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Easy formation of titanocene hydride–magnesium complexes in the $(C_5H_{5-n}Me_n)_2TiCl_2$ ($n = 3$–5)–dibutylmagnesium systems ☆

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Abstract

Complexes $[(C_5H_{5-n}Me_n)_2Ti(\mu\text{-}H)_2]_2Mg$ ($n = 3$–5) separate from the $(C_5H_{5-n}Me_n)_2TiCl_2$–Bu_2Mg (Bu = butyl) systems in toluene for Mg-to-Ti molar ratios 1–4 as crystalline materials. Crystal structures of the complexes ($n = 5$ (**1**): triclinic; $P\bar{1}$ ($Z = 2$); $a = 8.887(2)$ Å, $b = 12.142(4)$ Å and $c = 18.971(6)$ Å; $\alpha = 78.96(2)°$, $\beta = 86.29(3)°$ and $\gamma = 74.82(3)°$) ($n = 4$ (**2**): monoclinic; $C2/c$ ($Z = 4$); $a = 11.331(1)$ Å, $b = 13.177(2)$ Å and $c = 22.989(2)$ Å; $\beta = 99.18(1)°$) ($n = 3$ (**3**): triclinic; $P\bar{1}$ ($Z = 4$); $a = 12.603(3)$ Å, $b = 13.629(3)$ Å and $c = 19.561(6)$ Å; $\alpha = 70.77(2)°$, $\beta = 79.36(1)°$ and $\gamma = 83.41(1)°$) revealed a linear Ti–Mg–Ti arrangement with a pseudotetrahedral coordination of hydrogen atoms around the central magnesium atom. All the compounds show nearly identical electron spin resonance triplet-state spectra at $g = 1.990$ with $D = 0.012$–0.013 cm^{-1} and $E = 0$, in accordance with a nearly constant Ti(III)–Ti(III) distance of 5.54–5.72 Å. The complexes do not induce the polymerization of ethylene on the time scale of a month at room temperature.

Keywords: Magnesium; Titanocene; Hydride; Triplet state; Crystal structure; Catalysis

1. Introduction

Titanocene dichloride–alkylaluminium chloride systems are well-known homogeneous model systems for Ziegler–Natta polymerization catalysts [1,2]. These systems have been modified by changing the coordination capability of the central titanium atom both by introducing substituents at the cyclopentadienyl rings [3] and by changing the main group metal reducing agent. Among the reducing agents, various alkylaluminium compounds are most frequently used and, in the last decade, largely methylaluminoxanes [4,5]. Since numerous titanocene–aluminium complexes have been synthesized [6] and, since the presence of an organoaluminium component was often found to be inevitable for obtaining a suitable catalyst, binuclear Ti–Al complexes [7] or surface Al complexes on a bulk of $TiCl_3$ were proposed to be active centres of the olefin polymerization [8]. Achievements in this topic have been recently reviewed [9]. In the field of supported Ziegler–Natta catalysts the use of magnesium-containing carriers led to a discovery of highly active catalysts for polymerization of olefins [10–12]. The role of organomagnesium co-catalysts in homogeneous Ziegler–Natta systems have not been adequately investigated. The pioneering work by Brintzinger [13] on interactions in the $(C_5H_5)_2TiCl_2$–Grignard reagent systems opened the way to exploitation of such systems for the synthesis of allyltitanocenes [14,15]. An extension of Brintzinger's work to the complete series of methyl-substituted titanocene dichlorides combined with isopropyl Grignard reagents has recently occurred [16]. In the latter work, first X-ray structures of dimeric titanocene hydride–magnesium halohydride complexes $[(C_5HMe_4)_2Ti(\mu\text{-}H)_2Mg(OEt_2)(\mu\text{-}X)]_2$ (X = Cl or Br) were reported. The effect of methyl substituents was

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☆ Dedicated to Prof. Hans-H. Brintzinger on the occasion of his 60th birthday.

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observed in the case of the $(C_5Me_5)_2TiCl_2$–^{1}PrMgCl system where the dimeric product released one molecule of $MgCl_2$ to give a trinuclear Ti–Mg–Ti complex $[(C_5Me_5)_2Ti(\mu\text{-}H)_2]_2Mg$ (**1**) [17].

As the presence of ethereal solvents in the polymerization catalytic systems usually suppresses the catalytic activity, we have studied the reactions of the $(C_5H_{5-n}Me_n)_2TiCl_2$ complexes with commercially available dibutylmagnesium (Bu_2Mg) in hydrocarbon solvents. Here we report the formation of **1** and its analogues in the $(C_5H_{5-n}Me_n)_2TiCl_2$–Bu_2Mg systems, their crystal structures and some properties.

2. Experimental section

2.1. General data and methods

All operations with Ti(III) complexes were performed under vacuum in all-sealed devices equipped with magnetically breakable seals. A combined device equipped with a couple of quartz cuvettes (1 cm and 1 mm) and a quartz electron spin resonance (ESR) tube was used for the UV–visible and ESR measurements. Single crystals were adjusted into capillaries for X-ray analysis and KBr pellets were prepared in a glove-box (Braun) under purified nitrogen. UV–visible spectra were measured in the range 280–2000 nm on a Varian Cary 17D spectrometer using all-sealed quartz cuvettes (Hellma). ESR spectra were recorded on an ERS-220 spectrometer (Centre for Production of Scientific Instruments, Academy of Sciences, Berlin, Germany) in the X band. g values were determined using an Mn^{2+} ($M_I = -\frac{1}{2}$ line) standard at $g = 1.9860$ and a proton magnetometer MJ-110 R (Radiopan, Poznan, Poland). Concentrations of the paramagnetic compounds were estimated from integrated first derivation spectra. A variable-temperature unit STT-3 was used for the measurement in the range from −130 to +20°C. Samples in capillaries for mass spectroscopy (MS) analysis were opened and inserted into the direct inlet of a JEOL D-100 spectrometer under argon. IR spectra of KBr pellets in a gas-proof cuvette were recorded on a Mattson Galaxy 2020 spectrometer.

2.2. Chemicals

Toluene was purified by conventional methods, dried by refluxing over $LiAlH_4$ and stored as a solution of dimeric titanocene $(C_{10}H_8)[(C_5H_5)TiH]_2$. A 1.0 M solution of Bu_2Mg in heptane (Aldrich) was distributed into ampoules under argon and then degassed. The titanocene dichlorides $(C_5H_3Me_2)_2TiCl_2$ (1,3-dimethyl) [18], $(C_5H_2Me_3)_2TiCl_2$ (1,2,3-trimethyl), $(C_5HMe_4)_2TiCl_2$ and $(C_5Me_5)_2TiCl_2$ [19] were prepared according to literature procedures and were finally purified by crystallization from toluene.

2.3. Preparation of $[(C_5Me_5)_2Ti(\mu\text{-}H)_2]_2Mg$ (1)

$(C_5Me_5)_2TiCl_2$ (0.389 g, 1 mmol) was largely dissolved in 15 ml of toluene, and Bu_2Mg (3 mmol) in heptane was added while stirring. The red colour of the solution rapidly changed to dirty green and after 15 min to dirty brown. After standing overnight an agglomerate of dark needle crystals grew at the bottom and a pale-purple solution contained a slightly brown suspension of $MgCl_2$. The solution with most of the suspension was poured away and the crystals were washed with the same solvent mixture distilled backwards to remove the $MgCl_2$ suspension. Another crop of crystals was obtained from the mother liquor after the clear purple solution was separated from the sediment. Half of the solvent's volume was evaporated in vacuo and the remaining part was warmed to 100°C to dissolve all precipitated solid. Crystals were obtained by slow cooling. The crystals from both crops were collected and recrystallized from hot toluene. The yield of crystalline **1** was 80% (0.27 g).

ESR (toluene, 20°C): $g = 1.9896$, $\Delta H = 2.1$ mT, ESR (toluene, −130°C): $g = 1.9901$, $D = 0.01217$ cm^{-1}, $E = 0$. IR (KBr pellet): ν 1215 (s,b) cm^{-1}. MS (direct inlet, 200°C): m/e(%) slow decomposition, 664 M^+ in an envelope of m/e 656–668, 318 ($[(C_5Me_5)_2Ti]^+$, 100) and m/e 317–308. UV-visible (toluene, 20°C): λ 490, 590(sh), 760(sh) nm. The ESR and mass spectra are almost identical with those published earlier [17].

2.4. Preparation of $[(C_5HMe_4)_2Ti(\mu\text{-}H)_2]_2Mg$ (2)

$(C_5HMe_4)_2TiCl_2$ (0.36 g, 1 mmol) was largely dissolved in 15 ml of toluene and Bu_2Mg (3 mmol) in heptane was added. Following the isolation procedure described for **1**, crystalline **2** in the form of dark monoclinic platelets was obtained with a yield of 0.25 g (82%). An analogous procedure using 2 mmol of Bu_2Mg afforded 0.15 g of **2** (50%); using 4 mmol of Bu_2Mg, 0.2 g of **2** (65%) was obtained.

ESR (toluene, 20°C): $g = 1.9908$, $\Delta H = 1.2$ mT, ESR (toluene, −130°C): $g = 1.9907$, $D = 0.01327$ cm^{-1}, $E = 0$. IR (KBr pellet): ν 719(s), 764(m), 816(s), 1024(m), 1177(sh), 1235(vs) cm^{-1}. MS (direct inlet, 150–170°C): m/e(%) 610(1.4), 609(3.0), 608($M^{\cdot +}$, 5.7), 607(4.5), 606(7.1), 605(3.4), 604(3.9), 603(2.0), 602(2.3), 458(4.3), 292(9.8), 291(27), 290($[(C_5HMe_4)_2Ti]^+$, 100), 289(75), 288(29), 287(26), 286(11.5), 285(17), 284(9.3), 283(11), 282(4.1), 281(5.0), 273(6.1), 272(4.1), 271(6.8), 269(4.1). UV-visible (toluene, 20°C): λ 490, 590(sh), 740(sh) nm.

2.5. Preparation of $[(C_5H_2Me_3)_2Ti(\mu\text{-}H)_2]_2Mg$ (3)

$(C_5H_2Me_3)_2TiCl_2$ (1,2,3-trimethyl) (0.33 g, 1 mmol) was mixed with 7 ml of toluene and Bu_2Mg (3 mmol) in heptane was added under vigorous stirring. The mixture was further stirred at 50°C for 3 h until all solid titanocene dichloride had disappeared. After standing overnight at ambient temperature, several large dark-blue platelets crystallized out from a pale-purple solution and a light-brown sediment of $MgCl_2$. The crystals were isolated as described for **1** except that no attempt was made to obtain additional product from the mother liquor. The estimated yield was about 0.05 g (18%). Selected crystals were used for the X-ray analysis and spectroscopic measurements.

ESR (toluene, 20°C): $g = 1.9913$, $\Delta H = 1.2$ mT. ESR (toluene, −130°C): $g = 1.9919$, $D = 0.0132\ cm^{-1}$, $E = 0$. IR (KBr pellet): ν 723(m), 760(w), 781(s), 1026(m), 1190(s), 1223(sh), 1250(s) cm^{-1}. UV–visible (toluene, 20°C): λ 495, 600(sh), 700(sh) nm.

The mother liquor was evaporated in vacuum and the residue was extracted with hexane. Most of the coloured product had dissolved to give a clear purple solution. The hexane was replaced by toluene. The toluene solution gave a UV–visible spectrum identical with that of **3**. The ESR spectrum at 20°C was the same as that of **3**; in a glassy state at −130°C it showed a mixture of the spectrum of **3** and an asymmetric line at $g = 1.9913$, $\Delta H = 1.5$ mT, in comparable intensities.

2.6. Attempted preparation of $[(C_5H_3Me_2)_2Ti(\mu\text{-}H)_2]_2Mg$ (4)

An experiment analogous to that for obtaining **3** using $(C_5H_3Me_2)_2TiCl_2$ (1,3-dimethyl) resulted in a purple solution and a brownish sediment. The solution in pure toluene gave a strong ESR signal at $g = 1.9910$ but, upon cooling to −130°C, only a very weak spectrum of **4** with the parameters virtually identical with those of **3** was observed in addition to an asymmetric single line at $g = 1.9920$, $\Delta H = 1.5$ mT. All the titanium-containing products were very soluble in hexane.

2.7. Attempted reaction of 1 and 2 with ethylene

Ethylene from a gas reservoir (75 Torr in 4 l) was condensed into an ampoule (200 ml) equipped with breakable seals, and a saturated toluene solution of **1** or **2** (15 ml) was added. After 1 month at room temperature the pale-purple colour of the solution had not changed and only traces of white polymer were observed on walls. The mixture was cooled and ethylene was pumped off. Liquid solvent was distilled into a cooled trap and the residue was extracted with toluene. The solution gave UV–visible and ESR spectra of pure **1** or **2**. The yield of an insoluble polymer was less than 10 mg. The trapped solvent contained only toluene, according to gas chromatography–MS analysis.

Table 1
Crystallographic data and experimental details for **1**–**3**

	1	**2**	**3**
Crystal data			
Chemical formula	$C_{40}H_{64}MgTi_2$	$C_{36}H_{56}MgTi_2$	$C_{32}H_{48}MgTi_2$
Molecular weight ($g\ mol^{-1}$)	665.02	608.91	552.80
Crystal system	Triclinic	Monoclinic	Triclinic
Space group	$P\bar{1}$ (No. 2)	$C2/c$ (No. 15)	$P\bar{1}$ (No. 2)
a (Å)	8.887(2)	11.331(1)	12.603(3)
b (Å)	12.142(4)	13.177(2)	13.629(3)
c (Å)	18.971(6)	22.989(2)	19.561(6)
α (°)	78.96(2)	—	70.77(2)
β (°)	86.29(3)	99.18(1)	79.36(1)
γ (°)	74.82(3)	—	83.41(1)
V ($Å^3$)	1938.8	3388.6(6)	3111(3)
Z	2	4	4
D_{calc} ($g\ cm^{-3}$)	1.139	1.194	1.180
μ(Mo Kα) (cm^{-1})	4.46	4.9	5.0
Approximate crystal size (mm)	0.2 × 0.3 × 0.3	0.2 × 0.3 × 0.7	0.3 × 0.4 × 0.7
Data collection and refinement			
$2\theta_{max}$ (°)	44	52	44
Number of unique observed reflections, total	4459	3488	7652
$F_o > n(F_o)$	2733 ($n = 2$)	2353 ($n = 2$)	5378 ($n = 0$)
Number of variables	404	211	334
R	0.059	0.048	0.080
R_w	0.062	0.059	0.061

2.8. *X-ray crystal structure analysis of* ***1–3***

The crystal structure analysis of **1** was published in a short communication [17] and the crystal data have been deposited at the Cambridge Crystallographic Data Centre. Crystal fragments of **2** and **3** were fixed in capillaries under purified nitrogen in a glove-box (Braun) and were closed with a sealing wax. Data for **2** were collected on an Enraf–Nonius CAD-4 diffractometer and those for **3** on a Philips PW 1100 four circle diffractometer equipped with a STOE electronic control system, both at room temperature. Graphite-monochromated Mo Kα radiation was used in both cases. All the structures were solved by direct methods and Fourier syntheses. All non-hydrogen atoms were refined anisotropically and the four bridging H atoms isotropically. The hydrogen atoms of cyclopentadienyl ligands were included in calculated positions and refined riding on their attached carbon atoms. Calculations for **2** were performed by SHELX-86 and SHELX-76 programs those for **3** by use of the PC ULM package [20] incorporating the SHELX-76 program. Details of data collection and refinement for **1–3** are given in Table 1. Positional parameters and isotropic thermal factors are listed in Tables 2–4. Selected bond distances and bond angles are shown in Tables 5–7. A complete crystal structure report for **2** and **3** has been deposited at the Cambridge Crystallographic Data Centre.

Table 2
Positional parameters and B_{eq} values for **1**

Atom	x	y	z	B_{eq} (Å^2)
Ti(1)	0.2990(2)	0.7040(1)	0.64970(8)	2.64(3)
Ti(2)	0.1886(2)	0.3046(1)	0.83843(8)	3.36(4)
Mg	0.2392(4)	0.5050(3)	0.7434(2)	3.91(6)
C(1)	0.5361(9)	0.7508(7)	0.6001(5)	4.1(2)
C(2)	0.4963(9)	0.8039(7)	0.6607(5)	4.2(2)
C(3)	0.5055(9)	0.7158(7)	0.7216(5)	4.1(2)
C(4)	0.5515(9)	0.6078(7)	0.6973(5)	3.7(2)
C(5)	0.5662(9)	0.6301(7)	0.6229(5)	3.8(2)
C(6)	0.080(1)	0.7110(8)	0.5780(5)	4.6(2)
C(7)	0.160(1)	0.7870(8)	0.5396(5)	4.5(2)
C(8)	0.1514(9)	0.8761(7)	0.5771(5)	3.8(2)
C(9)	0.067(1)	0.8540(8)	0.6430(5)	4.8(2)
C(10)	0.0215(9)	0.7482(7)	0.6405(5)	4.1(2)
C(11)	0.196(1)	0.263(1)	0.9649(5)	10.2(4)
C(12)	0.256(1)	0.351(1)	0.9449(6)	10.0(4)
C(13)	0.140(2)	0.4414(8)	0.9153(5)	7.2(3)
C(14)	0.007(1)	0.403(1)	0.9183(5)	6.8(3)
C(15)	0.051(1)	0.2912(8)	0.9501(6)	9.1(3)
C(16)	0.319(1)	0.2064(8)	0.7443(5)	6.1(3)
C(17)	0.166(1)	0.2344(8)	0.7317(6)	7.5(3)
C(18)	0.096(1)	0.1774(8)	0.7831(7)	8.2(3)
C(19)	0.203(2)	0.1068(7)	0.8329(5)	7.8(3)
C(20)	0.348(1)	0.1315(8)	0.8087(5)	5.6(3)
C(21)	0.480(1)	0.9311(8)	0.6633(7)	7.4(3)
C(31)	0.492(1)	0.7355(9)	0.7981(5)	6.7(3)
C(41)	0.603(1)	0.4913(8)	0.7445(6)	6.4(3)
C(51)	0.624(1)	0.5434(8)	0.5761(6)	6.7(3)
C(61)	0.047(1)	0.6114(9)	0.5514(6)	8.1(3)
C(71)	0.227(1)	0.780(1)	0.4641(5)	7.7(4)
C(81)	0.189(1)	0.9905(9)	0.5473(7)	8.0(4)
C(91)	0.015(1)	0.931(1)	0.6980(6)	9.1(4)
C(100)	−0.090(1)	0.702(1)	0.6928(6)	7.7(4)
C(101)	0.575(1)	0.809(1)	0.5272(6)	7.3(3)
C(111)	0.215(2)	0.141(1)	1.0150(8)	17.8(9)
C(121)	0.423(1)	0.316(1)	0.9713(7)	18.2(8)
C(131)	0.187(2)	0.553(1)	0.9014(7)	18.6(8)
C(141)	−0.123(2)	0.511(2)	0.8921(7)	17.7(7)
C(151)	−0.101(2)	0.252(1)	0.9586(9)	17.9(6)
C(161)	0.447(2)	0.237(1)	0.6955(7)	16.2(5)
C(171)	0.098(2)	0.306(1)	0.6615(7)	16.8(7)
C(181)	−0.075(2)	0.184(1)	0.779(1)	17.1(6)
C(191)	0.173(2)	0.011(1)	0.8865(7)	17.0(8)
C(201)	0.500(2)	0.071(1)	0.8423(8)	16.3(5)
H(1)	0.250(6)	0.665(4)	0.735(3)	2(1)
H(2)	0.292(8)	0.560(6)	0.652(3)	1(1)
H(3)	0.335(8)	0.370(6)	0.806(4)	2(1)
H(4)	0.080(8)	0.426(6)	0.777(4)	2(1)

Table 3
Positional parameters and U_{eq} values for **2**

Atom	x	y	z	U_{eq} (Å^2)
Ti(1)	0.0860(1)	0.2513(1)	0.1431(1)	0.028(1)
Mg(1)	0.0000	0.2495(1)	0.2500	0.041(1)
H(1)	0.004(3)	0.177(3)	0.184(2)	0.05(1)
H(2)	0.095(3)	0.322(3)	0.212(2)	0.05(1)
C(1)	−0.0997(3)	0.2599(2)	0.0795(2)	0.039(2)
C(11)	−0.1847(3)	0.1703(3)	0.0712(2)	0.061(2)
C(2)	−0.0131(3)	0.2838(3)	0.0443(2)	0.039(2)
C(21)	0.0045(4)	0.2307(3)	−0.0117(2)	0.057(2)
C(3)	0.0433(3)	0.3762(2)	0.0659(2)	0.037(2)
C(31)	0.1351(3)	0.4330(3)	0.0372(2)	0.054(2)
C(4)	−0.0099(3)	0.4099(2)	0.1136(2)	0.042(2)
C(41)	0.0159(4)	0.5079(3)	0.1462(2)	0.064(2)
C(5)	−0.0964(3)	0.3367(3)	0.1226(2)	0.042(2)
C(6)	0.2959(3)	0.2522(2)	0.1496(2)	0.037(2)
C(61)	0.3701(3)	0.3465(3)	0.1509(2)	0.053(2)
C(7)	0.2748(3)	0.1956(2)	0.1991(2)	0.039(2)
C(71)	0.3238(4)	0.2202(3)	0.2622(2)	0.054(2)
C(8)	0.2100(3)	0.1070(2)	0.1791(2)	0.042(2)
C(81)	0.1776(4)	0.0223(3)	0.2180(2)	0.062(2)
C(9)	0.1904(3)	0.1073(2)	0.1169(2)	0.042(2)
C(91)	0.1344(4)	0.0233(3)	0.0778(2)	0.061(2)
C(10)	0.2436(3)	0.1976(2)	0.0986(2)	0.039(2)

3. Results and discussion

The $(C_5Me_5)_2TiCl_2$ and $(C_5HMe_4)_2TiCl_2$ compounds react with Bu_2Mg in a toluene–hexane mixture to give trinuclear Ti–Mg–Ti hydride-bridged complexes **1** and **2** with nearly quantitative yields. The ability to form complexes of this type is strongly diminished for titanocene dichlorides containing lower numbers of Me substituents at the cyclopentadienyl ligands. In an analogous reaction of $(C_5H_2Me_3)_2TiCl_2$, only a

Table 4
Positional parameters and U_{eq} values for molecules (1) and (2) of **3**

Atom	x	y	z	U_{eq} (Å^2)	Atom	x	y	z	U_{eq} (Å^2)
Molecule (1)					*Molecule (2)*				
Ti(1)	0.2133(1)	0.0967(1)	0.2899(1)	0.030(1)	Ti(3)	0.2136(1)	0.5957(1)	0.7898(1)	0.038(1)
C(10)	0.3758(4)	0.1484(4)	0.3022(3)	0.063(6)	C950)	0.3825(4)	0.6444(4)	0.8062(3)	0.037(4)
C(11)	0.3912(4)	0.1589(4)	0.2284(3)	0.049(5)	C(51)	0.3816(3)	0.6674(4)	0.7282(3)	0.045(4)
C(12)	0.3115(5)	0.2327(4)	0.2057(3)	0.053(5)	C(52)	0.3031(4)	0.7474(4)	0.6970(3)	0.048(4)
C(13)	0.2484(4)	0.2714(4)	0.2561(3)	0.051(5)	C(53)	0.2523(4)	0.7686(4)	0.7649(3)	0.054(5)
C(14)	0.2922(4)	0.2167(4)	0.3219(3)	0.053(5)	C(54)	0.2972(4)	0.7106(4)	0.8244(3)	0.049(5)
C(100)	0.4511(4)	0.0747(7)	0.3505(4)	0.084(7)	C(500)	0.4559(5)	0.5768(4)	0.8542(4)	0.074(7)
C(110)	0.4713(5)	0.1098(6)	0.1810(4)	0.094(8)	C(510)	0.4719(5)	0.6192(5)	0.6839(4)	0.076(7)
C(120)	0.2846(5)	0.2886(5)	0.1275(3)	0.067(5)	C(520)	0.2960(6)	0.7904(6)	0.6163(3)	0.095(7)
C(20)	0.0634(4)	0.1209(4)	0.3791(2)	0.034(4)	C(60)	0.0589(5)	0.6203(5)	0.8736(4)	0.073(6)
C(21)	0.1273(4)	0.0310(4)	0.4144(2)	0.041(4)	C(61)	0.1233(4)	0.5391(4)	0.9169(3)	0.051(5)
C(22)	0.1243(5)	−0.0491(4)	0.3817(3)	0.062(6)	C(62)	0.1293(4)	0.4569(3)	0.8889(3)	0.043(4)
C(23)	0.0637(4)	−0.0051(5)	0.3268(3)	0.058(6)	C(63)	0.0688(5)	0.4857(4)	0.8291(3)	0.057(5)
C(24)	0.0231(4)	0.0977(4)	0.3242(3)	0.065(6)	C(64)	0.0289(4)	0.5873(5)	0.8212(3)	0.054(5)
C(200)	0.0295(6)	0.2225(5)	0.3943(3)	0.078(6)	C(600)	0.0269(5)	0.7182(5)	0.8974(4)	0.070(6)
C(210)	0.1676(5)	0.0273(5)	0.4823(3)	0.068(6)	C(610)	0.1762(6)	0.5307(5)	0.9837(3)	0.075(6)
C(220)	0.1877(6)	−0.1548(4)	0.4107(4)	0.097(7)	C(620)	0.1730(7)	0.3472(5)	0.9154(4)	0.088(7)
Mg(1)	0.2433(1)	−0.0285(1)	0.1992(1)	0.049(2)	Mg(2)	0.2443(2)	0.4707(1)	0.7004(1)	0.050(2)
H(10)	0.168(5)	0.109(5)	0.191(5)	0.008(8)	H(50)	0.179(3)	0.369(3)	0.707(2)	0.017(5)
H(20)	0.304(5)	−0.004(5)	0.272(5)	0.008(8)	H(60)	0.300(3)	0.451(3)	0.624(2)	0.017(5)
H(30)	0.326(5)	−0.046(5)	0.101(5)	0.008(8)	H(70)	0.300(3)	0.473(3)	0.783(2)	0.017(5)
H(40)	0.163(5)	−0.162(5)	0.218(5)	0.008(8)	H(80)	0.189(3)	0.600(3)	0.704(2)	0.017(5)
Ti(2)	0.2487(1)	−0.1753(1)	0.1280(1)	0.040(1)	Ti(4)	0.2479(1)	0.3244(1)	0.6286(1)	0.038(1)
C(30)	0.4367(4)	−0.2270(5)	0.1231(4)	0.066(7)	C(70)	0.4330(4)	0.2743(4)	0.6316(4)	0.082(7)
C(31)	0.3891(5)	−0.3029(4)	0.1039(3)	0.057(5)	C(71)	0.3929(4)	0.2045(5)	0.6058(3)	0.056(5)
C(32)	0.3158(4)	−0.3532(4)	0.1670(3)	0.055(5)	C(72)	0.3141(5)	0.1463(4)	0.6623(3)	0.055(5)
C(33)	0.3174(6)	−0.3109(5)	0.2252(3)	0.068(6)	C(73)	0.3089(5)	0.1812(5)	0.7200(3)	0.061(6)
C(34)	0.3934(6)	−0.2331(5)	0.1914(6)	0.098(9)	C(74)	0.3800(5)	0.2582(5)	0.7043(3)	0.060(6)
C(300)	0.5291(5)	−0.1580(6)	0.0834(6)	0.13(1)	C(700)	0.5199(6)	0.3411(7)	0.5849(7)	0.14(1)
C(310)	0.4288(6)	−0.3187(7)	0.0323(4)	0.104(8)	C(710)	0.4257(7)	0.1716(5)	0.5378(3)	0.089(7)
C(320)	0.2570(5)	−0.4478(5)	0.1685(4)	0.082(7)	C(720)	0.2497(6)	0.0589(4)	0.6689(5)	0.093(7)
C(40)	0.0656(4)	−0.1290(6)	0.1054(3)	0.072(6)	C(80)	0.0656(6)	0.3879(8)	0.6059(4)	0.09(1)
C(41)	0.1273(4)	−0.0525(4)	0.0562(3)	0.045(5)	C(81)	0.1371(5)	0.4518(4)	0.5460(3)	0.057(6)
C(42)	0.1945(4)	−0.1018(4)	0.0110(3)	0.052(5)	C(82)	0.2081(4)	0.3916(4)	0.5083(3)	0.047(5)
C(43)	0.1819(5)	−0.2085(6)	0.0357(4)	0.069(7)	C(83)	0.1673(5)	0.2935(4)	0.5436(4)	0.066(6)
C(44)	0.0987(6)	−0.2234(4)	0.0935(5)	0.085(8)	C(84)	0.0875(5)	0.2885(8)	0.6029(3)	0.092(8)
C(400)	−0.0233(5)	−0.101(1)	0.1568(4)	0.18(1)	C(800)	−0.317(6)	0.4134(9)	0.6589(4)	0.13(1)
C(410)	0.1242(6)	0.0662(5)	0.0319(4)	0.082(7)	C(810)	0.1199(8)	0.5654(5)	0.5411(5)	0.13(1)
C(420)	0.2822(6)	−0.0637(6)	−0.0574(3)	0.093(7)	C(820)	0.2808(5)	0.4488(8)	0.4444(3)	0.126(9)

Table 5
Selected bond distances (Å) and bond angles (°) for **1**

Bond distances			
Ti(1)–H(1)	1.66(5)	Mg–H(3)	1.87(6)
Ti(1)–H(2)	1.75(7)	Mg–H(4)	1.92(8)
Ti(2)–H(3)	1.72(8)	Ti(1)–(C(1)–C(5))$_{av}$	2.398(8)
Ti(2)–H(4)	1.79(6)	Ti(1)–(C(6)–C(10)$_{av}$	2.392(8)
Mg–H(1)	1.94(5)	Ti(2)–(C(11)–C(15)$_{av}$	2.36(1)
Mg–H(2)	1.81(6)	Ti(2)–(C(16)–C(20)$_{av}$	2.37(1)
Ti(1) · · · Mg	2.860(4)	Ti(2) · · · Mg	2.857(4)
Bond angles			
H(1)–Ti(1)–H(2)	78(3)	H(3)–Ti(2)–H(4)	80(3)
H(1)–Mg–H(2)	70(3)	H(3)–Mg–H(4)	73(3)
Ti(1)–H(1)–Mg	105(3)	Ti(2)–H(3)–Mg	105(3)
Ti(1)–H(2)–Mg	107(4)	Ti(2)–H(4)–Mg	101(4)

Table 6
Selected bond distances (Å) and bond angles (°) for **2** [a]

Bond distances			
Ti(1)–H(1)	1.73(4)	Mg(1)–H(1)	1.81(4)
Ti(1)–H(2)	1.83(4)	Mg(1)–H(2)	1.77(4)
Ti(1)–CE(1)	2.059(3)	Ti(1)–CE(2)	2.050(3)
Ti(1) · · · Mg(1)	2.784(1)		
Bond angles			
H(1)–Ti(1)–H(2)	77.5(18)	H(1)–Mg(1)–H(2)	76.8(18)
Ti(1)–H(2)–Mg(1)	101.3(20)	Ti(1)–H(1)–Mg(1)	104.0(20)
CE(1)–Ti(1)–CE(2)	142.2(1)		

[a] Atoms Ti(1), C(1) etc. are related to atoms Ti(1′), C(1′) etc. respectively by the symmetry operation $-x$, y, $\frac{1}{2}-z$.

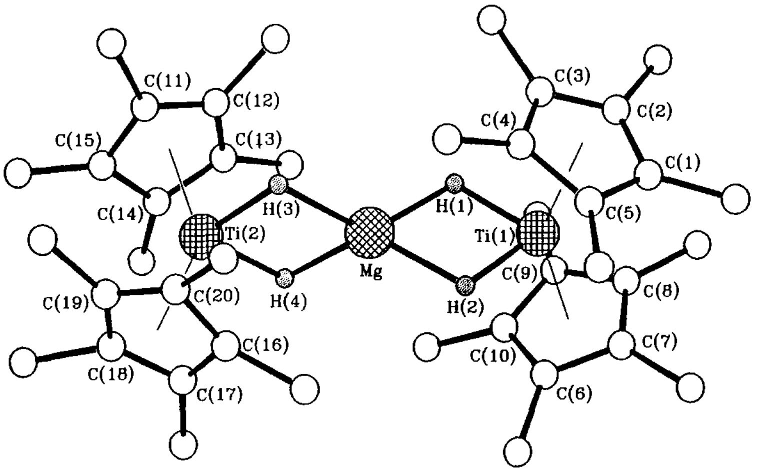

Fig. 1. PLUTO diagram and atom numbering scheme for 1.

low yield of 3 was isolated; however, a large amount of 3 remained in the mother liquor owing to its good solubility both in toluene and in hexane. No product of this structural type was isolated from the $(C_5H_3Me_2)_2$-$TiCl_2$–Bu_2Mg system, and the presence of 4 was deduced from the minor component in the ESR spectrum of the toluene solution of the reaction products only. On the contrary, 2 was formed for a wide Mg-to-Ti molar ratio range 1–4 with the optimum yield obtained for an Mg-to-Ti ratio of 3. The stoichiometry of the proceeding reactions is unknown; however, it follows from the structure of the product that intermediate titanocene alkyl–magnesium alkyl complexes dealkylate extremely easily.

The characterization and identification of the compounds are based on X-ray crystal structure analysis for **1–3** and on ESR spectra of their toluene solution in a glassy state for **1–4**. As follows from the molecular diagrams for **1–3** shown in Figs. 1–3, all the compounds consist, to some approximation (vide infra), of two mutually perpendicular titanocene fragments attached to one central magnesium atom through four Ti–H–Mg bridging bonds. The magnesium atom is thus pseudotetrahedrally coordinated. The ESR spectra of toluene solutions of **1–3** give a non-informative single line at a g value close to 1.990 with $\Delta H \approx 1.0$–2.0 mT; however, in frozen toluene glass, all the compounds show the spectra characteristic for the compounds in an electronic triplet state (Fig. 4). The g value is approximately the same as for the signal in solution; the zero-field splitting is in the range $D = 0.012$–0.013 cm^{-1} and $E = 0$. The value of D is inversely proportional to the distance between the unpaired electrons [21] and in the present case this corresponds well to the distance between the Ti(III) atoms in crystal structures, 5.5–5.7 Å (vide infra). Although a simple dependence between D (cm^{-1}) and d (Å) is a rather rough approximation, in the present case, where a comparison of structurally very similar compounds is carried out, a lower D value of 0.01217 cm^{-1} in **1**

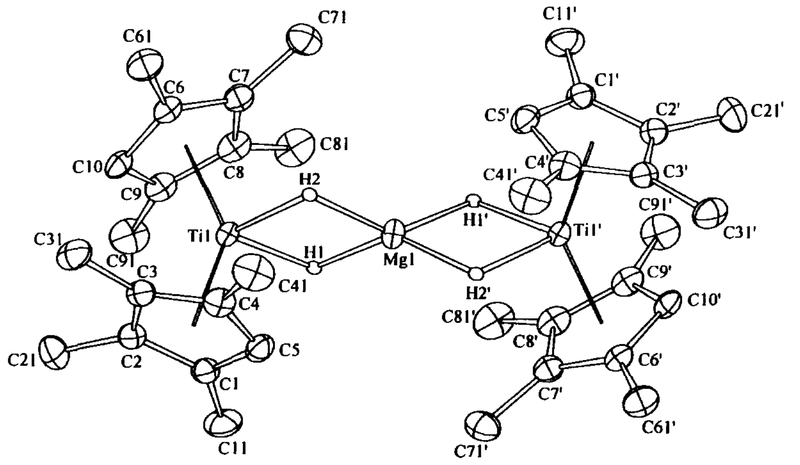

Fig. 2. ORTEP diagram of 2 with 50% probability thermal ellipsoids. The diagram shows the numbering scheme used in the tables.

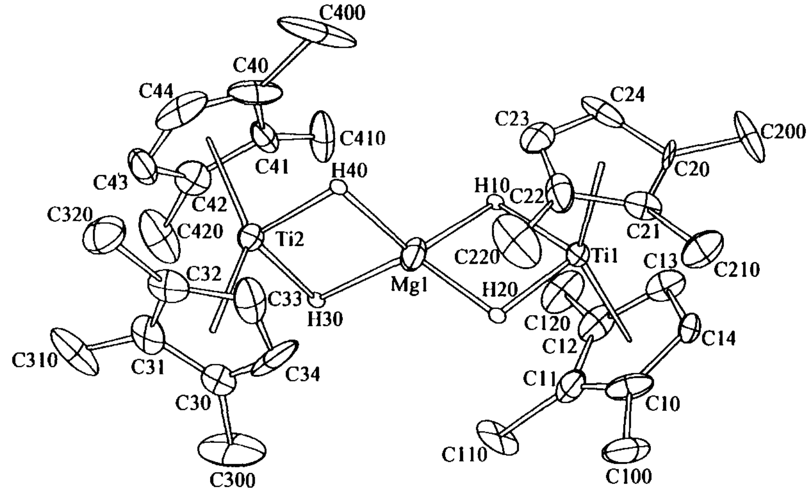

Fig. 3. ORTEP diagram of molecule (1) of **3** with 50% probability thermal ellipsoids. The diagram shows the numbering scheme used in the tables. The numbering scheme for molecule (2) contains cyclopentadienyl ring carbon atoms C(50)–C(84), H(50)–H(80), Mg(2) and Ti(3), Ti(4); methyl carbon atoms are labelled by adding zero to the number of the attached ring carbon atom.

reflects well the longer Ti–Ti distance; *d*(Ti–Ti) = 5.7 Å compared with *d*(Ti–Ti) = 5.5 Å in **2** and **3** which both afford $D = 0.0132$ cm^{-1}. The ESR spectrum of **4** which was discernible in addition to a much more intense single line at $g = 1.9913$ also implies the same value of *d*(Ti–Ti).

Table 7
Selected bond distances (Å) and bond angles (°) for molecule (1) and molecule (2) of **3**

Molecule (1)			
Bond distances			
Ti(1)–H(10)	2.07(5)	Mg(1)–H(10)	1.97(5)
Ti(1)–H(20)	1.76(5)	Mg(1)–H(20)	1.87(5)
Ti(2)–H(30)	1.98(5)	Mg(1)–H(30)	2.08(5)
Ti(2)–H(40)	1.94(5)	Mg(1)–H(40)	2.07(5)
Ti(1)–CE(1)	2.027(1)	Ti(2)–CE(3)	2.060(1)
Ti(1)–CE(2)	2.055(1)	Ti(2)–CE(4)	2.057(1)
Ti(1) · · · Mg(1)	2.793(2)	Ti(2) · · · Mg(1)	2.778(2)
Bond angles			
H(10)–Ti(1)–H(20)	83.5(21)	H(30)–Ti(2)–H(40)	96.4(20)
Ti(1)–H(10)–Mg(1)	87.7(19)	Ti(2)–H(30)–Mg(1)	86.4(19)
Ti(1)–H(20)–Mg(1)	100.6(24)	Ti(2)–H(40)–Mg(1)	87.6(19)
CE(1)–Ti(1)–CE(2)	142.2(2)	CE(3)–Ti(2)–CE(4)	140.0(2)
Molecule (2)			
Bond distances			
Ti(3)–H(50)	1.91(4)	Ti(4)–H(70)	1.86(4)
Ti(3)–H(60)	1.74(4)	Ti(4)–H(80)	1.88(4)
Mg(2)–H(50)	1.89(4)	Mg(2)–H(70)	1.66(4)
Mg(2)–H(60)	1.84(4)	Mg(2)–H(80)	1.63(4)
Ti(3)–CE(5)	2.055(5)	Ti(4)–CE(7)	2.044(6)
Ti(3)–CE(6)	2.052(6)	Ti(4)–CE(8)	2.043(7)
Ti(3) · · · Mg(2)	2.768(2)	Ti(4) · · · Mg(2)	2.785(2)
Bond angles			
H(50)–Ti(3)–H(60)	82.5(17)	H(70)–Ti(4)–H(80)	69.0(17)
Ti(3)–H(50)–Mg(2)	93.5(17)	Ti(4)–H(70)–Mg(2)	104.7(20)
Ti(3)–H(60)–Mg(2)	101.3(19)	Ti(4)–H(80)–Mg(2)	105.0(21)
CE(5)–Ti(3)–CE(6)	140.4(2)	CE(7)–Ti(4)–CE(8)	142.3(2)

The single-line ESR spectra at $g = 1.991$, which are only slightly anisotropic in a glassy state, were observed in the mother liquor after separation of a portion of **3** and in the attempted preparation of **4** where **4** was present as a very minor component. The natures of these compounds, which are highly soluble in hexane, are unknown. The UV–visible spectra of **1–3** show weak absorption bands at 490–760 nm which are attributable to titanocene Ti(III) hydride compounds [16,22] and the unknown highly soluble products give very similar spectra. This and virtually the same *g* values in both types of compound point to the same coordination surroundings of the Ti(III) atom in the so far unknown complexes. The high solubility in hexane and the absence of anisotropy in a frozen state can be compatible with some monomeric titanocene hydride

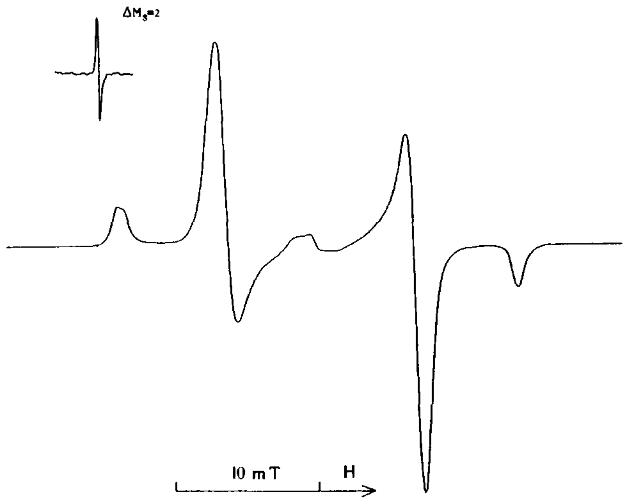

Fig. 4. ESR spectrum of **2** in toluene glass at −130°C. The $\Delta M_s = 2$ transition was observed at 166 mT and the signal was amplified four times.

species. Attempts at their isolation and identification are under way.

3.1. Description of crystal structures of 1–3

Compound **1** was obtained recently from the $(C_5Me_5)_2TiCl_2$–$^{i}PrMgCl$–OEt_2 system and its crystal structure (Fig. 1) was reported in a preliminary communication [17]. The crystal structures of **2** and **3** are shown in Figs. 2 and 3 respectively. Of these compounds, only **2** has a twofold axis of symmetry which is perpendicular to the Ti–Mg–Ti connection, contains the Mg atom and intersects the planes defined by atoms H(1), Mg(1) and H(2) and by H(1′), Mg and H(2′) at the angle 45°, perpendicular to the plane of Fig. 2. The molecular parameters for both halves of molecule **2** are identical. This symmetry does not hold exactly for **1** where both halves of the complex are only approximately equivalent. The unit cell of **3** contains two different molecules, differing markedly in the planarities of their bridges. In molecule (1) the central Mg atom is close (0.1 Å) to the plane defined by Ti(2), H(30) and H(40) whereas it is at the distance of 0.5 Å from the plane defined by Ti(1), H(10) and H(20). As a result, molecule (1) is bent by about 5° along the interconnection of H(10) and H(20). In molecule (2) this type of bending is exerted by both halves of the complex and the bending angles are about 2.5°. This diversity of molecules in the unit cell should be accounted for in the package effect. It is remarkable that the average Ti–Mg distance in **1** (2.858(4) Å) is slightly longer than the analogous distance in **2** (2.784(1) Å) and **3** (av. 2.785(2) Å) and that $(Ti–H)_{av}$ in **1** (1.73(7) Å) is distinctly shorter than $(Mg–H)_{av}$ (1.88(6) Å). In **2** and **3**, both bonds are equal but in **3** they are longer (1.95(5) Å) than in **2** (1.78(4) Å). Thus the strongest bridging bonds are in **2** whereas the weakest bonds in **3** imply its lower stability, as indeed is reflected by the low yield. The shortest Ti–H bonds in **1** correspond to a high reactivity of permethyltitanocene species towards hydrogen [23]. A somewhat longer Ti–Mg distance in **1** than in **2** may result from steric hindrance due to interaction of the C_5Me_5 ligands belonging to different halves of the molecule. This interaction is larger in **1** because the angle ϕ between the C_5Me_5 ring planes is only 36° as against 39.7° in **2** and on average 40.5° in **3**. Repulsion between the C_5Me_5 ligands in the cone of the angle ϕ brings about a lower value of this angle by about 4° compared with the C_5HMe_4 derivatives (cf. $(C_5Me_5)_2TiCl$ [24] and $(C_5HMe_4)_2TiCl$ [25]).

3.2. Impact of easy formation of 1–3 on the catalyst design

Complexes **1** and **2** were investigated for their catalytic activity in the polymerization of ethylene. However, they appeared to be unreactive with respect not only to ethylene but also to butadiene and they reacted only very slowly with terminal acetylenes on the time scale of months while the acetylenes dimerized to head-to-tail linear dimers [26]. It is highly probable that hydrides **1** and **2** will be formed even in systems containing largely organoaluminium compounds and only minor co-catalytic amounts of Bu_2Mg or butyloctylmagnesium as the more positive magnesium will successfully compete with aluminium. An analogous trinuclear permethyltitanocene hydride–aluminium hydride complex $[(C_5Me_5)_2Ti(\mu\text{-}H)_2]_2AlH$ is also known [27]; however, it is not certain whether it can arise also from dealkylation reactions in the $(C_5Me_5)_2TiCl_2$–R_3Al systems. Because of one accessible and reactive Al–H bond this compound is a catalyst of hydrogenation and isomerization of olefins. In general, the present results give a poor prospect for the exploitation of highly methyl-substituted titanocene derivatives in the polymerization catalysts.

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