

Synthesis and structure of trinuclear methoxy-bridged titanium(III)–magnesium complexes: $[(C_5H_{5-n}Me_n)_2Ti(\mu-OMe)_2]_2Mg$ ($n = 4$ and 5)

Róbert Gyepes^a, Jörg Hiller^b, Ulf Thewalt^b, Miroslav Polášek^a, Pavel Šindelář^c,
Karel Mach^{a,*}

^a J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, Dolejškova 3, 182 23 Prague 8, Czech Republic

^b Sektion für Röntgen- und Elektronenbeugung, Universität Ulm, D-89069 Ulm, Germany

^c Polymer Institute Brno, Tkalcovská 2, 656 49 Brno, Czech Republic

Received 11 November 1995

Abstract

The hydride complexes $[(C_5Me_5)_2Ti(\mu-H)_2]_2Mg$ (1) and $[(C_5HMe_4)_2Ti(\mu-H)_2]_2Mg$ (2) smoothly react with four equivalents of methanol to give the methoxy complexes $[(C_5Me_5)_2Ti(\mu-OMe)_2]_2Mg$ (3) and $[(C_5HMe_4)_2Ti(\mu-OMe)_2]_2Mg$ (4). The X-ray crystal analysis of 4 revealed a nearly linear arrangement of the metal atoms in an unsymmetrical molecule. The EPR spectra of the frozen toluene glass of 3 and 4 showed the triplet state spectra with very similar zero field splitting of rhombic symmetry. The distance between the unpaired electrons in 4 was estimated from the value of $D = 0.00958 \text{ cm}^{-1}$ to be 6.43 Å, in good agreement with the crystallographic $Ti^{III}-Ti^{III}$ distance of 6.329(1) Å. Complex 4 reacts with excess dibutyl magnesium to give a mixture of 2 and $[(C_5HMe_4)_2Ti(\mu-H)_2]_2Mg(\mu-OMe)_2$ (6). A mixture of 4 and methylalumoxane (1 : 100) did not induce the polymerization of ethylene.

Keywords: Titanium; Titanium(III)–magnesium complexes; EPR spectra; X-ray structure; Methoxy-bridged

1. Introduction

Titanium(IV)–magnesium complexes linked via μ -alkoxy and/or μ -chloro bridging bonds have attracted considerable attention as transition-metal components of catalysts for the olefin polymerization. In combination with ethylaluminium compounds or methylaluminoxane (MAO) they form a variety of model systems whose catalytic properties widely change from those of the homogeneous systems based, for example, on alkoxy derivatives of Ti and Zr, up to those of the heterogeneous systems based, for example, on $MgCl_2$ /organic ester–supported Ziegler–Natta systems [1]. Thus a dimer of the Ti_2Mg entities $[Ti_2(OEt)_7(\mu-OEt)(\mu-Cl)Mg(\mu-Cl)]_2$ [2] combined with MAO afforded effective catalysts for the polymerization of 1-olefins and diolefins. These catalysts mimicked the behaviour of homogeneous or heterogeneous systems depending on the na-

ture of the monomer [3,4]. The following Ti–Mg complexes have been synthesized and structurally characterized with a similar prospect: $[Mg_2(\mu-Cl)_2(THF)_6]$ $[TiCl_5(THF)]$ [5,6], $[(MeCO_2Et)_4Mg(\mu-Cl)_2TiCl_4]$ [7–9], $[MeCO_2Et)_4Mg(\mu-Cl)_2TiCl_3OH]$ [10], and $[(C_4H_7OCH_2CO_2Et)_2Mg(\mu-Cl)_2TiCl_4]$ [11].

The titanocene (Ti^{III})–magnesium coordination chemistry was first addressed by Stephan who prepared and determined structures of the chloro-bridged dimeric binuclear $(Ti-Mg)_2$ and trinuclear Ti_2Mg complexes $[(Cp_2Ti(\mu-Cl)_2Mg(THF)_2(\mu-Cl))]_2$ and $[(Cp_2Ti(\mu-Cl)_2)Mg(THF)_2]$ [12]. The similar hydride complexes $[(C_5HMe_4)_2Ti(\mu-H)_2Mg(OEt_2)(\mu-X)]_2$ ($X = Cl, Br$) [13] and $[(C_5H_{5-n}Me_n)_2Ti(\mu-H)_2]_2Mg$ ($n = 5-3$) [14,15] have been recently obtained from reactions of organomagnesium compounds with highly methylated titanocene dichlorides.

Here we report the formation and structures of methoxy-bridged Ti_2Mg complexes derived from the $[(C_5H_{5-n}Me_n)_2Ti(\mu-H)_2]_2Mg$ ($n = 4$ and 5) complexes and some of their properties.

* Corresponding author.

2. Experimental details

All manipulations with reagents, the synthesis, and most of spectroscopic measurements were carried out under vacuum using all-sealed glass devices equipped with breakable seals. The adjustment of single crystals into Lindemann glass capillaries for X-ray analysis, preparation of KBr pellets, filling of infrared cuvettes, and ethylene polymerization tests were performed in an atmosphere of purified nitrogen or argon.

2.1. Chemicals

The solvents toluene, hexane and 2-methyltetrahydrofuran (MTHF) were purified by conventional methods, dried by refluxing over LiAlH_4 and stored as solutions of dimeric titanocene $(\text{C}_{10}\text{H}_8)[(\text{C}_5\text{H}_5)\text{Ti}(\mu\text{-H})_2]$ [16]. Methanol (8 ml) was dehydrated by adding a piece of sodium. After the sodium was consumed the reaction mixture was degassed and methanol (MeOH) was distilled off in vacuo. A portion of 1 ml of the middle fraction was collected and diluted with toluene to give a 0.2 M solution. The hydride complexes $[(\text{C}_5\text{Me}_5)_2\text{Ti}(\mu\text{-H})_2]_2\text{Mg}$ (1) and $[(\text{C}_5\text{HMe}_4)_2\text{Ti}(\mu\text{-H})_2]_2\text{Mg}$ (2) were prepared from the corresponding titanocene dichlorides and a three-fold molar excess of dibutylmagnesium (Aldrich) in hydrocarbon solvents as recently described [15]. Polymerization-grade ethylene (Polymer Institute Brno) was purified by passing through columns filled with the Cu-catalyst (BASF, FRG) and molecular sieve 13X.

2.2. Methods

EPR 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+} ($M_1 = -1/2$ line) standard at $g = 1.9860$ and a proton magnetometer MJ-110 R (Radiopan, Poznan, Poland). A variable temperature unit STT-3 was used for the measurement in the range from -140 to $+20^\circ\text{C}$. Samples were measured as solutions in toluene or MTHF. The EPR spectra of triplet states were obtained in frozen glasses made of these solutions. Electronic absorption spectra were recorded on a Varian Cary 17D spectrometer in the range 280–2000 nm using all-sealed quartz cuvettes (Hellma). Electron impact mass spectra were measured on a JEOL D-100 spectrometer at 70 eV (only important mass peaks and peaks of intensity greater than 5% are reported). Samples in capillaries were opened and inserted into the direct inlet under argon. Hydrogen in the gaseous samples was identified on an MCH-1302 (USSR) mass spectrometer. The infrared spectrum of 3 (KBr pellet) was recorded on a Mattson Galaxy 2020

spectrometer. The pellet was measured in a gas-proof cuvette under nitrogen atmosphere.

2.3. Preparation of $[(\text{C}_5\text{Me}_5)_2\text{Ti}(\mu\text{-OMe})_2]_2\text{Mg}$ (3)

The crystalline complex $[(\text{C}_5\text{Me}_5)_2\text{Ti}(\mu\text{-H})_2]_2\text{Mg}$ (1) (0.6 g, 1 mmol) was mixed with 10 ml of toluene and 15 ml of a 0.2 M solution of MeOH in toluene were added. The pale purple colour of the hydride solution turned to a pale turquoise colour and the solid hydride complex dissolved. Another 5 ml of the MeOH solution was added subsequently in 3 ml and 2 ml portions. EPR spectra were measured at room temperature and at -130°C before and after additions of these portions. The colour of the solution finally turned to light green. A sample of the gas liberated in the reaction was sealed in an attached ampoule after cooling the reaction mixture by liquid nitrogen. The solution was evaporated in vacuo and the green crystalline residue was washed with 10 ml of hexane. The slightly yellow washing was discarded. The residue was dissolved in hot toluene to give a bright green solution. Thin pale green platelets crystallized out upon cooling to 0°C . Yield 0.64 g (82%).

MS (180°C): rapid decomposition of the sample; after cooling to 160°C the spectrum of $(\text{C}_5\text{Me}_5)_2\text{Ti}(\text{OMe})$ (m/e): 349 (M^+), 317 ($\text{M}-\text{MeOH}$), 213, 199, 197, 181, etc. was observed. UV-vis (toluene, green) (nm): 310 vs, sh, 840 ($\Delta H_{1/2} = 370$ nm) nm. EPR (toluene, 20°C): $g = 1.9779$, $\Delta H = 6.0$ G; (toluene, -130°C): $g_x = 1.9786$, $g_y = 1.9798$, $g_z = 1.9780$, $g_{\text{av}} = 1.9788$, $D = 0.00949$ cm^{-1} , $E = 0.00059$ cm^{-1} . The gas evolved during the reaction was according to MS solely dihydrogen.

2.4. Preparation of $[(\text{C}_5\text{HMe}_4)_2\text{Ti}(\mu\text{-OMe})_2]_2\text{Mg}$ (4)

Compound 4 was obtained from 1 mmol of $[(\text{C}_5\text{HMe}_4)_2\text{Ti}(\mu\text{-H})_2]_2\text{Mg}$ (2) by the same procedure as for obtaining 3. Light-green thin platelets of 4 were obtained from toluene. Yield 0.62 g (85%).

MS (200°C ; m/e , (%)): 728(M^+ ; 0.5), 607 ($[\text{M}-\text{C}_5\text{HMe}_4]^+$; 0.5), 407 ($[\text{M}-(\text{C}_5\text{HMe}_4)_2\text{Ti}(\text{OMe})]^+$; 4.0), 322(11.6), 321($[(\text{C}_5\text{HMe}_4)_2\text{Ti}(\text{OMe})]^+$; 42.8), 320(5.1), 291(15.5), 290(46.0), 289($[(\text{C}_5\text{HMe}_4)_2\text{Ti}-\text{H}]^+$; 100), 288(30.2), 287(62.6), 286(11.7), 285(19.6), 284(5.2), 283(7.3), 200(16.3), 199(18.6), 198(5.4), 197(9.2), 195(7.2), 186(7.0), 185(22.2), 184(5.7), 183(11.6), 181(13.2), 168(8.5), 167(21.3), 166(11.6), 165(8.2), 164(8.9), 163(8.1), 144.5($[(\text{C}_5\text{HMe}_4)_2\text{Ti}-\text{H}]^{2+}$; 6.5), 120(5.8), 105(16.4), 79(7.2), 77(5.4), 64(10.9), 32(8.0), 31(11.3), 18(14.6). IR(KBr pellet, light-green) (cm^{-1}): 2909 (vs); 2803 (s); 1441 (m); 1379 (w); 1368 (w); 1327 (w); 1082 (vs); 1020 (m); 841 (m); 824 (m); 718 (w); 565 (s); 490 (w); 451 (w); 405 (vs). UV-vis

(MTHF, green) (nm): λ 770 ($\Delta H_{1/2} = 320$ nm). EPR (toluene, 20°C): $g = 1.9798$, $\Delta H = 6.0$ G; (toluene, -130°C): $g_x = 1.9807$, $g_y = 1.9822$, $g_z = 1.9790$, $g_{av} = 1.9806$, $D = 0.00958$ cm⁻¹, $E = 0.00061$ cm⁻¹; (MTHF, 20°C): 1.9797 , $\Delta H = 6.0$ G; (MTHF, -140°C): $g_{\parallel} = 1.9787$, $g_{\perp} = 1.9828$, $g_{av} = 1.9801$, $D = 0.00876$ cm⁻¹, $E = 0$.

2.5. X-ray crystal structure analysis of 4

A large light-green platelet was cut under purified nitrogen in a glovebox (Braun) and a fragment $0.6 \times 0.5 \times 0.4$ mm³ was mounted in a glass capillary and sealed

by wax. The X-ray measurement was carried out on a Phillips PW 1100 four circle diffractometer equipped with a STOE electronic control system using graphite-monochromated Mo K α -radiation (λ 0.71069 Å) at room temperature.

Crystallographic data for 4: C₄₀H₆₄O₄MgTi₂, $M = 729.05$, orthorhombic, $P2_12_12_1$, No. 19, $a = 9.2086(5)$, $b = 15.8296(8)$, $c = 26.6504(8)$ Å, $V = 3884.8(2)$ Å³, $D_c = 1.247$ g cm⁻³, $Z = 4$, $\mu = 4.17$ cm⁻¹. Crystal data were collected by using the θ - 2θ method; $2\theta_{max} = 50^\circ$. A total of 3690 unique reflections out of 3866 observed reflections were used in the calculations. The structure was determined by the Patterson method which revealed

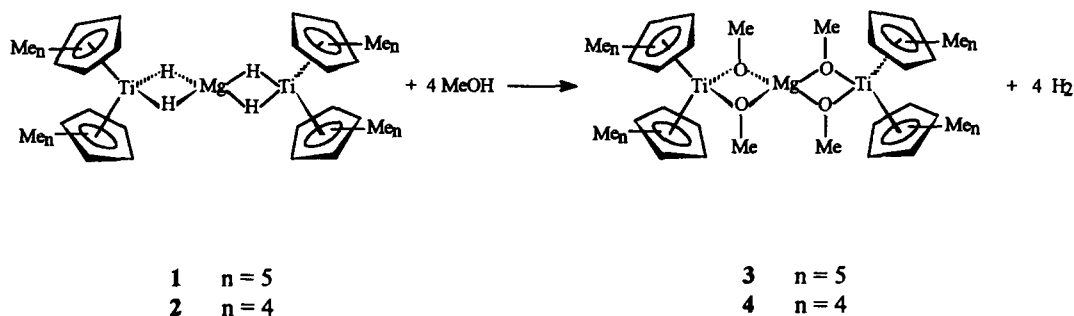
Table 1
Atomic coordinates and U_{eq} values of the non-hydrogen atoms of 4

Atom	x	y	z	U_{eq} (Å ²)
Ti(1)	0.1008(1)	0.0159(1)	-0.0839(1)	0.031(1)
Ti(2)	-0.0678(1)	-0.0101(1)	0.1458(1)	0.029(1)
Mg(1)	0.0148(1)	0.0058(1)	0.0311(1)	0.031(1)
O(1)	-0.0780(3)	0.0054(2)	-0.0345(1)	0.034(1)
C(1)	-0.2220(5)	0.0013(4)	-0.0521(2)	0.053(3)
O(2)	0.1825(3)	0.0234(2)	-0.0107(1)	0.035(1)
C(2)	0.3274(5)	0.0416(4)	0.0034(2)	0.054(3)
O(3)	-0.0044(3)	0.0766(2)	0.0902(1)	0.033(1)
C(3)	0.0016(6)	0.1655(3)	0.0957(2)	0.049(3)
O(4)	-0.0188(3)	-0.0812(2)	0.0813(1)	0.033(1)
C(4)	-0.0210(6)	-0.1696(3)	0.0816(2)	0.048(3)
C(5)	0.0447(6)	-0.1015(3)	-0.1396(2)	0.047(3)
C(51)	-0.0784(7)	-0.1045(4)	-0.1767(2)	0.069(4)
C(6)	0.0415(6)	-0.1393(3)	-0.0909(2)	0.044(3)
C(61)	-0.0823(6)	-0.1842(3)	-0.0672(2)	0.059(3)
C(7)	0.1844(6)	-0.1329(3)	-0.0706(2)	0.043(2)
C(71)	0.2294(7)	-0.1680(3)	-0.0212(2)	0.058(3)
C(8)	0.2755(5)	-0.0925(3)	-0.1064(2)	0.044(3)
C(81)	0.4398(6)	-0.0860(4)	-0.1022(2)	0.065(3)
C(9)	0.1883(6)	-0.0738(3)	-0.1482(2)	0.051(3)
C(10)	0.2313(5)	0.1289(3)	-0.1267(2)	0.042(2)
C(101)	0.3889(6)	0.1243(4)	-0.1424(2)	0.062(3)
C(11)	0.1085(6)	0.1119(3)	-0.1570(2)	0.044(3)
C(111)	0.1159(7)	0.0948(4)	-0.2132(2)	0.061(3)
C(12)	-0.0155(6)	0.1320(3)	-0.1309(2)	0.049(3)
C(121)	-0.1661(7)	0.1369(4)	-0.1524(2)	0.072(4)
C(13)	0.0269(6)	0.1652(3)	-0.0833(2)	0.049(3)
C(131)	-0.0724(8)	0.2020(3)	-0.0427(2)	0.075(4)
C(14)	0.1784(6)	0.1614(3)	-0.0809(2)	0.046(3)
C(15)	0.0704(7)	0.0417(4)	0.2167(2)	0.061(3)
C(151)	0.037(1)	0.1239(4)	0.2438(3)	0.106(6)
C(16)	0.1769(6)	0.0310(3)	0.1802(2)	0.050(3)
C(161)	0.2798(8)	0.0966(4)	0.1597(3)	0.095(5)
C(17)	0.1851(5)	-0.0540(3)	0.1683(2)	0.043(3)
C(171)	0.2955(6)	-0.0917(5)	0.1331(2)	0.075(4)
C(18)	0.0861(6)	-0.0989(3)	0.1969(2)	0.050(3)
C(181)	0.0780(8)	-0.1927(4)	0.2047(3)	0.087(5)
C(19)	0.0159(6)	-0.0385(4)	0.2285(2)	0.061(3)
C(20)	-0.2893(5)	0.0665(3)	0.1654(2)	0.040(2)
C(201)	-0.3011(6)	0.1578(3)	0.1816(2)	0.053(3)
C(21)	-0.3111(5)	0.0366(3)	0.1157(2)	0.036(2)
C(211)	-0.3370(6)	0.0912(3)	0.0701(2)	0.053(3)
C(22)	-0.3155(5)	-0.0516(3)	0.1173(2)	0.039(2)
C(221)	-0.3514(6)	-0.1078(3)	0.0728(2)	0.052(3)
C(23)	-0.2976(5)	-0.0792(3)	0.1670(2)	0.043(3)
C(231)	-0.3113(7)	-0.1677(3)	0.1869(2)	0.062(3)
C(24)	-0.2813(5)	-0.0046(3)	0.1965(2)	0.043(2)

the approximate positions of the Ti atoms. Atomic coordinates and anisotropic thermal parameters of all non-hydrogen atoms were refined by the least squares method. All hydrogen atoms were constrained to idealized geometries with a C–H distance of 1.08 Å. The PC ULM-package [17] was used for the calculations. The final *R* indices were $R = .044$, $R_w = 0.047$ for the 3581 reflections with $F_o > 1\sigma(F_o)$. The atomic coordinates and thermal parameters given in Table 1 refer to the absolute structure giving the lower *R* value. The *R* indices for the other enantiomorph were $R = 0.048$ and $R_w = 0.051$.

2.6. The reaction of 4 with dibutylmagnesium

The solution of 4 in toluene (0.04 M, 10 ml) was added to dibutylmagnesium in heptane (Aldrich, 1:1 *n*-butyl: *sec*-butyl) (1.0 M, 0.5 ml). The light-green color of 4 changed to reddish-blue within 30 min at room temperature. The reaction mixture was kept at 60°C for 2 h and then all volatiles (butenes and solvents) were evaporated in vacuum. The residue was extracted with 5 ml of toluene to give a clear solution which was separated from a small amount of a white sediment. The nature of products was established from EPR and UV–vis spectra of this solution. Attempts to isolate titanium products by crystallization in a larger-scale experiment failed because of the simultaneous precipitation of a white slurry.



Compounds 3 and 4 were obtained in high yields as light-green crystalline solids poorly soluble in hexane and moderately soluble in toluene. The structures of the compounds became apparent from their EPR spectra in frozen toluene glass, showing typical features of an electronic triplet state with a smaller zero field splitting parameter *D* than that found in the parent hydride complexes (vide infra). In agreement with Eq. (1), dihydrogen was identified by MS as the sole gaseous product. The composition of 4 was established by the EI-MS spectrum measured at 200°C. It showed the molecular mass peak (m/z 728) and the fragmentation pattern consistent with the structure suggested in Eq. (1). At variance with 4 compound 3 was thermolyzed in the direct inlet at only 180°C and yielded the MS spectrum attributable to $(C_5Me_5)_2Ti(OMe)$. The com-

EPR (toluene, $-50^\circ C$): $g = 1.9919$, $a_H = 5.2$ G, $a_{Ti} = 0.93$ G, $a_{Ti(7/2)} = 5.9$ G attributed to $[(C_5HMe_4)_2Ti(\mu-H)_2Mg(\mu-OMe)]_2$ (6) and a broad signal of 2 discernible at high signal amplification (see Fig. 1); ($-130^\circ C$): 2, $g = 1.9905$, $D = 0.01323$ cm^{-1} (lit. $g = 1.9907$, $D = 0.01327$ cm^{-1} [15]; 6, $g_1 = 2.0018$, $g_2 = 1.9922$, $g_3 = 1.9824$, $A_3 = 9.2$ G (triplet 1:2:1), $g_{av} = 1.9921$.

2.7. Ethylene polymerization tests

The polymerization tests were performed in a glass reactor equipped with a thermostated water jacket and a Teflon magnetic stirring bar. The reactor was connected through valves to a high vacuum line, to purified nitrogen and to feed of ethylene. Toluene (32 ml), 4 (0.04 mmol in 4 ml of toluene) and methylaluminoxane (4 mmol in 4 ml of toluene) were charged in the reactor under a stream of ethylene. The ethylene pressure was kept constant at 200 Torr during the test. The polymerization tests were carried out at 50 and 80°C for 3 h, always with negative results.

3. Results and discussion

The methylated titanocene–magnesium hydrides 1 and 2 smoothly react with four equivalents of methanol to give the methoxy complexes 3 and 4 and dihydrogen (Eq. (1)).

mon structure of 3 and 4 also follows from the same appearance of their UV–vis spectra showing a sole absorption band in the visible and near-infrared region. Its λ_{max} was found at 770 nm for 4 and at 840 nm for 3. Although the intensity of this band is low ($\epsilon \sim 10^1$ cm^2 $mmol^{-1}$) and hence compatible with the assignment to a d–d transition, a large dependence of λ_{max} on the number of Me groups at the cyclopentadienyl ligands is consistent with the assignment to a π –d or d– π^* transition. The solid state structure of 4 was further determined by an X-ray single crystal analysis.

3.1. Crystal structure of 4

The PLUTON drawing [18] of 4 with the atom numbering scheme is shown in Fig. 2. Selected bond distances

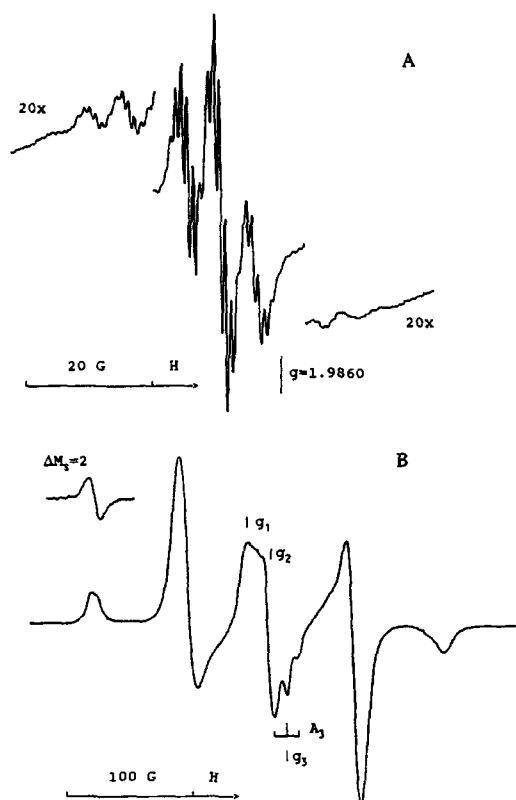


Fig. 1. EPR spectra of the reaction mixture of 4 with 3 equivalents of dibutylmagnesium in toluene: (A) solution at -50°C ; (B) glass at -130°C .

and bond angles are collected in Table 2. The molecule contains two non-equivalent octamethyltitanocene moieties each bonded through two bridging methoxy groups

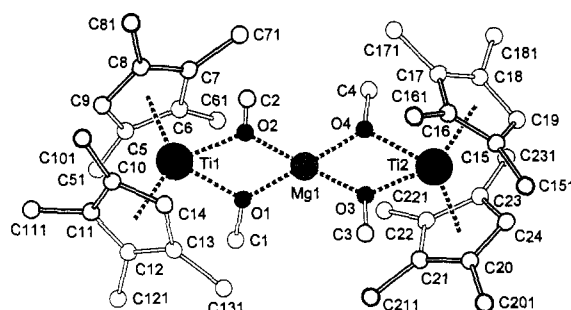


Fig. 2. A PLUTON drawing [18] of the molecular structure of 4 and the atom numbering scheme.

to the central magnesium atom. The magnesium atom is pseudotetrahedrally coordinated; however, the planes containing Mg(1), O(1) and O(2) atoms (denoted PL-1) and Mg(1), O(3) and O(4) atoms (PL-2) are not mutually perpendicular. The dihedral angle between them amounts to 79.1° . Nearly the same angle (80.4°) was observed between the planes of titanocene fragments defined by CE(1), Ti(1), CE(2), and CE(3), Ti(2), CE(4). The geometry of the bridging bonds is best understood by introducing the least squares planes through all elements in the bridges, i.e. Ti(1), O(1), O(2), Mg(1), and Ti(2), O(3), O(4), Mg(1). All the oxygen atoms are above and the Ti and Mg atoms are below the planes and their deviations from these planes are nearly twice as high for atoms generating the latter plane ($\pm 0.054 \pm 0.062 \text{ \AA}$). Accordingly, the dihedral angle between PL-1 and the plane through Ti(1), O(1) and O(2) is 175.3° and the dihedral angle between PL-2 and the plane

Table 2
Selected interatomic distances (\AA) and angles (deg) for 4^a

<i>Bond distances</i>			
Ti(1)–O(1)	2.115(3)	Ti(1)–O(2)	2.094(3)
Ti(1)–CE(1)	2.134(1)	Ti(1)–CE(2)	2.139(1)
Ti(2)–O(3)	2.101(3)	Ti(2)–O(4)	2.105(3)
Ti(2)–CE(3)	2.139(5)	Ti(2)–CE(4)	2.137(5)
Mg(1)–O(1)	1.947(3)	Mg(1)–O(2)	1.925(3)
Mg(1)–O(3)	1.941(3)	Mg(1)–O(4)	1.943(3)
O(1)–C(1)	1.408(6)	O(2)–C(2)	1.416(6)
O(3)–C(3)	1.417(6)	O(4)–C(4)	1.399(6)
<i>Non-bonding distances</i>			
Ti(1)–Mg(1)	3.170(1)	Ti(2)–Mg(1)	3.159(1)
Ti(1)–Ti(2)	6.329(1)		
<i>Bond angles</i>			
CE(1)–Ti(1)–CE(2)	134.7(1)	CE(3)–Ti(2)–CE(4)	134.3(1)
O(1)–Ti(1)–O(2)	72.8(1)	O(3)–Ti(2)–O(4)	73.4(1)
O(1)–Mg(1)–O(2)	80.3(1)	O(3)–Mg(1)–O(4)	80.6(1)
Ti(1)–O(1)–Mg(1)	102.5(1)	Ti(1)–O(2)–Mg(1)	104.1(1)
Ti(1)–O(1)–C(1)	122.0(3)	Mg(1)–O(1)–C(1)	135.5(3)
Ti(1)–O(2)–C(2)	126.7(3)	Mg(1)–O(2)–C(2)	129.2(3)
Ti(2)–O(3)–Mg(1)	102.7(1)	Ti(2)–O(4)–Mg(1)	102.5(1)
Ti(2)–O(3)–C(3)	126.0(3)	Mg(1)–O(3)–C(3)	130.8(3)
Ti(2)–O(4)–C(4)	121.8(3)	Mg(1)–O(4)–C(4)	135.7(3)

^a CE(1), CE(2), CE(3), and CE(4) refer to the centroids of the cyclopentadienyl rings.

through Ti(2), O(3) and O(4) is 171.6° . This means that the bridging oxygen bonds to Ti(2) are bent nearly twice as much around the O–O interconnection than those to Ti(1). Nevertheless, atoms Ti(1), Mg(1) and Ti(2) form nearly a line as the Ti(1)–Mg(1)–Ti(2) angle is 178.3° .

The two titanocene fragments differ by orientation of their C_5HMe_4 ligands, particularly in the mutual position of the proton-bearing ring carbon atoms. The Ti(1) fragment contains these carbon atoms on one side of the CE(1), Ti(1), CE(2) plane and the rings are mutually rotated by 45° . The angles between the above plane and the CE(1)–C(9) and the CE(2)–C(14) connections (see Fig. 2) are 6.6° and 51.6° respectively. The Ti(2) fragment is in a staggered configuration with C(19) and C(24) atoms placed symmetrically on both sides of the CE(3), Ti(2), CE(4) plane. However, the staggering angle of 18° is half the value for regularly staggered cyclopentadienyl ligands (36°). In spite of these differences, the CE(1)–Ti(1)–CE(2) angle (134.7°) is virtually the same as the CE(3)–Ti(2)–CE(4) angle (134.3°). The steric hindrance between the C(111) and C(51) Me groups is, however, responsible for a smaller angle between the C_5HMe_4 ring planes at Ti(1) (48.7°) against the analogous angle at Ti(2) (53.1°).

The methoxy groups have their carbon atoms situated above the bridging least squares planes as follows: C(1) 0.120 Å, C(2) 0.162 Å, C(3) 0.042 Å, and C(4) 0.144 Å. All the O–C bonds are inclined towards the titanium atoms but the difference between the Mg–O–C and Ti–O–C angles is larger for O(1) and O(4) ($13\text{--}14^\circ$) than for O(2) and O(3) ($3\text{--}4^\circ$) (see Table 2). The bond lengths and bond angles in the bridging skeleton do not differ considerably from those known for $[(C_5H_5)_2Ti(\mu\text{-OMe})_2]$ (**5**) [19]. The Ti–O bond lengths 2.094–2.115 Å are only slightly longer than the same bond in **5** (2.065(2) Å) and the O–C bond lengths 1.399(6)–1.417(6) Å do not differ practically from 1.401(7) Å in **5**. The symmetrical planar bridge in **5** contains angles O–Ti–O $71.24(3)^\circ$ and C–O–Ti $125.62(7)^\circ$ which differ from those of **4** only slightly (Table 2). From the

other side, the planar magnesium–*tert*-butoxy bridge in $[MgBr(\mu\text{-}^t\text{-Bu})(OEt_2)]_2$ gives the Mg–O bond length of 1.91 Å, and the O–Mg–O angle of 83.3° [20]. In the trinuclear complex $[Me_2Al(\mu\text{-OMe})_2]_2Mg(p\text{-dioxane})$ the Mg–O bond length was 2.05 Å and the O–C bond length 1.42 Å [21], both values being slightly longer than the average values 1.93 Å and 1.41 Å in **4**. The O–Mg–O angle (76°) was slightly smaller and the Mg–O–C (140°) slightly larger than the average values of analogous angles in **4**. These comparisons with model compounds are, however, of limited value because compound **4** contains bent bridging bonds whereas all the compared compounds have planar bridges. The reason for the deformation of **4** in the solid state is not clear, although packing effects apparently play an important role. This follows from an intermolecular distance of 3.38 Å between C(181) and C(151), which is the shortest contact distance in the structure and there are a great number of others in the range below 4.0 Å. Unfortunately, no apparent relation was disclosed between the orientation of the O–C bonds, the position of the proton-bearing ring carbon atoms in titanocene fragments and the bending of bridging bonds.

3.2. EPR investigation and the structures in solution

The parameters of EPR spectra of **3** and **4** and of their precursors **1** and **2** in the toluene solution and glass are listed in Table 3. In solution, only broad single line spectra were observed for all the complexes, not showing the coupling to the ^{47}Ti and ^{49}Ti isotopes with nuclear spins 5/2 and 7/2. These signals broadened with lowering of the measurement temperature, and in frozen glass they turned to typical spectra of the electronic triplet state of the cylindrical symmetry for the hydride precursors **1** and **2** and of the rhombic symmetry for **3** and **4**. This is demonstrated in Fig. 3, which shows EPR spectra in frozen toluene glass during the conversion of **1** into **3**. The records (B) and (C) also prove that an intermediate complex (**3'**) was formed during the reaction. This is in contrast to the **2**–MeOH

Table 3
EPR spectra observed in the $[(C_5H_5-nMe_n)_2Ti(\mu\text{-H})_2]_2Mg\text{-MeOH}$ ($n = 4$ and 5) systems in toluene solution (20°C) and glass (-130°C)

Compound	Solution		Glass							
	g_{iso}	$\Delta H(\text{mT})$	g_x	g_y	g_z	g_{av}	$D(\text{cm}^{-1})$	$E(\text{cm}^{-1})$	$R(\text{\AA})$	$d(\text{Ti-Ti})(\text{\AA})$
1	1.9896	2.1		1.9901			0.01217	0	5.96	5.72
2	1.9908	1.2		1.9907			0.01327	0	5.79	5.57
3	1.9797	0.6	1.9780	1.9790	1.9786	1.9785	0.00946	0.00060	6.44	—
3' ^a	1.982				1.9845		0.00897	0	6.58	—
4	1.9913	1.2	1.9790	1.9822	1.9810	1.9807	0.00958	0.00060	6.43	6.33
4' ^b	1.9797	0.6	g_{\parallel} 1.9787		g_{\perp} 1.9828	1.9814	0.00877	0	6.62	—

^a An intermediate complex formed in the $[(C_5Me_5)_2Ti(\mu\text{-H})_2]_2Mg\text{-MeOH}$ system.

^b The solution of **4** in MTHF at -140°C .

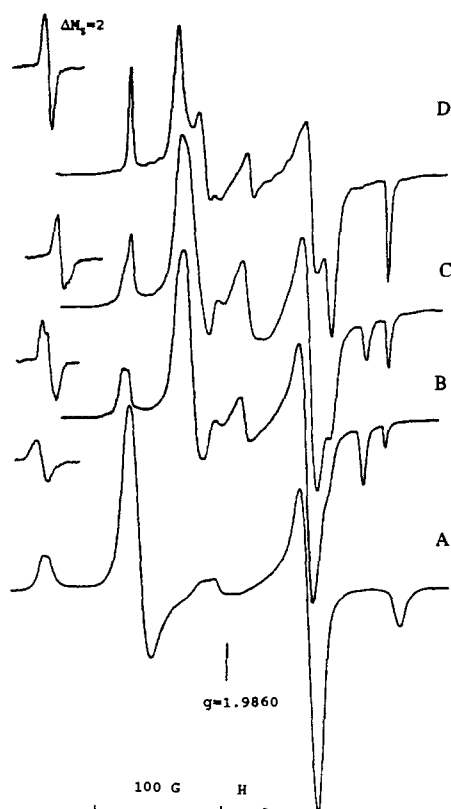


Fig. 3. EPR spectra of the reaction mixtures in frozen toluene glass after addition of MeOH to **1**. (A) compound **1**; (B) **1** + 3.0 equivalents of MeOH; (C) **1** + 3.3 equivalents of MeOH; (D) **1** + 4.0 equivalents of MeOH, after 3 days (compound **3**). Records of $\Delta M_s = 2$ transitions observed at about 1600 G are drawn at arbitrary place.

system where the analogous EPR investigation did not detect the presence of any intermediate complex.

The zero field splitting parameter D allows us to estimate the distance between the unpaired electrons in the triplet state. In particular, the dipolar component of D (denoted D_d) is related to the distance between the electrons (R , Å) for the system of the cylindrical symmetry by Eq. (2) [22] and for the system of rhombic symmetry by Eq. (3) [19].

$$R = (0.65 g_{\parallel} / D_d)^{1/3} \quad (2)$$

$$D_d = -\beta^2 / 3R^3 [2g_z^2 + (g_x^2 + g_y^2) / 2] \quad (3)$$

The contribution of a pseudodipolar component D_e to D ($D = D_d + D_e$) has been found to be low in most of dimeric titanium(III) complexes. A good agreement between the EPR values R and crystallographic distances $d(\text{Ti-Ti})$ was obtained for $[(\text{C}_5\text{H}_5)_2\text{Ti}(\mu\text{-Cl})_2]_2\text{Zn}$ ($R = 6.80$ Å; $d(\text{Ti-Ti}) = 6.84$ Å) [23], $[(\text{C}_5\text{H}_5)_2\text{Ti}(\mu\text{-OMe})_2]$ ($R = 3.38$ Å; $d(\text{Ti-Ti}) = 3.35$ Å) and $[(\text{C}_5\text{H}_5)_2\text{Ti}(\mu\text{-OEt})_2]$ ($R = 3.33$ Å; $d(\text{Ti-Ti}) = 3.35$ Å) [19]. The comparison of values R and $d(\text{Ti-Ti})$ for complexes **1**, **2**, and **4** (Table 3) gives even smaller

differences and confirms that neglecting the pseudodipolar component D_e is a reasonable approximation. The zero field splitting parameter D proved to be sensitive enough to follow the difference in $d(\text{Ti-Ti})$ distances for **1** and **2**, in agreement with the crystallographic data. The values of D for **3** and **4** thus predict that $d(\text{Ti-Ti})$ should be close to 6.4 Å for **3**. A rhombic symmetry of the zero field splitting in toluene glass indicates that the PL-1 and PL-2 bridging systems containing the magnesium atom are not mutually perpendicular and/or the molecule is bent, similar to the solid state. This has been changed in the MTHF solution where some coordination of the solvent, or at least the solvation of the magnesium atom, led to a more symmetric structure of **4** (denoted **4'**). The evidence was obtained from the EPR spectrum which was typical of the cylindrical symmetry; however, a large linewidth indicated only the approximate symmetry of **4'** (Fig. 4). A smaller value of D implies that the MTHF coordination was accompanied by loosening of the bridging bonds, resulting in a longer Ti-Ti distance (an estimate of 6.6 Å) (Table 3).

Somewhat puzzling is the structure of an intermediate complex **3'** observed by EPR spectroscopy in the **1**-MeOH system. Although the $D + 3E$ and $D - 3E$ components of the zero field splitting tensor were not determined because of the overlap with the spectrum of **3** the 2D component and g_z component of g -tensor for **3'** were clearly established (Table 3). The parameter $D = 0.00897 \text{ cm}^{-1}$, derived from them, unequivocally indicates that R about 6.6 Å is significantly longer than

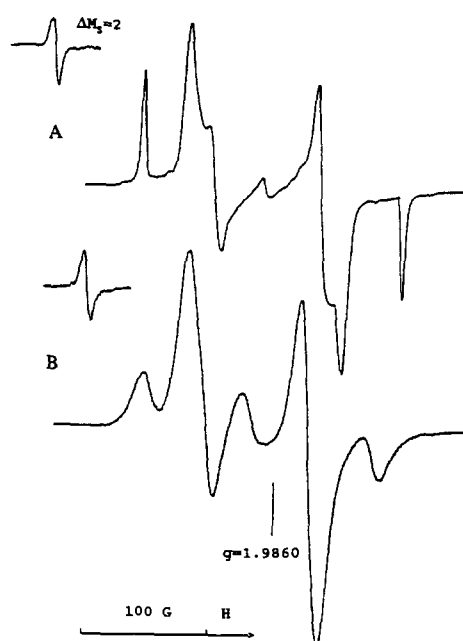


Fig. 4. EPR spectra of (A) **4** in the toluene glass (-130°C); (B) in MTHF glass (**4'**) (-140°C).

in both **1** and **3** (see Table 3). The maximum concentration of **3'** occurred at the molar MeOH–Ti ratio close to 3. This fact and a high g_z value (1.9845) are compatible with the view that it is a mixed μ -methoxy– μ -hydrido complex in spite of the expectation that such a complex should have $d(\text{Ti–Ti})$ longer than **1** and shorter than **3**. Since the reaction between the hydrides and MeOH is very slow for the ratios MeOH:Ti ≥ 3 a large value of R in **3'** can be brought about by a transient coordination of MeOH to the magnesium atom in a mixed μ -methoxy– μ -hydrido complex with the elongation effect on $d(\text{Ti–Ti})$ similar to that of MTHF demonstrated on **4'**. The absence of such a complex formation in the **2**–MeOH system, however, shows that similar intermediates strongly tend to disproportionate into the initial hydrido and final methoxy complexes.

3.3. Some properties of **4**

When mixed with a five-fold molar excess of Bu_2Mg , compound **4** disappeared within 30 min at room temperature. The electronic absorption spectrum of **4** (vide supra) was replaced by a broad absorption showing λ_{max} at 490 nm with a shoulder at 570 nm, and extending with decreasing intensity to 900 nm. The EPR spectrum of this solution revealed the presence of two compounds. The first one, denoted **6**, showed a well-resolved spectrum at $g = 1.9919$ exhibiting a large triplet (1:2:1) splitting ($a = 5.2$ G) and a superhyperfine splitting ($a = 0.93$ G). This spectrum overlapped a broad single line signal of the other compound. With decreasing measurement temperature the resolution of the spectrum of **6** improved to an optimum at -50°C , whereas the single line was broadened. The same sample measured in toluene glass revealed that the single line developed into a triplet state spectrum of **2** which was virtually identical with that of the authentic compound used for the synthesis of **4** [15]. An anisotropic spectrum of compound **6**, affording the triplet hyperfine splitting in solution, was observed in the middle part of the spectrum of **2** (see Fig. 1). A low anisotropy of its g -tensor is compatible with a high g_{iso} value, indicating a low occupancy of a d-orbital by the unpaired electron. The coupling to two equivalent hydride protons (ca. 9

G) was observed only for the A_3 component of the A-tensor. This value implies much lower magnitudes of A_1 and A_2 components in order to meet $a_{\text{iso}} = 5.2$ G.

Compound **6** is assigned to be a dimer $[(\text{C}_5\text{HMe}_4)_2\text{Ti}(\mu\text{-H})_2\text{Mg}(\mu\text{-OMe})]_2$ on the basis of its genesis and the comparison of its spectral parameters with those of known spectra of dimeric hydride complexes $[(\text{C}_5\text{HMe}_4)_2\text{Ti}(\mu\text{-H})_2\text{Mg}(\text{OEt}_2)(\mu\text{-X})]_2$ ($X = \text{Cl}, \text{Br}$) [13] and $[(\text{C}_5\text{HMe}_4)_2\text{Ti}(\mu\text{-H})_2\text{Mg}(\text{THF})(\mu\text{-Cl})]_2$ [24] (see Table 4). The structure of **6** as the methoxy-bridged hydride complex accounts for only minor differences in its EPR parameters compared with those of the halo-bridged compounds. Slightly smaller values of a_{H} and $a_{\text{H}}(\text{Cp})$ and a larger value of a_{Ti} can be connected with a changed electron density at the appropriate ligands or atoms due to different bridging bonds between Mg atoms. As no ether compounds were present in the reaction system the magnesium atoms have to be pseudotetrahedrally coordinated by two pairs of equivalent oxygen and hydrogen atoms. The origin of the superhyperfine multiplet splitting ($a = 0.93$ G for **6**), at least seven lines, is not specified for all the C_5HMe_4 compounds of this type [13] as the number of multiplet lines exceeds the number of lines which would arise from the coupling to a total of two protons at the two C_5HMe_4 rings. However, a very similar appearance of the multiplets, including the preserved odd multiplicity in the complexes containing different bridging elements between magnesium atoms and different additional ether molecules, indicates that the multiplet splitting must arise from the coupling to the methyl protons of the C_5HMe_4 ligands.

The electronic absorption spectrum of the reaction products confirms the above assignment since the absorption band at $\lambda_{\text{max}} = 490$ nm corresponds to the absorption band of **2** [15], and the shoulder at 570 nm is close to the absorption band at 590 nm of the $[(\text{C}_5\text{HMe}_4)_2\text{Ti}(\mu\text{-H})_2\text{Mg}(\text{THF})(\mu\text{-Cl})]_2$ complex [24]. Both the bands of the individual compounds show wings of decreasing intensity to ca. 900 nm in accord with the spectrum of a mixture.

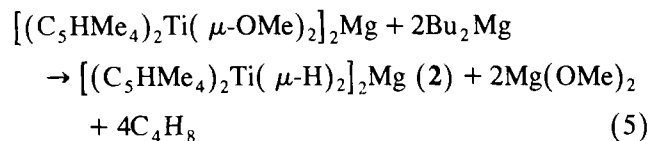
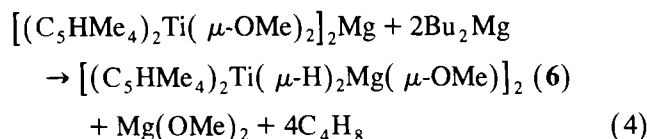
The formation of **2** and **6** in this system can be described by Eqs. (4) and (5), and the mechanism is analogous to the formation of **1** and **2** from the corre-

Table 4
EPR spectra of **6** and similar complexes of general formula $[(\text{C}_5\text{HMe}_4)_2\text{Ti}(\mu\text{-H})_2\text{Mg}(\text{L})(\mu\text{-X})]_2$ in solution

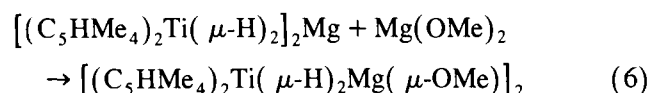
Compound L	X	g	$a_{\text{H}}(\text{G})$	$a_{\text{H}}(\text{C}_5\text{HMe}_4)(\text{G})^a$	$a_{\text{Ti}}(\text{G})$	Reference
—	OMe	1.9919	5.2	0.93	5.9	This work
OEt_2^b	Cl	1.9912	6.6	1.0	5.4	[13]
OEt_2^b	Br	1.9910	6.8	1.0	5.4	[13]
THF	Cl	1.9914	7.0	1.0	— ^c	[24]

^a Multiplets of odd number of lines (at least seven). ^b Measured in diethyl ether. ^c Measured in toluene; the solubility in toluene was not sufficient to observe a_{Ti} coupling.

sponding titanocene dichlorides with an optimum at a three-fold excess of Bu_2Mg [15].



Mutual abundance of compounds **2** and **6** is probably controlled by equilibrium (6)



Addition of MAO in excess to **4** also resulted in the disappearance of the green colour of **4**; however, the products were not studied in detail because the identification of the products would probably be impossible. Furthermore, the system **4**–MAO at the molar ratio 1:100 did not show any catalytic activity in the polymerization of ethylene. This would not be surprising, provided the interaction with MAO leads to the formation of complex hydrides, as the hydrides **1** and **2** also appeared to be unreactive towards ethylene [15].

4. Supplementary material available

Listings of atomic coordinates and isotropic thermal parameters, and all bond distances and angles are available from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76012 Karlsruhe by quoting the deposition number CSD-58526. Additional information such as anisotropic thermal parameters, least squares planes, dihedral angles, observed and calculated structure factors and views of unit cell may be obtained from the authors.

Acknowledgements

This investigation was supported by the Grant Agency of Academy of Sciences of the Czech Republic, grant no. 440403, by the Grant Agency of the Czech Repub-

lic, grant no. 203/93/0143, and by the Fonds der Chemischen Industrie.

References

- [1] G. Fink, R. Mülhaupt and H.H. Brintzinger (eds.), *Ziegler Catalysts*, Springer, Berlin and Heidelberg, 1995.
- [2] L. Malpezzi, U. Zucchini and T. Dall'Occo, *Inorg. Chim. Acta*, **180** (1991) 245.
- [3] T. Dall'Occo, F. Sartori, G. Vecellio, U. Zucchini and A. Maldotti, *Makromol. Chem.*, **194** (1993) 151.
- [4] U. Zucchini, T. Dall'Occo and A. Angelini, *J. Mol. Catal.*, **82** (1993) 45.
- [5] G. Valle, G. Ruisi and V. Russo, *Inorg. Chim. Acta*, **82** (1984) 81.
- [6] P. Sobota, J. Utko and T. Lis, *J. Chem. Soc. Dalton Trans.*, (1984) 2077.
- [7] L. Brun, *Acta Crystallogr.*, **20** (1966) 739.
- [8] D.A. Brown and M.G.H. Wallbridge, *Inorg. Chim. Acta*, **206** (1993) 209.
- [9] N.J. Clayden and P.J.V. Jones, *J. Chem. Soc. Perkin Trans. 2*, (1990) 175.
- [10] G. Giunchi, E. Albizzati, L. Malpezzi and E. Gianetti, *Inorg. Chim. Acta*, **147** (1988) 159.
- [11] P. Sobota, M. Wroblewska, S. Szaefert and T. Glowiak, *J. Organomet. Chem.*, **481** (1994) 57.
- [12] D.W. Stephan, *Organometallics*, **11** (1992) 996.
- [13] S.I. Troyanov, V. Varga and K. Mach, *J. Organomet. Chem.*, **461** (1993) 85.
- [14] S.I. Troyanov, V. Varga and K. Mach, *J. Chem. Soc. Chem. Commun.*, (1993) 1174.
- [15] R. Gyepes, K. Mach, I. Císařová, J. Loub, J. Hiller and P. Šindelář, *J. Organomet. Chem.*, **497** (1995) 33.
- [16] H. Antropiusová A. Dosedlová, V. Hanuš and K. Mach, *Transition Met. Chem.*, **6** (1981) 90.
- [17] R. Brüggemann, T. Debaerdemaeker, B. Müller, G. Schmid and U. Thewalt, *ULM-Programmsystem, 1. Jahrestagung der Deutschen Gesellschaft für Kristallografie, Mainz, 9–12 June, 1992*, Abstr., p. 33 (includes G.M. Sheldrick, *SHELX-76 Program for Crystal Structure Determination*, University of Cambridge, Cambridge, UK, 1976).
- [18] A.L. Spek, *PLUTON Molecular graphics program*, Utrecht University, Netherlands, 1995.
- [19] E. Samuel, J.F. Harrod, D. Gourier, Y. Dromzee, F. Robert and Y. Jeannin, *Inorg. Chem.*, **31** (1992) 3252.
- [20] P.T. Moseley and H.M.M. Shearer, *J. Chem. Soc. Chem. Commun.*, (1968) 279.
- [21] J.L. Atwood and G.D. Stucky, *J. Organomet. Chem.*, **13** (1968) 53.
- [22] R.L. Belford, N.D. Chasteen, H. So and R.E. Tapscott, *J. Am. Chem. Soc.*, **91** (1969) 4675.
- [23] D. Gourier, D. Vivien and E. Samuel, *J. Am. Chem. Soc.*, **107** (1985) 7418.
- [24] M. Horáček, R.Gyepes, V. Varga, I. Císařová and K. Mach, *XI. FEChEM Conf. Organomet. Chem., Parma, Italy, 1995*, Abstr., p. 89.