other 3d-transition metal terminal hydrides, but comparable with hydrides of the early transition metals of the 4d and 5d series.[7] Until now only structure determinations of titanium hydrides with bridging hydrogen atoms, e.g., complexes containing a Ti-H-Ti, Ti-H-Al, or Ti-H-B structural element, have been published. In these complexes the Ti-H distances vary between 1.69(10) and 1.94(7) Å.[7]

The location of the pyridyl fragment with respect to the Ti atom and especially the Ti-N distance (2.340(3) Å) indicates that we are dealing with a dative Ti-N bond.[8] The angle formed between the Ti atom and the centroids of the substituted cyclopentadienyl rings is 142.7°; the distances between Ti and the centroids (2.086 and 2.064 Å) are close to those found in unsubstituted Cp*₂Ti derivatives.[9]

The dihedral angle between the plane containing both ring centroids and Ti and the H-Ti-N plane is 61.5°. The C15-C20 bond deviates slightly from the ring plane (7.4°) toward the metal. The other C(ring)-C(methyl) bonds point away from the metal, thereby producing the normal “dish” shape of the Cp* ligands.[10] The C15-C20 angle (111.5(3)°) shows that C20 is almost perfectly sp² hybridized.

The ¹H-NMR spectrum of 2[11] affords assignments of the protons of the cyclopentadienyl ligands. Owing to the paramagnetism of 2, the signals are broad and shifted strongly. The hydride resonance could not be located, a problem also encountered for the related compound [Cp*₂TiH].[13] In the IR spectrum, ν(Ti-H) is found at 1475 cm⁻¹; slightly lower than for [Cp*₂TiH]. The assignment was confirmed by the synthesis of the deuteride: ν(Ti-D) was observed at 1065 cm⁻¹ (ν(Ti-H)/ν(Ti-D)= 1.38). The ESR spectrum shows a well-resolved doublet, centered at
In a Toeppler pump controlled experiment, 1 mole of ethylene per mole of Ti was consumed. Compound 3 was isolated as a dark brown, analytically pure crystalline material; it reacts with D₂ to form EtD and [D]-2 in a 1:1 molar ratio. \[ \text{TiH} + \text{CH}_2=\text{CH}_2 \rightarrow \text{[Ti]Et \rightarrow [Ti]D} + \text{EtD} \]

2     3     [D]-2

In a Toepler pump controlled experiment, 1 mole of ethylene and DCl also confirmed the presence of a Ti-H functionality. \[ \text{[Ti]H} + \text{DCl} \rightarrow \text{[Ti]Cl} + \text{HD} \]

2     4

In a Toepler pump controlled experiment, 1 mole of ethylene per mole of Ti was consumed. Compound 3 was isolated as a dark brown, analytically pure crystalline material; it reacts with D₂ to form EtD and [D]-2 in a 1:1 molar ratio. [1]

The formation of a Ti-H bond through hydrogen transfer from 2-methylpyridine is completely different from what is regularly observed in reactions with compounds of early transition metals of the type [Cp₂TiR][12] or [Cp*₂M] (M = Sc, [13] Y, [14] Lu[13]). In the case of a “tucked-in” bonding mode, metatation of the pyridine with hydrogen transfer to the fulvene ligand and formation of [Cp*₂Ti(η⁴-C₅H₄MeN)] is expected. A further outstanding feature is the conversion of a fulvene ligand into a functionalized pentamethylyclopentadienyl group. This reaction may be of considerable synthetic importance as an attractive route to bidentate Cp* ligands.

**Experimental Procedure**

2.1 (0.574 g, 1.81 mmol) was dissolved in Et₂O (20 mL) and cooled to -190°C. 2-Methylpyridine (0.168 g, 1.81 mmol) was added and the reaction mixture was warmed to -30°C to give beautiful dark blue crystals. Yield: 0.335 g (0.82 mmol, 45%) of 2. Correct elemental analysis.

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[5] [H-NMR: δ = 2.068 MHz, [D]₂Et₂O at 0°C. δ values relative to residual protons in the solvent at δ = 1.29; multiplicity, intensity, width at half maximum height (Hz) in parentheses: δ = 25.0 (s, 29 H, 280; C₅H₅N(Me)₂) 9.4 (m, 1 H, 280; C₅H₅N), 7.5 (m, 2 H, 170; C₅H₅N), 2.7 (s, 3 H, 50; C₅H₅N), IR (KBr/Nujol): ν = 2720, 1596, 1565, 1475, 1450, 1415, 1370, 1310, 1265, 1225, 1210, 1195, 1160, 1102, 1055, 1015, 992, 895, 835, 785, 728, 680, 610, 575, 437, 395 cm⁻¹.]