ORGANOMETALLICS

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Organometallics, **1993**, 12 (9), 3387-3389• DOI: 10.1021/om00033a004 • Publication Date (Web): 01 May 2002

Organometallics is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

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Synthesis and Structure of a Novel μ-Dimethyldimethylenecyclopentenyl Bis(μ-hydrido) Mixed-Valence Titanium(III)/Titanium(II) Compound

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Received April 29, 1993

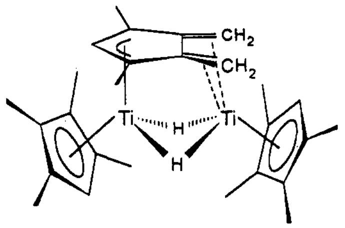
Summary: The binuclear compound (μ-η^4:η^3-1,4-dimethyl-2,3-dimethylenecyclopentenyl)bis(μ-hydrido)bis((η^5-tetramethylcyclopentadienyl)titanium), [μ-$C_5H(CH_3)_2(CH_2)_2$][(C_5HMe_4)Ti(μ-H)]$_2$ (1), was obtained by the reduction of (C_5HMe_4)$_2$$TiCl_2$ with $LiAlH_4$ in boiling mesitylene. Its X-ray crystal analysis revealed that each titanium atom of the folded Ti(μ-H)$_2$Ti fragment is bonded to remote parts of the bridging dimethyldimethylenecyclopentenyl ligand. Crystal data for 1: space group Pnma, a = 8.364(1) Å, b = 15.492(3) Å, c = 18.429(4) Å, Z = 4, 1712 reflections, R = 0.041.

Bis(cyclopentadienyl)titanium(II) species can be stabilized by coordination of suitable π or lone-pair electron donors which are able to accommodate d^2 electrons in their low-energy empty orbitals.[2] In the absence of such ligands, they dimerize with the formation of μ-η^5:η^5-fulvalene[3] or μ-η^1:η^5-cyclopentadienyl ligands as bridging elements[4] and with simultaneous oxidation to give Ti(III)/Ti(III) or Ti(III)/Ti(II) complexes, respectively. In permethyltitanocene chemistry, Ti(II) and Ti(III) derivatives are stabilized by the bonding interaction of Ti with exo methylene groups which are generated by hydrogen abstraction from one C_5Me_5 ligand.[5]

We have encountered products with both types of stabilization in the Cp'_2TiCl_2 ($Cp' = C_5H_{5-n}Me_n$; $n = 0, 1, 3-5$)–$LiAlH_4$ systems which, in the absence of ethereal solvents, were developed as practical catalysts for double-bond shifts, cis–trans isomerization, and intramolecular cyclizations of unsaturated hydrocarbons.[6] In boiling aromatic solvents, the dimeric titanocene [(C_5H_5)Ti(μ-H)]$_2$($C_{10}H_8$) was prepared in high yield,[7] while the same procedure with (C_5Me_5)$_2$$TiCl_2$ gave the well-known[5d] η^3:η^4-1,2,3-trimethyl-4,5-dimethylenecyclopentenyl (allyl diene, Ad*) complex (C_5Me_5)Ti(Ad*) in 30% yield.[8] Two isomers of an analogous compound were obtained from (C_5HMe_4)$_2$$TiCl_2$ by the same method, although in low yield.[8]

When the reduction of (C_5HMe_4)$_2$$TiCl_2$ with $LiAlH_4$ was carried out in boiling mesitylene for 4 h, the brown crystalline product 1 (eq 1) was isolated from the reaction solution.[9] Compound 1 was obtained practically pure by

$$(C_5HMe_4)_2TiCl_2 + 4\ LiAlH_4 \xrightarrow[165\ ^\circ C,\ 4\ h]{mesitylene,\ Ar}$$



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(9) A mixture of (C_5HMe_4)$_2$$TiCl_2$[8] (1.44 g, 4 mmol) and $LiAlH_4$ (0.6 g, 16 mmol) in dry, oxygen-free mesitylene was boiled with stirring under argon for 4 h. The solution was separated from a black sediment, and the mesitylene was replaced by benzene on the vacuum line. The clear brown solution was decanted from the remaining traces of the black sediment, and the benzene was evaporated in vacuo. The residue was then sublimed under high vacuum at 130 °C; the first blue fraction (traces) was separated, and the main brown fraction was collected in a trap at room temperature. The sublimate was rinsed out with hexane (4 mL) and dissolved in benzene (10 mL). Brown crystals of 1 were obtained by slow evaporation of the benzene solution in vacuo. No organometallic impurity was found by MS and EPR spectroscopy in the residue after evaporation of benzene from the mother liquor. Yield of crystalline 1: 0.17 g (18%). Anal. Calcd for $C_{27}H_{39}Ti_2$: C, 70.60; H, 8.55; Ti, 20.85. Found: C, 69.84; H, 7.98; Ti, 21.22. EPR: in toluene at 23 °C, (TiH_2Ti) triplet, $g = 1.9871$, $a_H = 4.3$ G, $\Delta H = 3.7$ G; in toluene glass at −130 °C, $g_1 = 2.0008$ ($A_1 < 7$ G), $g_2 = 1.9921$ (triplet, $A_2 = 7.8$ G), $g_3 = 1.9693$ (triplet, $A_3 = 8.8$ G), $g_{av} = 1.9874$. Satellites due to coupling to $^{47/49}$Ti nuclei were not observed. UV–vis (λ_{max} in benzene): 340 vs, sh; 520 m, sh; 800 w; 1140 m, vb nm. MS (direct inlet, 75 eV; m/e (%)): 462 (3.1), 461 (8.6), 460 (17.1), 459 (M^+, 44.3), 458 (24.3), 457 (45.0), 456 (46.0), 455 (100.0), 454 (32.5), 453 (39.3), 452 (17.5), 451 (26.4), 450 (14.6), 449 (21.0), 448 (11.4), 447 (14.6), 446 (7.8), 445 (11.4), 444 (5.0), 443 (7.1), 442 (3.6), 441 (3.8), 440 (1.4). Exact mass: m/e 455.1699, error -1×10^{-4} for $C_{27}H_{35}Ti_2$.

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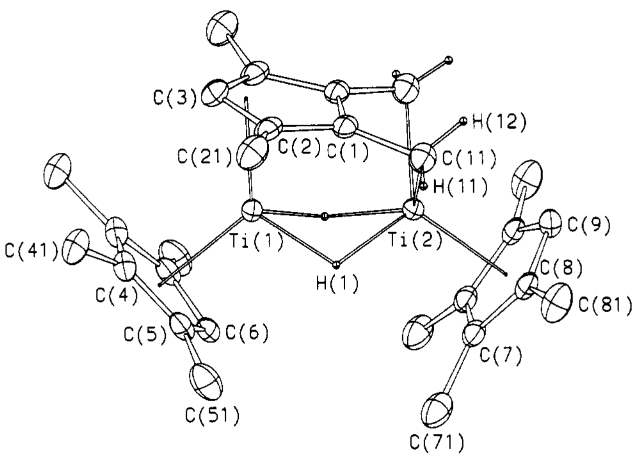

Figure 1. Molecular structure of 1. Important interatomic distances (Å) and angles (deg): Ti(1)–Ti(2) = 2.732(1), Ti(1)–C(1) = 2.467(3), Ti(1)–C(2) = 2.331(4), Ti(1)–C(3) = 2.290(5), Ti(1)–C(4) = 2.400(4), Ti(1)–C(5) = 2.354(4), Ti(1)–C(6) = 2.318(5), Ti(2)–C(1) = 2.372(3), Ti(2)–C(11) = 2.147(4), Ti(2)–C(7) = 2.359(4), Ti(2)–C(8) = 2.363(4), Ti(2)–C(9) = 2.350(4), C(1)–C(1′) = 1.440(5), C(1)–C(2) = 1.430(5), C(1)–C(11) = 1.459(5), C(2)–C(3) = 1.409(5), C(2)–C(21) = 1.499(6), Ti(1)–H(1) = 1.79(3), Ti(2)–H(1) = 1.82(3); H(1)–Ti(1)–H(1′) = 70(1), H(1)–Ti(2)–H(1′) = 69(1), Ti(1)–H(1)–Ti(2) = 98(2), Ti(2)–C(11)–C(1) 79.8(2), C(11)–Ti(2)–C(11′) = 84.2(1). The π-bonding interaction between Ti(2) and C(1) and C(11) is marked only by the Ti(2)–C(11) interconnection. Only bridging and methylene H atoms are shown for clarity.

sublimation under a high vacuum at 130 °C; traces of a byproduct, blue $(C_5HMe_4)(C_5HMe_2(CH_2)_2)Ti$,[8] sublimed at 100 °C and were collected separately. The MS spectrum of 1 gave its overall composition as $(C_5HMe_4)_3Ti_2$. The fragmentation pattern for M^+ showed extensive elimination of hydrogen (up to 4 H_2), which is typical for, e.g., dimeric titanocene[3d] or the allyl diene complexes.[5d,8] The molecular structure of 1 was determined by an X-ray single-crystal analysis[10] and is shown in Figure 1.

Compound 1 is a binuclear complex with two titanium atoms bridged by two hydrogen atoms and by one organic ligand derived from C_5HMe_4. Each titanium atom of the $Ti(\mu\text{-}H)_2Ti$ fragment is mostly π-bonded to remote parts of the bridging μ-η^4:η^3-1,4-dimethyl-2,3-dimethylenecyclopentenyl (μ-allyl diene, μ-Ad) ligand and π-bonded to one C_5HMe_4 ligand. Compound 1 is symmetrical with respect to a mirror plane containing both Ti atoms and C(3), C(6), and C(9) atoms, this plane bisecting both cyclopentadienyl rings and the bridging cyclopentenyl ring. The geometry of the Ti(μ-Ad)Ti skeleton is somewhat irregular with the Ti(1)–C(μ-Ad) bond lengths increasing in the following order: Ti(1)–C(3) = 2.290(5) Å, Ti(1)–C(2) = 2.331(4) Å, and Ti(1)–C(1) = 2.467(3) Å. This order and the overall geometry of μ-Ad with respect to Ti(1) and Ti(2) qualify carbon atoms C(2), C(3), and C(2′) as constituents of the η^3-allyl ligand. This is corroborated by the C(2)–C(3) bond length of 1.409(5) Å, which is the shortest in the μ-Ad ligand. The bond lengths C(1)–C(2) = 1.430(5) Å, C(1)–C(1′) = 1.440(5) Å, and C(1)–C(11) = 1.459(5) Å are close to the average of the double and single C–C bond lengths and indicate some electron delocalization over the diene system. The distances from Ti(2) to the diene system of the μ-Ad ligand are much shorter for the carbon atoms of the exo methylene groups (Ti(2)–C(11) = 2.147(4) Å) than the distances to the ring carbon atoms (Ti(2)–C(1) = 2.372(3) Å). The bond lengths to the $=CH_2$ carbon atoms are slightly shorter than the π-bond lengths between Ti and the ethylene carbon atoms in $(C_5Me_5)_2Ti(CH_2{=}CH_2)$ (2.16 Å)[11] or than the Ti—σ-CH_2^- bridging bond in (μ-η^1:η^5-tetramethylmethylenecyclopentadienyl)bis(μ-oxo)bis((pentamethylcyclopentadienyl)titanium(IV))[12] (2), which equals 2.176 Å. The substantial π-bonding character of the titanium–exo methylene interactions follows from the value for the C(1)–C(11)–Ti(2) angle, 79.8(2)°, which is far from the 102° required for sp^3 carbon atoms. In the case of the σ-bonded bridging $-CH_2-$ group in 2 this angle was exactly 102°.[12] The prevailing π-bonding mode of interaction between Ti(2) and the exo methylene double bond thus identifies Ti(2) as Ti(II).

The Ti–Ti distance of 2.732(1) Å for the $Ti(\mu\text{-}H)_2Ti$ folded fragment in 1 is much shorter than that for metallic α-Ti (2.896 Å).[13] The reason for this short distance should not be sought either in the Ti–Ti bonding interaction or in the binding effect of the hydrogen bridge but rather in the attracting effect resulting from the short distance between binding sites in the bridging ligands. An only slightly longer distance of 2.745 Å has recently been found in a μ-indenyl complex, (μ-η^5:η^6-indenyl)[(η^5-indenyl)Ti(μ-H)]$_2$[14] (3), whereas the fulvalene ligand in dimeric titanocene exerts a pulling-away effect to yield the Ti–Ti distance 2.99 Å.[15] A strong attractive effect of the bridging ligand was also found in 2, where the Ti–Ti distance of 2.725 Å required a strongly folded $Ti(\mu\text{-}O)_2Ti$ bridge.[12]

The evidence that 1 is a paramagnetic Ti(III)/Ti(II) complex was provided by the ESR spectra of its toluene solution at 296 K and at 77 K. The triplet splitting (a = 4.3 G) at g = 1.9871 found at ambient temperature is due to the interaction of the Ti(1) d^1 electron with two μ-H equivalent nuclei. In frozen glass, the triplet splitting was observed for two components of the rhombic **g** tensor. Coupling to $^{47/49}Ti$ isotopes was not observed. In the structurally similar complex 3, low values of $a_{iso,H}$ (4.8 G) and $a_{iso,Ti}$ (4.0 G) were explained by the unpaired electron exchanging sites at the low-spin Ti(II) and Ti(III) centers.[14] The assumption of a mixed-valence Ti(III)/Ti(II) complex is corroborated by the presence of the absorption band in the near-infrared region at λ_{max} = 1040 nm.[4b] The d electrons of Ti(II) may partly reside in a low-energy MO involving the LUMO of the bridging ligand. The evidence for such as electronic structure in $(C_5Me_5)TiAd^*$ was obtained from UPS spectra.[16]

Structurally analogous compounds were obtained by the same treatment of $(C_5Me_5)_2TiCl_2$ and $(C_5H_2Me_3)_2TiCl_2$

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(10) Crystal data for 1: $C_{27}H_{39}Ti_2$, M_r = 459.4; orthorhombic, *Pnma*; a = 8.364(1), b = 15.492(3), c = 18.429(4) Å; Z = 4, R = 0.041, R_w = 0.043 for 1712 observed reflections ($I \geq 2\sigma(I)$) of 2975 measured. All non-hydrogen atoms were refined anisotropically and all H atoms isotropically. A full X-ray structure report for 1 has been deposited as supplementary material.

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as the thermally robust products. Further studies of the electronic structure and chemical reactivity of this series of compounds are under way.

Acknowledgment. This work was supported by the Grant Agency of the Academy of Sciences of the Czech Republic (No. 44014). Chemetall, GmbH, Frankfurt, FRG, is acknowledged for a gift of lithium aluminum hydride. We wish to thank Dr. V. Hanuš for the mass spectrometric analysis.

Supplementary Material Available: A complete crystal structure report for 1, including tables of crystal data, positional parameters, general displacement parameter expressions (*U*'s), bond distances, and valence angles (8 pages). Ordering information is given on any current masthead page.

OM930278I