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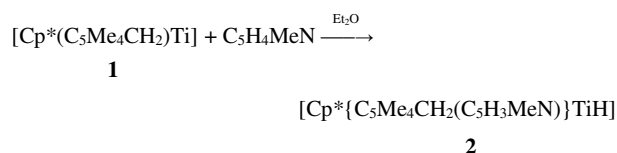
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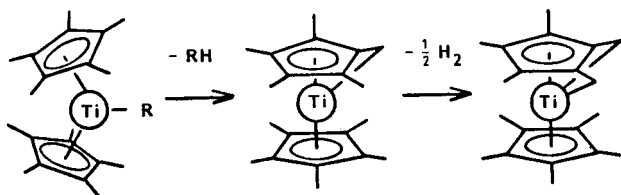
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Titanium Hydride Formation through Hydrogen Transfer from 2-Methylpyridine to a Titanium Fulvene Compound; the First Structurally Characterized Terminal Titanium Hydride

By Johannes W. Pattiasina, Fré van Bolhuis, and Jan H. Teuben*

In a study of the thermolysis of compounds of the type $[\text{Cp}^*_2\text{TiR}]$ ($\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$; $\text{R} = \text{H}$ 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 Et_2O 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]

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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.

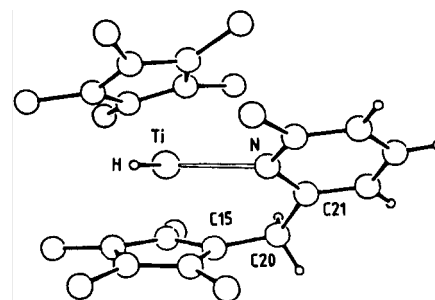


Fig. 1. Molecular crystal structure of $[\text{Cp}^*\{\text{C}_5\text{Me}_4\text{CH}_2(\text{C}_5\text{H}_3\text{MeN})\}\text{TiH}]$ **2**.

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]

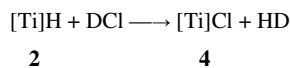
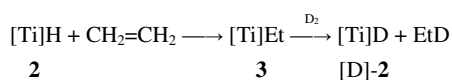
The location of the pyridyl fragment with respect to the Ti atom and especially the Ti-N distance (2.340(3) Å) indicate that we are dealing with a dative Ti-N bond.^[8] The angle formed between the Ti atom and the centroids of the substituted cyclopentadienyl rings is 142.7° ; the distances between Ti 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 91.6° ; the H-Ti-N angle is $91(2)^\circ$. From this it is clear that **2** has all the characteristics of a regular $\text{Cp}^*_2\text{M(L)X}$ molecule. 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-C21 angle ($111.5(3)^\circ$) shows that C20 is almost perfectly sp^3 hybridized.

The $^1\text{H-NMR}$ spectrum of **2**^[5] 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 $[\text{Cp}^*_2\text{TiH}]$.^[3] In the IR spectrum, $\bar{\nu}(\text{Ti-H})$ is found at 1475 cm^{-1} , slightly lower than for $[\text{Cp}^*_2\text{TiH}]$. The assignment was confirmed by the synthesis of the deuteride: $\bar{\nu}(\text{Ti-D})$ was observed at 1065 cm^{-1} ($\bar{\nu}(\text{Ti-H})/\bar{\nu}(\text{Ti-D})=1.38$). The ESR spectrum shows a well-resolved doublet, centered at

$g = 1.985$ ($a_{\text{H}} = 11.5$ G), and a clear hyperfine splitting due to interaction with titanium isotopes (^{47}Ti , $I = 5/2$, ^{49}Ti , $I = 7/2$, natural abundance 7.28% and 5.51%, respectively, $a_{\text{Ti}} = 9.3$ G).

Reaction of **2** with ethylene and DCl also confirmed the presence of a Ti-H functionality.



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 D_2 to form EtD and [D]-**2** in a 1:1 molar ratio.^[11]

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 $[\text{Cp}_2\text{TiR}]^{[12]}$ or $[\text{Cp}^*_2\text{MR}]$ ($\text{M} = \text{Sc}^{[13]}$, $\text{Y}^{[14]}$, $\text{Lu}^{[15]}$). In the case of a "tucked-in" bonding mode, metalation of the pyridine with hydrogen transfer to the fulvene ligand and formation of $[\text{Cp}^*_2\text{Ti}(\eta^2\text{-C}_5\text{H}_3\text{MeN})]$ is expected.

A further outstanding feature is the conversion of a fulvene ligand into a functionalized pentamethylcyclopentadienyl 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 Et_2O (20 mL) and cooled to -196°C . 2-Methylpyridine (0.168 g, 1.81 mmol) was added and the reaction mixture was warmed to -80°C . Upon gradually warming the mixture to room temperature, the color of the solution changed from red-purple to dark green and finally dark blue. After stirring for 4 h, the solution was filtered, concentrated to 15 mL, and slowly cooled 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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CAS Registry numbers:

1, 53436-87-6; **2**, 107116-24-5; [D]-**2**, 107116-25-6; **3**, 107116-26-7; **4**, 107116-27-8; 2-methylpyridine, 109-06-8.

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[5] $^1\text{H-NMR}$ (200.068 MHz, $[\text{D}_{10}]\text{Et}_2\text{O}$ at 0°C ; δ values relative to residual protons in the solvent at $\delta = 1.29$; multiplicity, intensity, width at half maximum height (Hz) in parentheses: $\delta = 25.0$ (s, 29 H, 280; $\text{C}_5\text{Me}_5(\text{C}_5\text{Me}_4\text{CH}_2)$), 9.4 (m, 1 H, 280; $\text{C}_5\text{H}_3\text{MeN}$), 7.5 (m, 2 H, 170; $\text{C}_5\text{H}_3\text{MeN}$), 2.7 (s, 3 H, 50; $\text{C}_5\text{H}_3\text{MeN}$); IR (KBr/Nujol): $\bar{\nu} = 2720, 1596, 1565, 1475, 1450, 1415, 1370, 1310, 1265, 1225, 1210, 1195, 1160, 1102, 1055, 1015, 990, 925, 895, 835, 785, 728, 680, 610, 575, 437, 395$ cm^{-1} .

- [6] Cell data: $a = 10.045(4)$, $b = 19.333(5)$, $c = 11.504(4)$ Å, $\beta = 96.45(3)^\circ$, $V = 2220.2$ Å³, $\rho_{\text{calcd}} = 1.228$ g cm^{-3} , $\mu = 3.9$ cm^{-1} , $Z = 4$, $P2_1/m$, 4818 unique reflections, 2827 reflections with $I \geq 3 \sigma(I)$, 398 parameters refined, $R = 0.052$, $R_w = 0.057$. Further details of the crystal structure investigation are available on request from the Fachinformationszentrum Energie, Physik, Mathematik GmbH, D-7514 Eggenstein-Leopoldshafen 2 (FRG), by quoting the depository number CSD-52363, the names of the authors, and the journal citation.
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