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Dimeric titanocene hydride–hydridomagnesium chloride and bromide complexes. Crystal structures of the tetramethylcyclopentadienyl derivatives

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Abstract

Cp'_2TiX_2–^iPrMgX (Cp′ = C_5HMe_4, $C_5H_2Me_3$, C_5H_5; X = Cl or Br) systems afford blue crystalline products, with low solubility in diethyl ether. X-Ray single crystal analysis of the C_5HMe_4 derivatives revealed dimeric centrosymmetric structures of $[(C_5HMe_4)_2Ti(\mu\text{-H})_2Mg(OEt_2)(\mu\text{-Cl})]_2$ (**Ia**) and $[(C_5HMe_4)_2Ti(\mu\text{-H})_2Mg(OEt_2)(\mu\text{-Br})]_2$ (**Ib**). The solution EPR spectra of all the compounds ($g = 1.9910$–1.9934, $a_H = 0.66$–0.75 mT, $a_{Ti} = 0.54$–0.66 mT, a(multiplet) = 0.04–0.1 mT) can be assigned either to the dimers or to the dissociated monomeric species.

1. Introduction

Cp_2TiCl_2–Grignard reagent systems have been extensively studied because of their catalytic activity in the isomerization [1], hydrogenation [2], hydrometallation [3] and oligomerization of unsaturated hydrocarbons [4] and in the fixation of molecular nitrogen [5]. They were also used as reducing agents in organic synthesis [6] and as systems for the preparation of (η^3-allyl)titanocenes from dienes [7].

Cp_2TiCl_2–RMgCl (R = Me, Et, $^iPr = CH(CH_3)_2$) systems have been thoroughly studied by means of EPR spectroscopy [8]. At a large excess of Grignard reagents (Mg/Ti = 20–50) dialkylated $(Cp_2TiR_2)^-$ species were stabilized at low temperature, showing the hyperfine coupling to protons at α-carbon atoms. These species for R = Et, ^iPr eliminated olefins upon warming and yielded highly reactive but thermally stable $(Cp_2TiH_2)^-$ anionic species. The olefin was more easily eliminated for ^iPr than for Et derivatives. The composition of the dihydride species was deduced from their EPR spectra exerting a triplet splitting ($a_H = 0.7$ mT) at $g = 1.993$ which indicated the interaction of the unpaired electron of Ti^{III} with two equivalent hydrogen nuclei. Alkyl groups of Grignard reagents were identified as the main source of hydrogen for $(Cp_2TiH_2)^-$ using deuterated Grignard compounds, however, obtaining the same EPR spectrum in the Cp_2TiCl_2–Mg system proved that the ether solvent can participate as the hydrogen source. In another study of the latter system [9], the evidence was obtained that cyclopentadienyl protons also serve as a source of hydrides. Further detailed investigation of the EPR spectra of the $(Cp_2TiH_2)^-$ species obtained with various metal alkyls concluded that the anionic form is present in systems containing Li^+ and Na^+ as counter-cations whereas the product of interaction of Cp_2TiBr_2 with ^iPrMgBr should be formulated as $Cp_2Ti(\mu\text{-H})_2MgBr$ [10].

Here we report the preparation of crystalline complexes $[Cp'_2Ti(\mu\text{-H})_2Mg(OEt_2)(\mu\text{-X})]_2$ (Cp′ = C_5H_5

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(Cp), C_5H_2(1,2,4-)Me_3 and C_5HMe_4; X = Cl or Br) from the reaction between Cp'_2TiX_2 and ^iPrMgX in diethyl ether, X-ray crystal structures for the Me_4Cp derivatives and the solution EPR spectra of all the complexes.

2. Experimental details

2.1. Chemicals

Titanocene dihalides Cp'_2TiX_2 (Cp′ = Cp, Me_3Cp and Me_4Cp; X = Cl or Br) were prepared according to literature procedures [11]. Partly deuterated $(C_5HMe_4)_2TiCl_2$ was obtained by using $LiAlD_4$ (99.3% D) for the reduction of a mixture of 2,3,4,5-tetramethylcyclopentenones in diethyl ether. The content of C_5DMe_4 ligand in $(C_5HMe_4)_2TiCl_2$ was 55% as determined by MS analysis. Diethyl ether and tetrahydrofuran (THF) were dried using $LiAlH_4$ and were stored on a vacuum-argon line as solutions of dimeric titanocene. Isopropyl chloride (^iPrCl) and isopropyl bromide (^iPrBr) (both Fluka) were dried over CaH_2 and finally by adding a small piece of sodium; then they were fractionated under argon. Isopropyl Grignard reagents were prepared in the usual way to obtain an approximately 2 M solution in diethyl ether. Their concentration was assessed by acido-basic titration and the solutions were diluted with diethyl ether to 0.05 M.

2.2. Preparation of crystalline $[Cp'_2Ti(\mu\text{-}H)_2Mg(OEt_2)(\mu\text{-}X)]_2$ complexes

All the complexes were prepared from the above listed titanocene dihalides by the procedure given below for the Me_4Cp chloro compound **Ia**. Crystalline $(Me_4Cp)_2TiCl_2$ (0.225 g, 0.625 mmol) was evacuated and ^iPrMgCl in ether (0.05 M, 50 ml) was added under argon. The ampoule with the reaction mixture was cooled in liquid nitrogen, evacuated and sealed off. After warming to room temperature, the mixture was shaken until all the dichloride dissolved, affording a blue solution. After standing for 3 days, the product crystallized out on the walls as blue platelets. A fine white sediment of $MgCl_2$ separated at the bottom whereas the supernatant solution was only pale blue. Fine $MgCl_2$ was washed out from crystalline **Ia** using a silica wool plug to hold the large crystals of **Ia**. The yield of large crystals of **Ia** was 0.17 g (0.21 mmol, 68%); the conversion to **Ia** was, however, nearly quantitative as no byproducts were detected.

Analogous Me_3Cp and Cp products also formed blue crystals but their size was much smaller. This did not allow their separation from $MgCl_2$. On the other hand, in the systems containing bromine, $MgBr_2$ remained in solution and the products could be isolated nearly quantitatively. The yield of crystalline $[(Me_4Cp)_2Ti(\mu\text{-}H)_2Mg(OEt_2)(\mu\text{-}Br)]_2$ (**Ib**) was 87%. Yields of the Me_3Cp and Cp compounds were 64% and 24% as a result of the increasing solubility of the products in ether.

All the crystalline products were blue, well soluble in THF, yielding blue paramagnetic solutions. Their ESR spectra in ether and THF differed negligibly, all showing hyperfine triplet splitting ($a_H \sim 0.7$ mT at g close to 1.9910–1.9934).

2.3. X-Ray data collection and structure determination for *Ia* and *Ib*

The blue triangle platelets of **Ia** and **Ib** were mounted into the Pyrex capillaries under argon and sealed. About 20 crystals of each of the compounds were examined by Laue photographs to find satisfactory crystals for the X-ray measurements. The crystallographic quality of both the selected crystals was not, however, very good.

The lattice parameters were determined on an automatic Enraf-Nonius CAD-4 diffractometer from the setting angles of 20 centred reflections, with 12° < θ < 15°. All the crystals showed no evidence of decomposition during data collection at room temperature. The

TABLE 1. Details of the structure determination of **Ia** and **Ib**

	Ia	**Ib**
(a) Crystal data		
Chemical formula	$[(C_5HMe_4)_2Ti(\mu\text{-}H)_2Mg(OEt_2)(\mu\text{-}X)]_2$	
	X = Cl	X = Br
Crystal system	Triclinic	Monoclinic
Space group (no.)	$P\bar{1}$ (2)	$P2_1/b$ (14)
a (Å)	8.504(3)	8.533(2)
b (Å)	10.011(4)	9.985(3)
c (Å)	15.372(7)	30.614(5)
α (°)	76.69(3)	90.0
β (°)	87.13(3)	90.0
γ (°)	64.83(3)	115.62(2)
V (Å^3)	1150.9	2352.0
Z	1	2
D_{calc} (g cm^{-3})	1.227	1.326
μ (cm^{-1})	5.18	20.76
Approx. crystal dimensions (mm)	0.2×0.2×0.08	0.3×0.2×0.1
(b) Data collection and refinement		
Radiation, monochromator	Mo Kα, graphite	
Temperature (K)	293	
θ_{max} (°)	21	24
Total data	2679	4052
Unique observed data $F^2 \geq 2\sigma(F^2)$	1681	1465
No. of refined parameters	229	230
R	0.093	0.089
R_w	0.098	0.094
ESD of the unit weight	2.7	5.3

TABLE 2. Positional and thermal parameters for **Ia** and **Ib**

Atom	x	y	z	B (Å^2)
Ia				
Ti	0.7836(3)	0.1974(3)	0.7233(2)	2.44(6)
Cl	1.1269(5)	0.0894(4)	0.9828(2)	3.89(9)
Mg	0.9976(6)	0.0001(5)	0.8814(3)	3.3(1)
O	1.221(2)	−0.192(1)	0.8740(8)	6.5(4)
C(1)	0.679(2)	0.141(2)	0.6048(8)	3.6(4)
C(2)	0.844(2)	0.013(1)	0.6324(7)	3.3(4)
C(3)	0.969(2)	0.071(1)	0.6157(8)	3.5(3)
C(4)	0.885(2)	0.228(1)	0.5795(8)	3.2(4)
C(5)	0.707(2)	0.269(1)	0.5714(9)	3.6(3)
C(6)	0.545(2)	0.298(2)	0.8136(9)	3.9(4)
C(7)	0.499(2)	0.408(2)	0.7290(9)	3.6(4)
C(8)	0.623(2)	0.469(1)	0.7145(9)	3.9(4)
C(9)	0.745(2)	0.404(1)	0.7900(8)	3.5(4)
C(10)	0.700(2)	0.298(1)	0.8496(8)	2.6(3)
C(11)	0.513(2)	0.120(2)	0.599(1)	5.2(4)
C(12)	1.395(3)	−0.169(3)	0.839(1)	9.4(8)
C(13)	1.519(4)	−0.222(3)	0.906(2)	13(1)
C(14)	1.281(4)	−0.342(3)	0.886(2)	14(1)
C(15)	1.119(5)	−0.347(3)	0.878(2)	5(1)
C(21)	0.873(2)	−0.151(2)	0.664(1)	5.5(5)
C(31)	1.165(2)	−0.033(2)	0.626(1)	5.4(5)
C(41)	0.983(2)	0.329(2)	0.550(1)	5.2(4)
C(61)	0.446(2)	0.206(2)	0.856(1)	5.1(4)
C(71)	0.335(2)	0.463(2)	0.670(1)	5.1(5)
C(81)	0.609(2)	0.599(2)	0.642(1)	4.9(5)
C(91)	0.887(2)	0.449(2)	0.803(1)	4.8(4)
H(1)	0.793	0.054	0.812	2.0
H(2)	0.981	0.162	0.780	2.0
Ib				
Ti	0.4611(4)	0.1018(4)	0.3592(1)	2.61(8)
Br	0.7322(3)	0.0932(3)	0.49707(7)	4.27(5)
Mg	0.4908(9)	−0.0431(6)	0.4380(2)	3.0(2)
O	0.495(2)	−0.243(2)	0.4381(5)	7.2(5)
C(1)	0.626(3)	0.331(2)	0.3944(6)	3.0(5)
C(2)	0.568(3)	0.373(2)	0.3544(8)	4.4(6)
C(3)	0.388(2)	0.309(1)	0.3591(6)	3.2(4)
C(4)	0.327(3)	0.238(2)	0.3972(7)	4.0(5)
C(5)	0.483(3)	0.247(2)	0.4202(7)	4.1(5)
C(6)	0.296(2)	−0.004(2)	0.2953(6)	3.1(5)
C(7)	0.335(3)	−0.119(3)	0.3131(6)	5.0(7)
C(8)	0.516(2)	−0.064(2)	0.3116(5)	3.0(5)
C(9)	0.591(2)	0.083(2)	0.2932(5)	3.0(4)
C(10)	0.453(2)	0.118(2)	0.2845(6)	3.5(5)
C(11)	0.823(3)	0.392(3)	0.4044(8)	5.3(7)
C(12)	0.296(6)	−0.388(4)	0.431(1)	11(1)
C(13)	0.260(5)	−0.462(4)	0.472(1)	10(1)
C(14)	0.580(9)	−0.317(7)	0.439(2)	14(2)
C(15)	0.767(5)	−0.210(4)	0.431(1)	12(1)
C(21)	0.675(3)	0.478(3)	0.3184(8)	5.9(8)
C(31)	0.261(3)	0.335(2)	0.3270(8)	6.0(7)
C(41)	0.140(3)	0.152(3)	0.4163(7)	4.9(7)
C(61)	0.113(2)	−0.021(2)	0.2876(8)	5.0(6)
C(71)	0.196(3)	−0.272(2)	0.3265(8)	5.8(7)
C(81)	0.615(3)	−0.150(2)	0.3233(8)	6.7(7)
C(91)	0.778(3)	0.180(3)	0.2837(8)	6.1(7)
H(1)	0.335	−0.015	0.399	2.0
H(2)	0.627	0.088	0.392	2.0

structures were solved using the direct method and successive Fourier synthesis and were refined by the full-matrix least-square method. The Me groups of the diethyl ether ligands were disordered due to their intense thermal movement; improved results were obtained for several closely positioned C atoms with partial occupancy. Among hydrogen atoms, only those bridging the Ti and Mg atoms were found in the difference map. They were included in the atom sets with constrained Ti–H vectors. All non-hydrogen atoms except the C atoms of the Me groups of OEt_2 ligands were refined anisotropically. All the calculations were carried out on a VAX-2 computer using SDP programs.

The crystal data for **Ia** and **Ib** and further details of the structure determination are summarized in Table 1. Positional and equivalent thermal parameters for **Ia** and **Ib** are listed in Table 2. Selected bond distances and valence angles are given in Table 3.

2.4. EPR spectroscopy

EPR spectra were measured on an ERS-220 spectrometer (German Academy of Sciences, Berlin) in the X-band at +30 to −30°C using the variable temperature unit STT-3. g-Factors were determined using a Mn^{2+} ($M_i = -1/2$ line) standard at $g = 1.9860$ and a proton magnetometer MJ-110 R (Radiopan, Poznan, Poland).

TABLE 3. Bond distances (Å) and bond angles (°) in the structures **Ia** and **Ib**

	Ia	**Ib**		**Ia**	**Ib**
Ti···Mg	2.880(4)	2.880(8)	Ti–C(1)	2.34(2)	2.37(2)
Ti–H(1)	1.72	1.71	Ti–C(2)	2.44(1)	2.46(2)
Ti–H(2)	1.79	1.79	Ti–C(3)	2.42(1)	2.41(2)
Mg–X	2.467(7)	2.634(6)	Ti–C(4)	2.33(1)	2.42(3)
Mg–X′	2.451(7)	2.645(7)	Ti–C(5)	2.32(1)	2.32(2)
Mg–H(1)	1.89	1.89	Ti–C(6)	2.38(1)	2.38(2)
Mg–H(2)	1.93	1.93	Ti–C(7)	2.46(1)	2.44(2)
Mg–O	2.07(1)	2.01(2)	Ti–C(8)	2.44(1)	2.40(2)
O–C(12)	1.64(3)	1.70(4)	Ti–C(9)	2.41(2)	2.35(2)
O–C(14)	1.33(3)	1.23(9)	Ti–C(10)	2.33(1)	2.30(2)
C–C(av., C_p)[a]	1.42	1.41	Ti–C(av.)	2.39	2.39
CE1–Ti–CE2[b]	138.2	138.9	X–Mg–X′	84.2(4)	85.4(2)
H(1)–Ti–H(2)	80.4	80.3	Mg–X–Mg′	95.8(4)	94.6(2)
H(1)–Mg–H(2)	72.5	72.5	X–Mg–O	96.3(5)	99.5(6)
Ti–H–Mg(av.)	104	104	X′–Mg–O	102.3(6)	97.6(5)

[a] The C–CH_3 distances are in the ranges 1.48–1.55 Å (**Ia**) and 1.49–1.56 Å (**Ib**). [b] CE1 and CE2 centroids of the C_p-rings C(1)–C(5) and C(6)–C(10), respectively.

3. Results and discussion

All the $Cp'_2TiX_2/{}^iPrMgX$ ($Cp' = Cp$, $C_5H_2Me_3$, C_5HMe_4; $X = Cl$ or Br) systems in diethyl ether at Mg/Ti molar ratios of 4–20 afforded blue crystalline products, slightly soluble in diethyl ether. In the series of chloro compounds, the products, denoted **Ia**, **IIa** and **IIIa** for the C_5HMe_4, $C_5H_2Me_3$ and Cp derivatives, respectively, were obtained as slurries of blue crystals with a white sediment of $MgCl_2$. In the series of bromo compounds, denoted analogously **Ib**, **IIb** and **IIIb**, the $MgBr_2$ formed remained in solution and blue crystals of the products were easily separated. The formation of the products is apparently quantitative because the blue colouration of the mother liquors decreased in intensity from **IIIb** to nearly colourless **Ib** and all the liquors exerted only EPR spectra at $g = 1.993$ with the triplet splitting $a_H \sim 0.7$ mT in intensity proportional to the colouration. Although the EPR spectra differ in superhyperfine splitting (*vide infra*), their main parameters (g, a_H) are very close to those found earlier in the spectra of Cp_2TiCl_2–MR (M = alkali metal, MgX; R = Et or ${}^iPr$) systems and assigned to either $(Cp_2TiH_2)^-M^+$ or $Cp_2Ti(\mu\text{-}H)_2MgBr$ [8,10]. X-Ray single crystal analysis was performed for the C_5HMe_4 compounds **Ia** and **Ib** because **Ia** was the only chloro compound yielding sufficiently large crystals which could be separated from the precipitate of $MgCl_2$.

3.1. X-Ray structures of Ia and Ib

The X-ray analysis revealed that both the compounds form practically identical dimeric centrosymmetrical molecules $[(C_5HMe_4)_2Ti(\mu\text{-}H)_2Mg(OEt_2)(\mu\text{-}Cl)]_2$ (**Ia**) and $[(C_5HMe_4)_2Ti(\mu\text{-}H)_2Mg(OEt_2)(\mu\text{-}Br)]_2$ (**Ib**). The structure of **Ia** with atom numbering scheme is shown in Fig. 1. The titanium atom is coordinated to two η^5-C_5HMe_4 ligands and is connected through bridging hydrogen atoms to one magnesium atom. The magnesium atom is further bonded to two bridging halogen atoms (X and X′) and to the oxygen atom of the coordinated diethyl ether. The structures of **Ia** and **Ib** differ remarkably only in the Mg–X bond lengths and in the packing mode of the molecules in the crystals. The bridging hydrogen atoms were localized by the difference synthesis at reasonable distances from both the Ti and Mg atoms, however, the refinement of their positions could not be carried out because of insufficient quality of the intensity measurement. The position of H atoms at mean distances Ti–H = 1.75 Å and Mg–H = 1.91 Å are virtually the same as in $[(C_5Me_5)_2Ti(\mu\text{-}H)_2]_2Mg$ (**IV**) (1.73 Å and 1.89 Å, respectively) [12]. The distance of 2.88 Å between Ti and Mg atoms in **Ia** and **Ib** is nearly the same as in **IV** (2.86 Å). It is, however, slightly longer than the Ti–Al distances (2.75–2.79 Å) in a number of titanocene hydride–aluminium hydride complexes [13,14]. Among the latter complexes, the structure of $[(C_5Me_5)_2Ti(\mu\text{-}H)_2AlH(\mu\text{-}H)]_2$ [14] most closely resembles those of **Ia** and **Ib**.

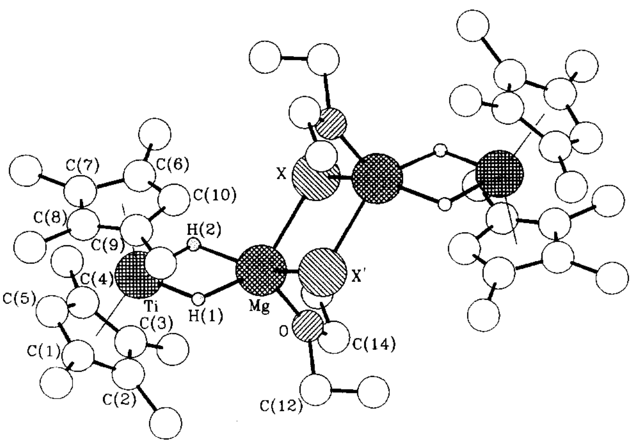

Fig. 1. The molecular structure and atom numbering scheme for **Ia** and **Ib**.

The halogen bridged cycles Mg–X–Mg′–X′ are planar as follows from the presence of the centre of inversion; these cycles form rhombs with the X–Mg–X′ angle of 85°. The Mg–X bonding distances are close to those currently found in bridges where one halogen atom binds two magnesium atoms. For instance, the Mg–Cl and Mg–Cl′ distance, on average 2.46 Å, in the $Mg(\mu\text{-}Cl)_2Mg$ skeleton of **Ia**, where the coordination number of Mg (CN(Mg)) is 5, is slightly longer than the average value of 2.42 Å for $[(C_5Me_5)Mg(\mu\text{-}Cl)(THF)]_2$ with CN(Mg) = 4 [15] but slightly shorter than the average 2.49 Å in $[Cp_2Ti(\mu\text{-}Cl)_2Mg(THF)_2(\mu\text{-}Cl)]_2$, where CN(Mg) = 6 [16]. The Mg–Br distance (av. 2.64 Å) in **Ib** is longer than the distances of 2.57 Å in $[EtMg(\mu\text{-}Br)(NEt_3)]_2$ [17] and 2.58 Å for $[EtMg(\mu\text{-}Br)(OPr_2]_2$ [18]; this is compatible with CN(Mg) = 5 in **Ib** and CN(Mg) = 4 in the compared complexes.

The Mg–O distances 2.07 Å for **Ia** and 2.01 Å for **Ib** fall into the range 2.0–2.1 Å found for the coordination of ethers in Grignard reagents [19]. The terminal Me groups in OEt_2 ligands exert an intense thermal movement which is reflected in high values of thermal factors and even in the partial occupancy of close positions for corresponding C atoms.

The formation of dimeric molecules is compatible with the coordination of only one ether molecule at the Mg atom. It is known from the stereochemistry of Grignard reagents [19] that alkyl groups of coordinated OEt_2 and OPr_2 effectively prevent the magnesium atom attaining a coordination number higher than 4.

The fine control of dimerization by ether molecules is illustrated by dimeric $[EtMg(\mu\text{-}Br)(OPr_2)]_2$, where $Mg:OPr_2 = 1:1$, [18] whereas $EtMg(Br)(OEt_2)_2$, where $Mg:OEt_2 = 1:2$, is monomeric [20]. In **Ia** and **Ib**, the coordination number 5 is, however, possible because bridging hydrogen atoms occupy a smaller coordination space compared to other ligands.

In octamethyltitanocene moieties, the orientation of the C_5HMe_4 ligands is remarkable. In the $(C_5HMe_4)TiCl$, $(C_5HMe_4)TiI$, and $(C_5HMe_4)TiCl_2$ compounds, the ring carbon atoms bearing the hydrogen atom are in positions of close contact with the C_5HMe_4 ligands to minimize steric hindrance [21]. In **Ia** and **Ib**, the C_5HMe_4 ligand (C(6)–C(10)) which is in proximity to bridging halogen atoms has the opposite orientation. This is apparently caused by repulsion between Me groups of this ligand and bridging halogen atoms (see Fig. 1). Both the C_5HMe_4 ligands are slightly displaced so that the Ti–C(5) and Ti–C(10) distances are the shortest (*cf.* values of Ti–C distances in Table 2). In spite of these differences, the CE–Ti–CE angles are virtually the same in **Ia** (138.2°), **Ib** (138.9°) and in other molecules containing the $(C_5HMe_4)_2Ti$ moiety (139°) [21].

3.2. EPR spectra of the Cp'_2TiX_2–^iPrMgX systems

The EPR spectra of the reacting mixtures revealed that the $(C_5HMe_4)_2TiX_2$ and $(C_5H_2Me_3)_2TiX_2$ compounds are first reduced to monomeric monohalides Cp'_2TiX ($X = Cl$, $g = 1.964$–1.965, $\Delta H = 1.2$–1.3 mT; $X = Br$, $g = 1.960$–1.962, $\Delta H = 2.3$ mT) (*cf.* [22]). In addition to these dominating signals, two minor signals in the range $g = 1.983$–1.986 and $g = 1.975$–1.979 were transiently observed, which could be tentatively attributed to the $[Cp'_2Ti(\mu\text{-}X)_2]_2Mg(OEt_2)_n$ and $[Cp'_2Ti(\mu\text{-}X)_2Mg(OEt_2)_n(\mu\text{-}X)]_2$ ($n = 1$–2) compounds (*cf.* [16]). The EPR spectra showing a triplet hyperfine splitting of *ca.* 0.7 mT at $g = 1.9910$–1.9919 occurred when the formation of the Cp'_2TiX compounds was completed and grew in intensity until blue crystals started to precipitate on the walls. In the Cp_2TiCl_2 system, the grey-green dimer $(Cp_2TiCl)_2$, slightly soluble in ethyl ether reacted rapidly to a blue product (**IIIa**) characterized by the known EPR spectrum with triplet splittings [8,10]. The parameters of the solution EPR spectra of all the compounds are listed in Table 4. Compared to the published EPR spectrum for the $Cp_2TiBr_2/{}^iPrMgBr$ system in THF, which showed coupling to magnesium (^{25}Mg, $I = 5/2$, 10% abundance) [10], the resolution in none of our systems was sufficient to observe these features, although further hyperfine splitting was well discernible in all the spectra at optimum temperature 0–10°C. This splitting was ascribed earlier to the interaction of the Ti^{III} unpaired electron with hydrogen protons of the C_5H_5 rings [8–10]. The present results show that the origin of this splitting is rather puzzling in methylated derivatives

TABLE 4. EPR parameters of the $[Cp'_2Ti(\mu\text{-}H)_2Mg(OEt_2)(\mu\text{-}X)]_2$ complexes [a] (values of coupling constants in mT)

Cp′	X	g	a_H	$a_{H(Cp')}$	Multiplicity	a_{Ti}
C_5HMe_4	Cl	1.9912	0.66	0.10	Odd	0.54
	Br	1.9910	0.68	0.10	Odd	0.54
$C_5H_2Me_3$ [b]	Cl	1.9919	0.67	0.06	Odd	0.58
	Br	1.9917	0.70	0.06	Odd	0.58
C_5H_5	Cl	1.9934	0.74	0.04	Even	0.68
	Br	1.9932	0.75	0.04	Even	0.66

[a] Diluted solutions in diethyl ether, measured at 0°C. [b] 1,2,3-trimethylcyclopentadienyl isomer.

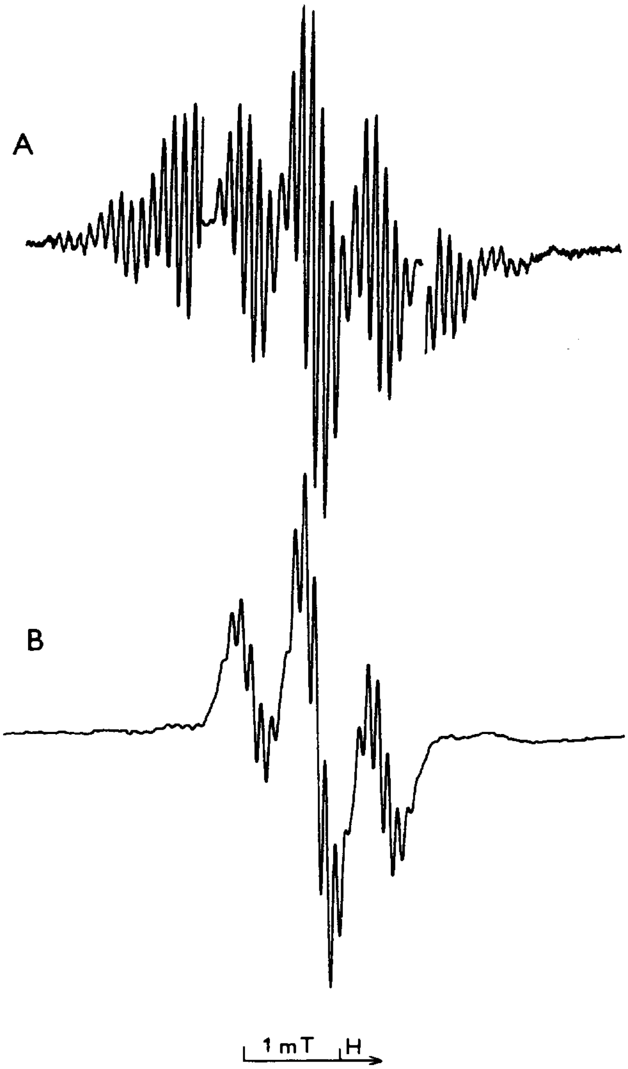

Fig. 2. EPR spectra of **Ia** (A) and of the same compound containing 55% of the C_5DMe_4 ligand (B) (diethyl ether solution, 0°C, wings of the spectrum A were amplified 20 times showing the features due to the ^{47}Ti and ^{49}Ti isotopes).

since the number of lines in the multiplets does not decrease proportionally with the number of hydrogen atoms at the Cp rings. The C_5HMe_4 and $C_5H_2Me_3$ compounds exert multiplets consisting of at least of 7 and 9 lines, respectively, which cannot be accounted for by the presence of 2 or 4 equivalent ring protons in both the titanocene moieties. Compound **Ia** containing 55% of the C_5DMe_4 ligands showed the same splitting pattern as the undeuterated sample but in decreased intensity (Fig. 2). This means that the ring proton is responsible for the occurrence of the multiplet spectra and some mode of induction of unpaired electron spin density on Me substituents must be considered. The presence of the ring proton is substantial for this effect because the analogous C_5Me_5 chloro compound yields an EPR spectrum with triplet splitting ($a_H = 0.67$ mT) at $g = 1.9904$ but without further hyperfine splitting [12]. The origin of multiplets cannot be explained by the inequivalence of the C_5HMe_4 rings in **Ia** and **Ib** (*vide supra*). The solution EPR spectra cannot distinguish between the presence of dimeric or monomeric compounds in ether solution since any electronic Ti^{III}–Ti^{III} interaction can hardly be assumed in the dimers.

Further study of the title compounds by spectroscopic means and the examination of their chemical reactivity are under way.

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