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Preliminary Communication

A titanium-magnesium complex containing perpendicularly bridging bis(trimethylsilyl)acetylene ligands: $[(\eta^5\text{-}C_5H_5)Ti][(\eta^5\text{-}C_5H_5)Mg][\mu\text{-}\eta^2:\eta^2\text{-}C_2(SiMe_3)_2]_2$

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Abstract

The complex $[(\eta^5\text{-}C_5H_5)Ti][(\eta^5\text{-}C_5H_5)Mg][\mu\text{-}\eta^2(Ti, Mg):\eta^2(Ti, Mg)\text{-}C_2(SiMe_3)_2]_2$ (**1**) was obtained by the reaction of $(\eta^5\text{-}C_5H_5)_2Ti(\eta\text{-}C_2(SiMe_3)_2)$ (**2**) with Mg and bis(trimethylsilyl)acetylene in THF. Crystals of **1** contain two slightly different molecules in the asymmetric unit. Both molecules contain Ti and Mg atoms in the apical positions of a nearly symmetrical rectangular bipyramid whose base is formed by four equivalent acetylenic carbons atoms. Each metal atom is capped by one $\eta^5\text{-}C_5H_5$ ligand.

Whereas a large number of titanocene binuclear and trinuclear Ti-Al complexes bridged through hydrogen [1] or halogen [2] atoms are known, the first titanocene-Mg complexes were structurally characterized only recently when the crystalline $[(Cp)_2Ti(\mu\text{-}Cl)_2]_2Mg(THF)_2$($Cp = \eta^5\text{-}C_5H_5$) and $[Cp_2Ti(\mu\text{-}Cl)_2Mg(THF)_2(\mu\text{-}Cl)]_2$ complexes were isolated from the $Cp_2TiCl_2 + Mg + THF$ system [3]. In the presence of disubstituted acetylenes, the titanocene (Ti^{II}) species generated in the above system are stabilized by the coordination of the acetylene in a π-bonding manner. The structures of the $(C_5Me_5)_2Ti(Me_3SiC{\equiv}CSiMe_3)$ [4], $Cp_2Ti(PhC{\equiv}CSiMe_3)$ and $(C_5Me_5)_2Ti(PhC{\equiv}CSiMe_3)$ [5] complexes were established by X-ray single crystal analysis and the structures of $Cp_2Ti(Me_3SiC{\equiv}CSiMe_3)$ (**2**) [6], $Cp_2Ti(PhC{\equiv}CPh)$ [7,8], and $Cp_2Ti(MeC{\equiv}CMe)$ [8] were inferred from their NMR and infrared spectral data and chemical properties. Among these complexes **2** shows a very low reactivity in addition reactions; it does not react with an excess of $Me_3SiC{\equiv}CSiMe_3$ (BTMSA) and the acetylene is displaced by diphenylacetylene, acetone, or benzophenone [6]. The ready displacement of BTMSA by 1,4-bis(trimethylsilyl)-1,3-butadiyne followed by the scission of the diyne ligand has recently been shown to afford $[(Cp_2TiC{\equiv}CSiMe_3]_2$ in high yield [9].

Here we describe the preparation and X-ray structure of a binuclear Ti-Mg complex $(CpTi)(CpMg)[(\mu\text{-}C_2(SiMe_3)_2]_2$ (**1**) arising from the reaction of $Cp_2Ti(Me_3SiC{\equiv}CSiMe_3)$ (**2**) [6] with Mg and BTMSA in THF (eqn. (1)).

$$\underset{(\mathbf{2})}{Cp_2Ti(\eta\text{-}C_2(SiMe_3)_2)} + Mg + Me_3SiC{\equiv}CSiMe_3 \rightarrow \underset{(\mathbf{1})}{(CpTi)(CpMg)\left[\mu\text{-}\eta^2:\eta^2\text{-}C_2(SiMe_3)_2\right]_2} \quad (1)$$

The same product was also obtained when after the formation of **2** by reduction of Cp_2TiCl_2 with an excess of Mg in the presence of an excess of BTMSA in THF the reaction was prolonged [10 *].

The X-ray single crystal analysis of **1** [11 *] revealed that there are two slightly different molecules, denoted by **1** (1) and **1** (2), in the asymmetric unit. The molecular structure of **1** (1) is shown in Fig. 1. Selected interatomic distances and valence angles for **1**(1) and **1**(2) are listed in Table 1. The acetylenic carbon atoms of the $Me_3SiC{\equiv}CSiMe_3$ ligands form the base of a nearly rectangular bipyramid (maximum deviation from the least square plane 0.013 Å for **1** (1) and 0.006 Å for **1** (2)) with the Ti and Mg atoms at its apexes. Both the metal atoms are capped with η^5-Cp ligands in a slightly staggered configuration. The coordination environments of the Ti and Mg atoms are apparently so similar that they are disordered within each independent molecule. The refinement of a site occupation factor shows that this disorder has to be taken into account in the interpretation in particular of bond distances and angles involving the metal atoms. Estimation of the individual metal–C (acetylene) bond distances by extrapolation by the least square method indicates that the Ti–C (acetylene) bond distances (av.

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* Reference number with asterisk indicates a note in the list of references.

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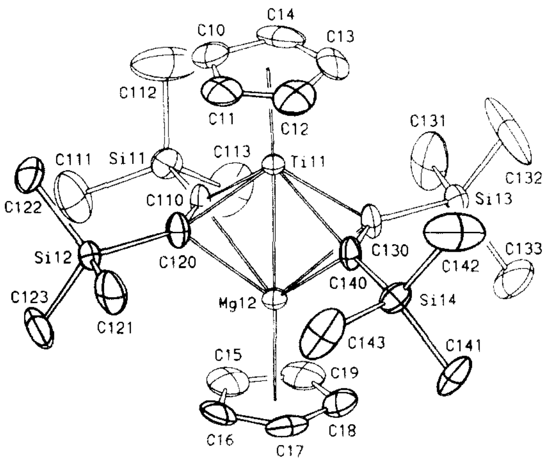

Fig. 1. The molecular structure and atom numbering scheme for **1**(1).

2.03 (±0.03) Å) are distinctly shorter than the Mg–C(acetylene) bond distances (av. 2.44 (±0.03) Å) whereas the metal–C(Cp) bond lengths are nearly the same (Ti–CE av. 2.08 (±0.02) and Mg–CE av. 2.03 (±0.02) Å). The difference in metal–C(acetylene) bond lengths is reflected in a slight displacement of the Si atoms from the bipyramid base plane towards Mg by a mean of about 0.10 Å. The BTMSA ligands show a C–C bond length of 1.31(1) Å for **1**(1) and 1.33(1) Å for **1**(2), and the C–C–Si angle is on average 140(2)°. The values of both of the parameters indicate a change from sp to sp^2 hybridization at the carbon atoms upon coordination. These values differ only slightly from those found in $(C_5Me_5)_2Ti(Me_3SiC{\equiv}CSiMe_3)$ (1.309 Å, av. 135.4°) [4]; the latter values should not differ considerably from those for $Cp_2Ti(Me_3SiC{\equiv}CSiMe_3)$ as only negligible differences in these parameters were found between the $(C_5Me_5)_2Ti(PhC{\equiv}CSiMe_3)$ and $Cp_2Ti(PhC{\equiv}CSiMe_3)$ complexes [5]. It must be emphasized that the distances between neighbouring carbon atoms of the base of the bipyramid belonging to different BTMSA ligands, on average 3.24(3) Å, prove the absence of a cyclobutadiene ring in **1**. The Ti–Mg distance (av. 2.776(2) Å) is only slightly longer than the sum of the covalent radii of Ti (1.32 Å) and Mg (1.36 Å) [13], but considerably shorter than the sum of the valence radii of metallic Ti (1.448 Å) and metallic Mg (1.599 Å) [14]. Hence, the presence of a Ti–Mg single bond can be regarded as established in **1**.

TABLE 1. Selected bond distances (Å) and valence angles (°) for **1**(1) and **1**(2) (esd's in parentheses)

Bond distances			
Ti(11)–Ce(Cp ring)	2.064(12)	Mg(12)–CE(Cp ring)	2.056(10)
Ti(11)–C(Cp) (av.)	2.371(14)	Mg(12)–C(Cp)av.	2.370(9)
Ti(11)–C(110)	2.224(7)	Mg(12)–C(110)	2.291(7)
Ti(11)–C(120)	2.183(7)	Mg(12)–C(120)	2.266(7)
Ti(11)–C(130)	2.208(7)	Mg(12)–C(130)	2.296(7)
Ti(11)–C(140)	2.194(7)	Mg(12)–C(140)	2.231(7)
C(110)–Si(11)	1.855(7)	C(110)–C(120)	1.308(10)
C(120)–Si(12)	1.860(7)	C(130)–C(140)	1.307(9)
C(130)–Si(13)	1.865(7)	Ti(11)–Mg(12)	2.777(2)
C(140)–Si(14)	1.861(7)		
Ti(21)–CE(Cp ring)	2.068(10)	Mg(22)–CE(Cp ring)	2.050(11)
Ti(21)–C(Cp) (av.)	2.379(6)	Mg(22)–C(Cp) av.	2.361(15)
Ti(21)–C(210)	2.158(6)	Mg(22)–C(210)	2.263(7)
Ti(21)–C(220)	2.150(7)	Mg(22)–C(220)	2.373(7)
Ti(21)–C(230)	2.156(7)	Mg(22)–C(230)	2.290(7)
Ti(21)–C(240)	2.143(7)	Mg(22)–C(240)	2.369(7)
C(210)–Si(21)	1.856(7)	C(210)–C(220)	1.329(9)
C(220)–Si(22)	1.857(7)	C(230)–C(240)	1.330(9)
C(230)–Si(23)	1.848(7)	Ti(21)–Mg(22)	2.774(2)
C(240)–Si(24)	1.868(7)		
Valence angles			
Ti(11)–C(110)–Mg(12)	75.9(2)	Si(11)–C(110)–C(120)	143.0(6)
Ti(11)–C(120)–Mg(12)	77.2(2)	Si(12)–C(120)–C(110)	138.9(6)
Ti(11)–C(130)–Mg(12)	76.1(2)	Si(13)–C(130)–C(140)	140.3(6)
Ti(11)–C(140)–Mg(12)	77.7(2)	Si(14)–C(140)–C(130)	137.7(6)
Ti(21)–C(210)–Mg(22)	77.7(2)	Si(21)–C(210)–C(220)	138.8(5)
Ti(21)–C(220)–Mg(22)	75.5(2)	Si(22)–C(220)–C(210)	140.7(5)
Ti(21)–C(230)–Mg(22)	77.2(2)	Si(23)–C(230)–C(240)	138.9(5)
Ti(21)–C(240)–Mg(22)	75.7(2)	Si(24)–C(240)–C(230)	141.2(5)

Atoms of **1**(1) are denoted by numbers (1...), those of **1**(2) by (2...).

A solution of compound **1** in THF or hexane gives no ESR signal. The well-resolved ^1H and ^{13}C NMR spectra of **1** indicate that it is a diamagnetic complex containing two nonequivalent Cp ligands and two equivalent BTMSA ligands. The ^{13}C NMR chemical shift of the acetylene C atoms (269.07 ppm) differs considerably from that of **2** (244.70 ppm) [6], in agreement with the assumed delocalization of electron density over the acetylene ligands in **1** (*vide infra*).

The structure of **1**, and its genesis, diamagnetism and high thermal stability, allow us to regard both the Ti and Mg atom as bivalent. One of the valencies in each case participates in the regular metal–Cp bond whereas the other must be involved in mutual bonding of the (CpTi) and (CpMg) moieties. The latter is achieved either through a direct Ti–Mg single bond (*vide supra*) or through the bridging bonds, generating a negative charge at each of the acetylene ligands. Both the bonding modes were found to be acceptable by an MO study of a number of transiton metal complexes with perpendicularly bridging acetylene ligands [15]. The d^2 electrons of Ti^{II} are presumably delocalized in low-energy MO orbitals involving $\pi\star$ orbitals. The absence of d^2 electrons in **1** follows from its electronic absorption spectrum which shows an absorption band at 525 nm (ϵ *ca.* 10^2 cm^2 $mmol^{-1}$) that can be tentatively assigned to a π–d transition. The analogous delocalization of d^2 electrons has been established by UPS and electronic absorption spectroscopy for exomethylene derivatives of permethyltitanocene [16]. In contrast to **1**, a pentacoordinated Ti^{II} in the square pyramidal (η^6-arene)$TiAl_2Cl_{8-x}Et_x$ (X = Cl, Br; $x = 0–2$) complexes gives a d–d absorption band at 800 nm (ϵ *ca.* 10 cm^2 $mmol^{-1}$) [17,18].

A large number of transition metal complexes with perpendicularly-bridging bent acetylene ligands possess common structural features, including a C–C bond length of 1.3–1.4 Å, a C–C–R angle of 130–150°, and metal–metal distance ranging between 2.2 and 3.5 Å [15,19], but only a few complexes with two perpendicularly bridging acetylenes are known, namely the homonuclear $Nb_2(CO)_2Cp_2(\mu\text{-}C_2R_2)_2$ [20] and $Fe_2(CO)_4(\mu\text{-}C_2t\text{-}Bu_2)_2$ [21] and the heteronuclear $CpM(CO)(\mu\text{-}CF_3C{\equiv}CCF_3)_2Co(CO)_2$ (M = Mo, W) complexes [22]. Complex **1** is the first titanium complex with perpendicularly bridging acetylene ligands and the first heteronuclear complex of this type containing a Main Group element.

The structural chemistry of magnesium has been recently reviewed [23]. The bonding of Mg in **1**, mimicking that of a transition-metal, presents new aspects of the nature of Mg–C bonding [24], and opens up new perspectives for the coordination chemistry of Main Group metals.

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10 Preparation of **1**. Cp_2TiCl_2 (1 g, 4 mmol) and magnesium turnings (Fluka, for Grignard reagents) 1 g, 44 mmol) were placed in an ampoule and BTMSA (1.8 ml, 8 mmol) and THF (40 ml) were distilled in under vacuum. The frozen mixture was sealed off, warmed to ambient temperature and magnetically stirred. The red colour of the mixture gave way to the yellow colour of the $Cp_2Ti(\eta\text{-}C_2(SiMe_3)_2)$ complex within 1 h, and the colour subsequently slowly changed to green. After overnight stirring the clear green solution was evaporated in vacuum and the red residue extracted with hexane to give a clear red solution and a white residue of $MgCl_2$. Dark red crystals of **1** were obtained by cooling of the concentrated hexane solution. Yield of crystalline **1** 1.85 g, 85%. Toluene solution of **1** was stable to 150°C. MS (direct inlet, 135–155°): m/z (relative intensity) 542 (M^+, 0.5), 372 (1.0), 348 (6.7), 283 (1.5), 281 (2.5), 277 (1.5), 275 (3.3), 243 (0.6), 241 (1.3), 202 (Cp_2TiMg, 4.8), 178 (Cp_2Ti, 100), 155 (93), 113 (CpTi, 10), 89 (CpMg, 4.5), 73 (73), 65 (11). Elemental analysis: 542.1992, error $+1.4\cdot10^{-3}$ for $C_{26}H_{46}MgSi_4Ti$; 202.0115, error $-3\cdot10^{-4}$ for $C_{10}H_{10}MgTi$. ^1H NMR (400 MHz, C_6D_6, 25°C): δ 0.132 s (36 H), 5.983 s (5 H), 6.402 s (5 H); ^{13}C NMR (100 MHz, C_6D_6, 25°C): δ 1.43 q, 107.87 d, 110.62 d, 269.07 s; UV-Vis (hexane): 377 (vs), 525 (m, sh) nm.

11 Crystal structure determination of **1** (Phillips PW 1100 single crystal diffractometer, graphite monochromator, Mo K_α radiation (λ 0.71069 Å), room temperature): $C_{26}H_{46}MgSi_4Ti$, M = 543.18, monoclinic, $P2_1/c$, a 16.242(1), b 24.934(2), c 16.328 (1) Å, β 90.647(8)°, V 6612.06 $Å^3$, D_c 1.091 g cm^{-3}, $Z = 8$, μ 3.90 cm^{-1}. A dark red, nearly rectangular crystal fragment of 0.40× 0.50×0.60 mm was mounted in a glass capillary under purified nitrogen. Crystal data were collected by $\theta/2\theta$-method; $2\theta_{max}$ = 48°. A total of 7019 unique reflections with $F_o > 2\sigma(F_o)$, out of 9860 observed reflections, were used for further calculations. The structure was solved by iterative symbolic addition. Two different

molecules denoted **1**(1) and **1**(2) were found in the asymmetric unit. Further refinement showed that the Ti and Mg atoms were disordered within each independent molecule. A site occupation factor (sof) was therefore refined for both the **1**(1) and **1**(2) molecules in such a way that the Ti(sof) position is partly occupied by Mg(1-sof) and the Mg(sof) position is partly occupied by Ti(1-sof). Coordinates and temperature factors were set equal for Ti(sof), Mg(1-sof) and Mg(sof), Ti(1-sof), respectively. Final values of sof were found to be 0.5989(8) for **1**(1) and 0.7054(7) for **1**(2). Hydrogen atoms were included in calculated positions. All non-hydrogen atoms were refined with anisotropic temperature factors. The final R indices were $R = 0.086$, $R_w = 0.086$. The PC ULM-package [12] was used for all the calculations. Further details concerning the crystal structure analysis are available upon request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, W-7514 Eggenstein-Leopoldshafen 2 (Germany) by quoting the deposition number CSD-55608, the name of the author and the journal citation.

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