

Synthesis and X-Ray Crystal Structure of the Permethyltitanocene Hydride–Magnesium Hydride Complex $[\{(C_5Me_5)_2Ti(\mu-H)_2\}_2Mg]$

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The trinuclear hydride complex $[\{(C_5Me_5)_2Ti(\mu-H)_2\}_2Mg]$ **1** was obtained from the $[(C_5Me_5)_2TiCl_2]-Pr^iMgCl-Et_2O$ system; the X-ray crystal structure of **1** shows two mutually perpendicular permethyltitanocene moieties coordinated through four bridging hydride bonds to the central pseudotetrahedrally coordinated magnesium atom.

The $[(C_5Me_5)_2TiCl_2]-Pr^iMgCl$ (1:2) system has been reported to be a specific catalyst for linear head-to-tail dimerization of terminal acetylenes.¹ The nature of the catalytically active species was proposed mostly on a speculative basis and therefore we have studied the catalytic system by EPR spectroscopy in detail. A rapid reduction of $[(C_5Me_5)_2TiCl_2]$ to $[(C_5Me_5)_2TiCl]^{2-}$ ³ was followed by much slower conversion of the latter into a complex characterized by a poorly resolved EPR spectrum at $g = 1.9906$ showing a triplet splitting ($a = 0.68$ mT). EPR spectra with similar parameters were previously observed in $[(C_5H_5)_2TiCl_2]-Grignard$ reagent systems and were tentatively ascribed to the $[(C_5H_5)_2TiH_2]$ anion.⁴ EPR evidence for the presence of a $[(C_5H_5)_2Ti(\mu-H)_2MgBr]$ complex in such a system was reported later.⁵ After 3 days at room temperature, the purple $[(C_5Me_5)_2TiCl]-Pr^iMgCl$ reaction mixture containing precipitated $MgCl_2$ was evaporated *in vacuo* and the residue was extracted with hexane to remove the blue product affording the above EPR spectrum. The residue was then extracted with toluene. The pale purple solution obtained showed a single EPR signal at $g = 1.9896$, $\Delta H = 2.1$ mT, at room temperature and in a frozen glass at -130 °C an EPR spectrum typical of a triplet electronic state. Its parameters, $g_{x,y} = g_z = 1.9901$, $D = 0.01217$ cm⁻¹ and $E = 0$, imply cylindrical symmetry in a two-electron system. Partial evaporation of the toluene solution afforded a crop of dark platelet crystals of $[\{(C_5Me_5)_2Ti(\mu-H)_2\}_2Mg]$ **1**.[†] A toluene solution prepared from these crystals gave the same EPR spectrum as that of the mother liquor.

The X-ray crystal structure of **1** was determined.[‡] The trinuclear complex consists of two mutually perpendicular $(C_5Me_5)_2Ti(\mu-H)_2$ fragments attached to one central Mg atom through four equivalent Ti–H–Mg bridges. The Mg atom is

pseudotetrahedrally coordinated by four H atoms at distances in the range 1.81–1.94 Å. The average value of 1.88 Å corresponds well with the Mg–H distance of 1.96 Å in the Mg–H–Al bridge in magnesium μ -9,10-dihydro-9,10-anthrylene-aluminate containing a five-coordinated Mg atom,⁶ and with the Mg–H distance of 1.95 Å for the six-coordinated Mg in MgH_2 .⁷ The Ti–H distances in the planar $Ti(\mu-H)_2Mg$ bridges range from 1.66 to 1.79 Å (av. 1.73 Å). These values are in accord with the Ti–H distances in the $Ti(\mu-H)_2Ti$ bridge in dimeric titanocene (av. 1.73 Å)⁸ or with the Ti–H distance of 1.72 Å in Ti–H–Al bridges.⁹ The H–Mg–H angles in the planar $Mg(\mu-H)_2Ti$ rings are 70(3) and 73(3)° and the analogous H–Ti–H angles are 78(3) and 80(3)°. The planes of the $Mg(\mu-H)_2Ti$ bridges in **1** are virtually perpendicular. The angle between the best planes of the C_5Me_5 rings of both $(\eta^5-C_5Me_5)_2Ti$ moieties (36°) is within 1° of that in $(\eta^5-C_5Me_5)_2TiCl$.²

Compound **1** is another example of a trinuclear bis(titanocene) (Ti^{III}) complex with a central main group metal element giving a triplet electronic state. The crystallographic $Ti \cdots Ti$ distance of 5.7 Å in **1** fits well with the value found for the zero-field splitting parameter D . Known compounds of this type are the $[\{(C_5H_5)_2Ti(\mu-X)_2\}_2Zn]$ ($X = Cl, Br$) complexes¹⁰ with a $Ti \cdots Ti$ distance of 6.84 Å for the chloro compound.¹¹ On the other hand, the only structurally characterized titanocene–Mg complexes $[\{(C_5H_5)_2Ti(\mu-Cl)_2\}_2Mg]$ and $[\{(C_5H_5)_2Ti(\mu-Cl)_2Mg(\mu-Cl)_2\}_2]$, did not show any $Ti^{III}-Ti^{III}$ electron spin interaction.¹²

Compound **1** is probably formed from the complex characterized by the EPR spectrum with triplet splitting (*vide supra*) whose structure is tentatively assumed to be $[(C_5Me_5)_2Ti(\mu-H)_2Mg](OEt)_nCl$ ($n = 1$ or 2) (*cf.* ref. 4) or its chloride

[†] Preparation of **1**: $[(C_5Me_5)_2TiCl_2]$ (0.50 g, 1.28 mmol) was suspended in dry, degassed Et_2O and Pr^iMgCl in Et_2O (2.5 mol l⁻¹, 5 ml) was added. The stirred mixture turned intense blue within 30 min and after 3 days had changed to a purple colour. The ether was evaporated off *in vacuo* and the residue was extracted with hexane to give a blue solution. The residue was extracted with toluene, yielding a pale purple solution. Dark needles separated upon cooling of the concentrated toluene solution. The yield of crystalline **1** was 0.12 g (28%).

[‡] Crystal Data for **1**: $C_{40}H_{64}MgTi_2$, $M = 665.01$, triclinic, space group $P\bar{1}$, $a = 8.887(2)$, $b = 12.142(4)$, $c = 18.971(6)$ Å, $\alpha = 78.96(2)$, $\beta = 86.29(3)$, $\gamma = 74.82(3)^\circ$, $V = 1938$ Å³, $Z = 2$, $D_c = 1.14$ g cm⁻³, $\mu(Mo-K\alpha) = 4.46$ cm⁻¹, $R = 0.059$, $R_w = 0.062$ for 2733 observed reflections with $I > 2\sigma(I)$. Data were collected on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated $Mo-K\alpha$ radiation ($1 \leq \theta \leq 22^\circ$). The structure was solved using direct methods and Fourier syntheses. All non-hydrogen atoms were refined anisotropically and the four bridging H atoms isotropically. Methyl hydrogen atoms were included in calculated positions and refined riding on their attached carbon atoms. Unusually high thermal parameters were observed for the carbon atoms of the C_5Me_5 ligands attached to $Ti(2)$, indicating some disorder. Crystallographic calculations were carried out using SDP programs. Atom coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

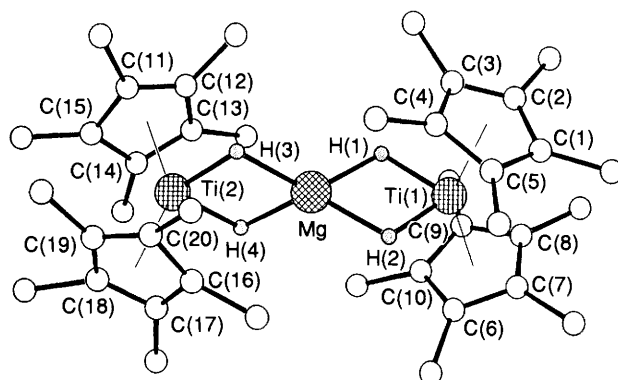


Fig. 1 Molecular structure of **1**. Atoms are represented by spheres of arbitrary radius. Selected interatomic distances (Å) and valence angles (°) are given for one half of the molecule; the corresponding values for the other half are virtually the same. $Ti(1) \cdots Mg$ 2.860(4), $Ti(1)-H(1)$ 1.66(5), $Ti(1)-H(2)$ 1.75(7), $Ti(1)-C(1)$ 2.411(9), $Ti(1)-C(2)$ 2.42(1), $Ti(1)-C(3)$ 2.405(9), $Ti(1)-C(4)$ 2.388(7), $Ti(1)-C(5)$ 2.368(7), $Ti(1)-C(6)$ 2.42(1), $Ti(1)-C(7)$ 2.404(8), $Ti(1)-C(8)$ 2.384(7), $Ti(1)-C(9)$ 2.358(8), $Ti(1)-C(10)$ 2.392(8), $Mg-H(1)$ 1.94(5), $Mg-H(2)$ 1.81(6); $H(1)-Ti(1)-H(2)$ 78(3), $H(1)-Mg-H(2)$ 70(3), $Ti(1)-H(1)-Mg$ 105(3), $Ti(1)-H(2)-Mg$ 107(4).

bridged dimer.¹³ Thorough study of the reactions yielding **1** is under way.

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