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### Formation of a Novel $\eta^3$

Pattiasina, Johannes W.; Hissink, Catharina E.; Boer, Jan L. de; Meetsma, Auke; Teuben, Jan H.; Spek, Anthony L.

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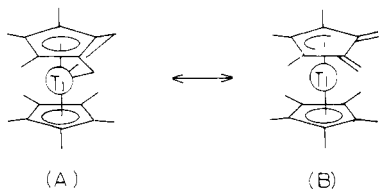


Figure 1. Modes of bonding in  $\text{Cp}^*(\text{C}_5\text{Me}_3(\text{CH}_2)_2)_2\text{Ti}$ .

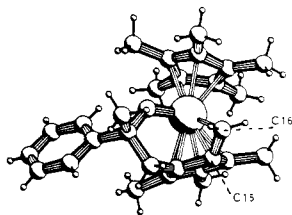


Figure 2. Molecular structure of  $\text{Cp}^*\text{Ti}(\text{C}_5\text{Me}_3(\text{CH}_2)_2\text{CH}_2\text{CO}(\text{Me})(\text{Ph}))$ .

a blue, diamagnetic organotitanium compound III.<sup>9</sup> The elemental analyses, molecular weight (cryoscopy in benzene), mass spectrum, IR spectrum, but especially  $^1\text{H}$  and  $^{13}\text{C}$  NMR data are in complete accordance with a formulation as a monomeric  $(\eta^5\text{-Cp}^*)(\eta^3\text{-}\eta^4\text{-C}_5\text{Me}_3(\text{CH}_2)_2)_2\text{Ti}$  complex with a unique 1,2,3-trimethyl-4,5-dimethylenecyclopentenyl ligand. The bonding in this compound is very intriguing, given the possibility of two resonance structures (Figure 1).

The main difference is the formal oxidation state of the metal, which varies from +4 in A to +2 in B. Structure A is an analogue of regular  $\text{Cp}^*_2\text{TiR}_2$  with two Ti-C  $\sigma$  bonds to the cyclopentadienyl methylene groups. In structure B the trimethyldimethylenecyclopentenyl ligand is in an  $\eta^3$ -allyl- $\eta^4$ -butadiene bonding fashion and in this sense analogous to complexes of the type  $\text{Cp}^*\text{M}(\text{1-methallyl})(\text{butadiene})$  ( $\text{M} = \text{Ti}, \text{Zr}, \text{Hf}$ ).<sup>10</sup>

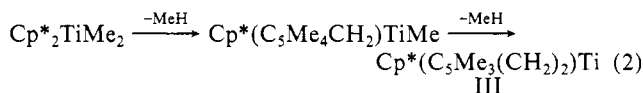
NMR data indicate that structure B is the best representation. The coupling constants for both methylene groups ( $^2J_{\text{HH}} = 4.4$  Hz and  $^1J_{\text{CH}} = 160$  Hz) are typical for  $\text{sp}^2$  hybridized carbon atoms, thus favoring B.

An X-ray structure determination of III to verify both relative position and the bonding situation of the methylene groups is hampered by disorder problems. Conformation of the proposed structure comes from the molecular structure of the acetophenone reaction product IV of III<sup>11</sup> (Figure 2). The acetophenone carbonyl function is inserted in a titanium methylene bond, forming an alkoxide bridging titanium and a (substituted) 1,2,3,4-tetramethylfulvene ligand. Compound IV is the first

structurally characterized monomeric titanium fulvene complex. Relevant for the structure of III is the fact that the two methylene functions are indeed on neighboring ring C-atoms, thus confirming the 1,2,3-trimethyl-4,5-dimethylenecyclopentenyl structure proposed for III. The bonding of the fulvene methylene group is very interesting. The short  $\text{C}=\text{CH}_2$  bond (1.437 (5) Å), the angle  $\text{HC}(16)\text{H}$  (116 (3)°), and the rather small deviation of the  $\text{CH}_2$  hydrogen atoms from a planar array with C(15) and C(16) (the angle between C(15)-C(16) and the plane  $\text{HC}(16)\text{H}$  is 27.8 (2)°) indicate that in first approximation we are dealing with an  $\text{sp}^2$  hybridized methylene carbon atom. The coupling constants ( $^2J_{\text{HH}} = 3.6$  Hz and  $^1J_{\text{CH}} = 150$  Hz) are in agreement with this view. However, the deviation of the  $\text{C}=\text{CH}_2$  fragment from the ring plane (36.3°) indicates an  $\eta^2$ -bonding of this olefinic function to the metal. Comparison with a real titanium olefin complex  $\text{Cp}^*_2\text{TiC}_2\text{H}_4$ <sup>12</sup> reveals indeed a strong similarity. The C-Ti-C angle (37.8 (1)° in IV and 38.9 (1)° in  $\text{Cp}^*_2\text{TiC}_2\text{H}_4$ ) is virtually the same in both compounds. The Ti-C distances, however, (Ti-C(15) = 2.317 (3), Ti-C(16) = 2.281 (3) Å against 2.160 (4) Å in  $\text{Cp}^*_2\text{TiC}_2\text{H}_4$ ) differ considerably.

In conclusion we may state that both molecular structure and NMR data for IV favor bonding structure B for III, containing a so far unknown bifunctional, e.g., an  $\eta^3$ -allyl,  $\eta^4$ -diene organic ligand.

Compound III is not accessible through II only. Thermal decomposition of  $\text{Cp}^*_2\text{TiMe}_2$  is known to undergo hydrogen abstraction from a  $\text{Cp}^*$  ligand giving  $\text{Cp}^*(\text{C}_5\text{Me}_4\text{CH}_2)\text{TiMe}$ .<sup>3</sup> We observed that heating of the latter compound in mesitylene at 160 °C also produces III (obtained yield 22%) (eq 2).



This stepwise hydrogen abstraction from  $\text{Cp}^*$  ligands is not limited to titanium. The group 4 homologue  $\text{Cp}^*_2\text{ZrMe}_2$ <sup>13</sup> gives the same reaction.  $\text{Cp}^*(\text{C}_5\text{Me}_3(\text{CH}_2)_2)_2\text{Zr}$  could be isolated in 4% yield as a red crystalline material after heating  $\text{Cp}^*_2\text{ZrMe}_2$  at 160 °C in mesitylene.<sup>14</sup>

We are at the moment investigating the reactivity of the new  $\eta^3$ - $\eta^4$ -1,2,3-trimethyl-4,5-dimethylenecyclopentenyl ligand and the scope of the stepwise hydrogen abstraction from  $\text{Cp}^*$  ligands in metal carbyls.

**Note Added in Proof:** Recently, observations similar to ours have been reported for the tungsten system  $\text{Cp}^*_2\text{WH}_2$ , which under irradiation produces tungsten analogues of II and III.<sup>15</sup>

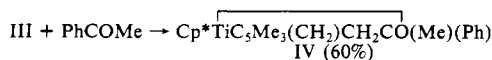
**Acknowledgment.** We thank H. J. Heeres for his enthusiastic assistance in the study of the thermal decomposition of  $\text{Cp}^*_2\text{ZrMe}_2$ . The investigation was supported by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for Advancement of Pure Research (ZWO).

**Supplementary Material Available:** Details of the synthesis of and analytical data for I, thermal decomposition of I, thermolysis of  $\text{Cp}^*_2\text{MMe}_2$  ( $\text{M} = \text{Ti}, \text{Zr}$ ), and synthesis of IV and tables of fractional atomic coordinates, thermal parameters, bond distances, and structure of IV (10 pages). Ordering information is given on any current masthead page.

(9) 4.0 g (12.5 mmol) of II was heated to 150 °C for 120 h in 15 mL of *o*-xylene. The solvent was stripped and the product crystallized from pentane. Yield 2.8 g (9.3 mmol, 75%) of III. Anal. Calcd for  $\text{C}_{20}\text{H}_{28}\text{Ti}$ : C, 75.93; H, 8.92; Ti, 15.14. Found: C, 75.79; H, 8.89; Ti, 15.03. IR (KBr/Nujol) 3020, 2710, 1480, 1365, 1335, 1160, 1070, 1020, 872, 830, 810, 800, 725, 660, 620, 580, 550, 445, 410  $\text{cm}^{-1}$ ;  $^1\text{H}$  (200.068 MHz) and  $^{13}\text{C}$  (50.31 MHz) NMR in  $\text{C}_6\text{D}_6$ :  $^1\text{H}$  (ppm relative to residual protons in deuterated solvent at  $\delta$  7.15)  $\delta$  1.79 (s, 15,  $\text{Cp}^*$ ), 1.34 (s, 3, Me), 1.14 (s, 6, 2 Me), 0.92, 0.86 (d, d, 2, 2,  $^2J_{\text{HH}} = 4.4$  Hz, 2  $\text{CH}_2$ );  $^{13}\text{C}$  data (ppm relative to  $\text{C}_6\text{D}_6$  at  $\delta$  127.96)  $\delta$  144.60, 133.18, 122.70 (all s,  $\text{C}_5\text{Me}_3(\text{CH}_2)_2$ ), 119.06 (s,  $\text{C}_5\text{Me}_3$ ), 67.64 (t,  $^1J_{\text{CH}} = 160$  Hz,  $\text{C}_5\text{Me}_3(\text{CH}_2)_2$ ), 11.79 (q,  $^1J_{\text{CH}} = 125$  Hz,  $\text{C}_5\text{Me}_3$ ), 10.13, 9.98 (both q,  $^1J_{\text{CH}} = 125$  Hz,  $\text{C}_5\text{Me}_3(\text{CH}_2)_2$ ); MS, parent peak at  $m/e$  316. Cryoscopic molecular weight determination in  $\text{C}_6\text{H}_6$ : calcd 316; found 332.

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(11) Acetophenone reacts with III in pentane (reaction time 24 h at 22 °C) according to



Compound IV was identified by elemental analyses (C, H, Ti), mass spectrum, IR, and  $^1\text{H}$  and  $^{13}\text{C}$  NMR. Suitable crystals of IV were grown from a pentane solution. The structure of IV was determined by X-ray crystallography. Crystal data:  $\text{C}_{28}\text{H}_{36}\text{OTi}$ ,  $M_r = 436.5$ ; monoclinic,  $P2_1/c$ ;  $Z = 4$ ;  $a = 15.969$  (3) Å,  $b = 9.721$  (2) Å,  $c = 16.193$  (2) Å;  $\beta = 112.75$  (1)°;  $R = 0.043$ ,  $R_w = 0.040$  ( $w = 1/\sigma^2(F)$ ); based on 2715 reflections with  $I > 2.5\sigma(I)$  out of 4076 unique CAD4 diffractometer data. Hydrogen atoms, located from a difference electron density map, were refined isotropically all other atoms anisotropically. Full details will be published elsewhere.

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(14) IR (KBr/Nujol) 3020, 2720, 1480, 1375, 1340, 1070, 1020, 855, 825, 800, 705, 550, 405  $\text{cm}^{-1}$ ;  $^1\text{H}$  (200.068 MHz) and  $^{13}\text{C}$  (50.31 MHz) NMR in  $\text{C}_6\text{D}_6$ :  $^1\text{H}$  data (ppm relative to  $\text{Me}_4\text{Si}$  at  $\delta$  0.00)  $\delta$  1.93 (s, 15,  $\text{Cp}^*$ ), 1.46 (s, 3, Me), 1.27 (s, 6, 2 Me), 0.97, 1.17 (d, d, 2, 2,  $^2J_{\text{HH}} = 6.2$  Hz, 2  $\text{CH}_2$ );  $^{13}\text{C}$  data (ppm relative to  $\text{C}_6\text{D}_6$  at  $\delta$  127.96)  $\delta$  137.12, 131.51, 128.25 (all s,  $\text{C}_5\text{Me}_3(\text{CH}_2)_2$ ), 119.48 (s,  $\text{C}_5\text{Me}_3$ ), 56.52 (t,  $^1J_{\text{CH}} = 148$  Hz,  $\text{C}_5\text{Me}_3(\text{CH}_2)_2$ ), 11.51 (q,  $^1J_{\text{CH}} = 126$  Hz,  $\text{C}_5\text{Me}_3$ ), 10.96, 10.45 (both q,  $^1J_{\text{CH}} = 126$  Hz,  $\text{C}_5\text{Me}_3(\text{CH}_2)_2$ ).

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