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Paramagnetic NMR of Titanocene–Aluminum $(\eta^5\text{-}C_5H_5)_2TiCl_2AlX(C_2H_5)$, X = C_2H_5 and Cl, Complexes and some Related Titanocene–Aluminum Hydride Derivatives*

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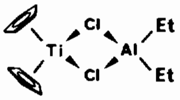
Abstract

The NMR paramagnetic shifts and the calculated proton and carbon hyperfine coupling constants are reported for $(\eta^5\text{-}C_5H_5)_2TiCl_2Al(X)(C_2H_5)$, X = C_2H_5 (**I**) and Cl (**II**). The reaction of $(\eta^5\text{-}C_5H_5)_2TiCl$ with $HAl(C_2H_5)_2$ (1:2) was followed by NMR. A transient species believed to be the Shilov type bimetallic monomeric hydride was observed. The spectrum of the isolated hydride product shows non-equivalent cyclopentadienyl ring protons and is similar to the NMR spectra reported for oligomeric titanium hydrides. Moreover, microanalysis and spectroscopic results are consistent with the oligomeric structure for the isolated hydride (**III**), which is believed to be another example of a $\mu\text{-}(\eta^1\text{:}\eta^5\text{-}C_5H_5)$ cyclopentadienyl bridged complex.

Introduction

Bimetallic aluminium compounds of the type $(\eta^5\text{-}C_5H_5)_2TiCl_2AlX_2$ (X = alkyl) have been extensively studied in the past tree decades primarily because of their role in key catalytic reactions [1]. The structure determined by X-ray crystallography is shown here for the ethyl complex **I** [2].



The arrangement of the ligands about Ti and Al is tetragonal and both metal atoms are approximately on the principal molecular axis.

EPR has been extensively used to probe the physico-chemical properties of the alkyl derivatives [3–6]. It was first thought that the parasite octet resonance which appears in the spectra of **I** was due to spin coupling with aluminum and two equivalent protons of the ethylene ligands, but no reasonable explanation could be given for the doublet resonance observed in a second intermediate spectra [7]. The intrinsic tendency of aluminum alkyls to eliminate hydrogen has focussed interest on the hydride derivatives. Shilov *et al.*, were the first to relate the new resonances to monomeric hydrides derived from the titanocene–aluminum alkyls [8]. The detailed EPR study of X = iso-butyl, ethyl, and several other alkyl groups, reveals that the new spectra could satisfactorily be explained by assuming the *in situ* formation of hydrogen bridge complexes, $(\eta^5\text{-}C_5H_5)_2TiX'_2AlX_2$, X'_2 = (H)(Cl) and H_2 [3, 8]. Since, combined deuteration experiments [8] and elimination or hydrogenation reactions [1, 9–11] involving principally the alkyl groups have shown that in solution the dichloro-bridge complexes are in fact in equilibrium with the mono and dihydrido-bridge derivatives. The interpretation of the EPR spectra of the analogue dichloro and tetrahydrido compounds is also consistent with the monomeric structure [12, 13]. A bimetallic structure is also found for the gas and solid phase titanocene tetrahydrido borate molecule $(\eta^5\text{-}C_5H_5)_2TiBH_4$, adding further evidence in favor of the hydrido-bridge as a general structure for the titanocene–group IIIA hydrides [14].

Interestingly, the titanocene–aluminum hydride compounds isolated so far are structurally quite different from each other. A few compounds have been found to have the double-bridge titanium–aluminum center. For instance, X-ray analysis has shown that this type of structure exists for the adduct compound $[(\eta^5\text{-}C_5H_5)_2TiAlH_4]_2\cdot[(CH_3)_2NCH_2CH_2N(CH_3)_2]$ [15]. Similarly, the bridged-ring 1,1′-methylenetitanocene complex $CH_2(\eta^5\text{-}C_5H_4)_2TiAlH_4$ is also believed to belong to this class [16]. However, compared to their boron analogues these monomeric tetrahydrido aluminates are less stable. Stabilization in the above complexes is achieved by nitrogen dative bonding to the aluminum metal and by linking the two cyclopentandienyl rings. The inherent molecular instability in monomeric titanocene aluminates leads to oligomeric hydrides.

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The complexes $[(C_5H_5)(C_5H_4)TiHAl(C_2H_5)_2]_2$ [17, 18], $\{[(C_5H_5)Ti]_2(H)(H_2Al(C_2H_5)_2(C_{10}H_8)$, $[(C_5H_4)$-$TiHAl(C_2H_5)_2]_2(C_{10}H_8)\}$ [19], and $[(C_5H_5)_4Ti_2$-$AlH_3]_2$ [20] are some examples and all have a Ti–H–Al bridge with either μ-(η^1:η^5-C_5H_4) cyclopentadienyl or μ-(η^5:η^5-$C_{10}H_8$) fulvalenyl ligands in their molecular structure.

In view of this rich chemistry we decided to examine by NMR the paramagnetic spin distribution between the titanocene and aluminate moieties for the paramagnetic titanium(III) complexes **I** and **II**. Moreover, the reaction of $(\eta^5$-$C_5H_5)_2TiCl$ and the neutral trimeric $[HAl(C_2H_5)_2]_3$ hydride was followed by NMR. A titanocene aluminum hydride was isolated and characterized by elemental analysis, MS, NMR, EPR, and IR spectroscopy.

Experimental

The titanocene monochloride, $(\eta^5$-$C_5H_5)_2TiCl$, complex was prepared by direct synthesis from $TiCl_3$ and $Tl(C_5H_5)$ [21]. The chloro aluminum alkyl derivatives **I** and **II** were prepared following a known method [22] from $(\eta^5$-$C_5H_5)_2TiCl_2$, purchased from Strem Chemicals, and $Cl_2Al(C_2H_5)$ and $ClAl(C_2H_5)_2$, respectively. The aluminum alkyl compounds (neat liquids) and titanium trichloride, $TiCl_3$ 98%, were purchased from Thiocol-Alpha, thallium sulfate, $Tl_2(SO_4)$, from Aldrich Chemical Co., and lithium diethyldihydridoaluminum, $Li[H_2Al(C_2H_5)_2]$, 2.75 M in toluene, was supplied by Alpha Products. All the chemicals were used as received from the manufacturer without any additonal purification.

The compounds are extremely air sensitive. All reactions and subsequent manipulations were performed in a Schlenk-type apparatus filled with purified nitrogen or in an argon filled dry box (O_2 and $H_2O < 5$ ppm). The solvents were refluxed, over sodium for toluene, or molecular sieves for heptane and pentane, before being distilled under a nitrogen atmosphere.

Mass spectra of the solid complexes were recorded on a Varian M66 instrument. Glass capillaries containing the samples were introduced in the instrument on a heated metal rod. Spectra were recorded periodically while the temperature reached 200 °C at a rate of 64 °C/min. Elemental microanalysis were carried out by Schwarzkopf Microanalytical Laboratories, New York, U.S.A. The nuclear magnetic resonance (NMR) spectra were recorded on either a Bruker WP-80 instrument (80 MHz, ^{1}H), a Bruker HX-90 continuous wave (90 MHz, ^{1}H), or a Bruker WH-400 Fourier transform (400 MHz, ^{1}H and 101 MHz, ^{13}C) multinuclear instrument. Electron paramagnetic resonance (EPR) experiments were carried out with the samples in 3 mm O.D. quartz tubing using a Jeol JES-ME-3X spectrometer. The diphenylpicrazyl (DPPH) radical ($g = 2.0036$) was used for calibration. Infrared (IR) spectra of the samples were recorded on a Beckman IR-4250 instrument from KBr wafers prepared in the dry box. The spectra were calibrated using a polystyrene film.

In the following discussion the NMR shifts quoted will be in $\Delta H/H$ units, *i.e.* in ppm with positive values increasing upfield from either the ring solvent proton (toluene-d_7) or quaternary carbon resonances.

Synthesis of the Hydride (III)

First, the following modification to a protocol given by Ziegler *et al.* for preparing the neutral aluminum hydride, $HAl(C_2H_5)_2$ [23] was made. A magnetic stirring bar is introduced into a three neck 500 ml Schlenk flask mounted with a dropping funnel, a glass stopper, and a water cooled reflux column. Then, 200 ml of freshly distilled toluene and 7 ml (53.0 mmol) diethylaluminum chloride, $ClAl(C_2H_5)_2$ (95%), were transferred into the flask. From the dropping funnel, 120 ml (55.0 mmol) of $Li[H_2Al(C_2H_5)_2]$, 0.458 M in toluene, were added dropwise to the magnetically stirred solution over a period of 1 h. Once the addition was completed, the solution was stirred for another hour at ambient temperature. Next, the reaction mixture was left standing on dry ice over night.

In a typical preparation the flask was warmed to room temperature. The clear hydride solution above the white solid was then transferred through a small bore PTFE tubing to a second magnetically stirred 125 ml toluene solution containing 11.80 g (55.4 mmol) $(C_5H_5)_2TiCl$. The khaki-green color of the monochloride solution immediately turned dark violet. The reaction flask was then connected to a vacuum line and heated at 70 °C for 3 h under nitrogen. The solvent was taken off under reduced pressure and ambient temperature till heavier volatiles stopped condensing onto the line's liquid nitrogen traps. Freshly distilled heptane, 150 ml, was added to the oily residue. The deep violet solution was stirred and the flask left standing on dry ice for several days. A black powder formed which was collected by filtration on a fritted glass disk while the solution was still cold. The heptane filtrate was recovered and its volume reduced so a second crop of the black solid could be collected in the same way. This yielded 7.5 g of the black solid. The solid decomposed at 170 °C. *Anal.* Calc. for C_{44}-$H_{50}Cl_4AlTi_4$: C, 56.27; H, 5.37; Cl, 15.09; Al, 2.87; Ti, 20.40. Found: C, 55.50; H, 5.06; Cl, 14.74; Al, 2.41; Ti, 21.99% (total mass = 100.7%). IR (KBr): 3100w,br; 2915s; 2890w; 2857s; 2790vw; 2715vw; 1700m,br; 1512w; 1445s; 1427m; 1410m; 1367s; 1260w,sh; 1237w,sh; 1227s,br; 1022s; 1010m,sh; 800s; 666s; 540w; 440w; 390w,br; base

TABLE I. Ion Abundance Observed in Mass Spectrum of III

m/z	Relative abundance (%)[a]	Ion	*m/z*	Relative abundance (%)[a]	Ion	*m/z*	Relative abundance (%)[a]	Ion
57	17	$HAlEt^+$	112	12	$Ti(C_5H_4)^+$	148	99	$Ti(C_5H_5)_2Cl^+$
65	34	$C_5H_5^+$	113	18	$Ti(C_5H_5)^+$	149	14	$Al(C_2H_5)_2(C_5H_4)^+$
66	33	$C_5H_6^+$	120	14	$Al(C_5H_4)(C_2H_5)^+$	150	42	$Al(C_2H_5)_2(C_5H_4)H$[c]
77[b]	17	$C_6H_5^+$	121	10	$Al(C_5H_5)(C_2H_5)^+$	178	28	$Ti(C_5H_5)_2^+$
79[b]	26	$C_6H_7^+$	122	25	$Ti(C_3H_3)Cl^+$	183	11	$Ti(C_5H_5)Cl_2^+$
83	31	$TiCl^+$	124	13	$Ti(C_3H_5)Cl^+$ [c]	211	13	$Ti(C_5H_4)_2Cl^+$
85	26	$Al(C_2H_5)_2^+$ [c]	146	13	$Ti(C_5H_3)Cl^+$	212	12	$Ti(C_5H_4)(C_5H_5)Cl^+$
91	22	$Al(C_5H_4)^+$	147	14	$Ti(C_5H_4)Cl^+$	213	100	$Ti(C_5H_5)_2Cl^+$
						214	20	$Ti(C_5H_5)_2HCl^+$
						215	37	$Ti(C_5H_5)_2H_2Cl^+$

[a] Percent relative abundance. Only fragments above *m/z* = 50 and with intensities equal or greater than 10% are given in the Table. [b] From solvation toluene in the solid sample. [c] No correction has been made to the intensity because of chlorine-37. Hence, a significant amount of the intensity reported here, one fourth of the (*m/z*-2) peak, is due to this isotope fragment.

TABLE II. Paramagnetic Proton NMR Shifts for III and Other Titanocene–Aluminium Hydrides[a]

Complexes	Chemical groups (relative intensity)					
	C_5H_5	C_2H_5	C_5H_4	$C_{10}H_8$	TiHAl	TiHTi
III[b]	1.98(5)	5.43(3), 5.62(3)[c], 6.26(2), 6.36(2)[d]	0.11(1), 1.14(1), 2.11(1), 2.71(1)		13.77(1)	
$[(C_5H_5)(C_5H_4)Ti(H)Al(C_2H_5)_2]_2$[e]	2.05	5.64, 5.78, 6.46, 6.64	0.24, 1.27, 2.17 2.81		14.12	
$[(C_5H_5)Ti]_2(H)[H_2Al(C_2H_5)_2]$[f]	1.84(10)	5.73(3), 5.89(3), 6.75(2), 6.97(2)		0.65(2), 2.49(4), 3.30(2)	18.72(2)	28.9(1)
$[(C_5H_4)TiHAl(C_2H_5)_2]_2C_{10}H_8$[g]		5.57(3), 5.87(3) 6.31(2), 7.10(2)	−1.17(1), 0.71(1), 1.26(1), 2.27(1), 2.55(1), 2.85(1), 2.94(2)		13.69(1)	

[a] Shifts are given relative to the intense toluene ring resonance. [b] Spectrum taken at 333 K in toluene-d_8. [c] The first two frequencies are quartets with $J = 8$ Hz for both. [d] The last two frequencies are triplets with $J = 8$ Hz for both. [e] Taken from ref. 18; spectrum temperature and solvent conditions not defined. [f] Taken from ref. 19; at 225 K in toluene-d_8. [g] Taken from ref. 19; at 296 K in C_6D_6.

line deformation 950–500 cm^{-1}. The main ionic fragments in the electron impact mass spectrum are given in Table I. The characteristic NMR frequency of the hydride is given in Table II and its EPR features are discussed in the following sections.

All spectroscopic experiments were carried out on samples of the pure isolated products. Elemental microanalytic results for complexes **I** and **II** are: *Anal.* Calc. for $C_{14}H_{20}Cl_2AlTi$ (**I**): C, 50.33; H, 6.03; Cl, 21.23%, molecular weight 334.10, reported melting point (m.p.) 126–130 °C [22]. Found: C, 50.01; H, 5.97; Cl, 21.10%. MS 333 *m/z* (9% relative intensity), m.p. 123–128 °C. Calc. for $C_{12}H_{15}Cl_3AlTi$ (**II**): C, 42.33; H, 4.44; Cl, 31.24%, molecular weight 340.49, reported m.p. 88–92 °C [22]. Found: C, 41.89; H, 4.40; Cl, 29.04%, MS 339 *m/z* (2% relative intensity), m.p. 85–89 °C. Similarly, their room temperature solution EPR spectra were identical to those reported in the literature [6].

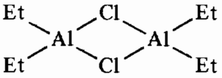
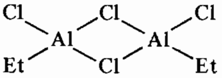
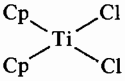
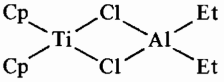
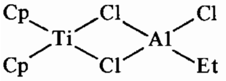
Results

The NMR shifts for **I** and **II** are given in Table III together with their reference diamagnetic molecules. The band widths at half-height ($W_{1/2}$), and the calculated hyperfine coupling constants, A_h, are also given. The diamagnetic complex $(\eta^5\text{-}C_5H_5)_2TiCl_2$ was used to calculate the cyclopentadienyl isotropic shift. The aluminum alkyl compounds, $ClAl(C_2H_5)_2$ and $Cl_2Al(C_2H_5)$, were used as reference for the ethyl groups. The ethyl proton shifts for **I** and **II** vary linearly with the inverse absolute temperature as shown in Fig. 1. Also, the shift variations for the cyclopentadienyl ring carbons were found to be inversely proportional to the absolute temperature. Excessive line broadening in the spectra recorded below 254 K made it impossible to verify this linearity over the full 183 to 373 K temperature range covered. The ring protons were also not observed below 254 K for the same reason.

The proton paramagnetic shifts for the hydride complex **III** are given in Table II. Values found in the literature for other titanocene–aluminum hydrides have also been included. Variable temperature NMR shows that the temperature dependence is less than that observed for **I** and **II**. This can be seen from the shift *versus* temperature curves given in Fig. 2. The probable error for the reported shifts is based on the band width at half-height (0.29 $W_{1/2}$) and are shown as vertical bars on the curves, Figs. 1 and 2.

In summary, the cyclopentadienyl temperature dependent shifts in **I** and **II** move upfield for the carbon resonances as the temperature is lowered.

TABLE III. NMR Shifts of some Diamagnetic Compounds and Paramagnetic Complexes I and II in Toluene-d_8

Compound[a]	Ligand	Nuclei	Chemical shift, $\Delta H/H$[b] (ppm)		A_h; A_h (mean)[c] (Gauss)	Temperature (K)
	CH_2	H	6.81[d]			333
		C	133.3			
	CH_3	H	5.93[e]			
		C	128.7			
	CH_2	H	6.71[d]			333
		C	136.5			
	CH_3	H	6.02[e]			
		C	131.1			
$[HAlEt_2]_3$	AlHAl	H	4.14			333
	CH_2	H	3.43[f]			
	CH_3	H	[g]			
	C_5H_5	H	1.10			333
		C	12.0			
			Paramagnetic shift	Isotropic shift		
	C_5H_5	H	−27(1440)	−28	0.48	373[h]
I		C	81(220)	69	−0.30	368
			97(420)	85	−0.30 (−0.37 ± 0.05[i]	307
			120(900)	108	−0.32	254[h]
	CH_2	H	7.8(48)	1.0	−0.017/−0.018 ± 0.015[j]	373
		C	133(120)[k]	0	0	368
			130.9(54)	−2.4	0.009	308
			136(120)[k]	3	−0.007	187
	CH_3	H	4.6(48)	−1.3	0.022/0.023 ± 0.003[j]	373
		C	133(120)[k]	4	−0.017	368
			136.3(54)	7.6	−0.027	308
			136(120)[k]	7	−0.015	187
	C_5H_5	H	−26(1200)	−27	0.47	373
II		C	83(660)	71	−0.30	368
			95(420)	83	−0.30 −0.27 ± 0.09[l]	307
			103(840)	91	−0.35	294[h]

(continued)

TABLE III. *(continued)*

Compound[a]	Ligand	Nuclei	Chemical shift, $\Delta H/H$[b] (ppm)		A_h;A_h (mean)[c] (Gauss)	Temperature (K)
	CH_2	H	8.2(48)	1.5	−0.026/0.02 ± 0.02[m]	373
			136(120)[k]	−1	0.004	368
		C	133.6(40)	−2.9	0.010	307
			140(240)[k]	4	−0.009	187
	CH_3	H	4.2(48)	−1.8	0.031/0.042 ± 0.009[i]	373
			136(120)[k]	5	−0.021	368
		C	140.0(60)	8.9	−0.032	307
			140(240)[k]	9	−0.020	187

[a] The aluminium alkyl concentration was 20% (*v*/*v*). For the titanium complexes the solutions were saturated. [b] The shifts were measured relative to the intense ring proton resonance of toluene-d_7 impurities or to the solvent quaternary carbon resonances. The band widths at half-height ($W_{1/2}$) are given in parenthesis. [c] The first value in this column is the calculated hyperfine coupling constant for the given temperature. In some cases, when the Curie law is obeyed, the mean value and standard deviation calculated from the $\Delta H/H$ versus T^{-1} plots, is given. [d] Quadruplet with $J = 8.0$ Hz. [e] Triplet with $J \mp 8.0$ Hz. [f] Two partially resolved quadruplets were observed. J (quadruplet) = 10.0 Hz and J (doublet) = *ca.* 1 Hz. [g] The methyl protons were partially masked by triethylaluminium impurities at 5.90 ppm. [h] The cyclopentadienyl resonances were too broad ($W_{1/2} > 3000$ Hz) below this temperature to permit accurate determination of the frequency. [i] Linear correlation coefficient = 0.99. [j] Linear correlation coefficient = 0.89. [k] Only one resonance was observed for the ethyl ligand. [l] Linear correlation coefficient = 0.87. [m] Linear correlation coefficient = 0.80.

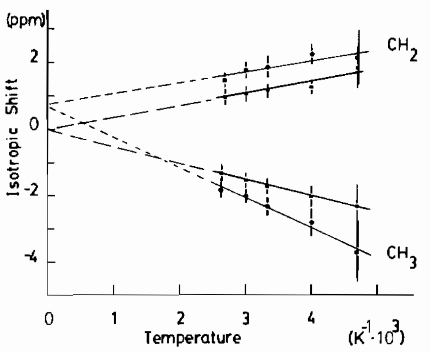


Fig. 1. Ethyl proton isotropic shifts for I (squares) and II (circles) *vs.* the inverse temperature.

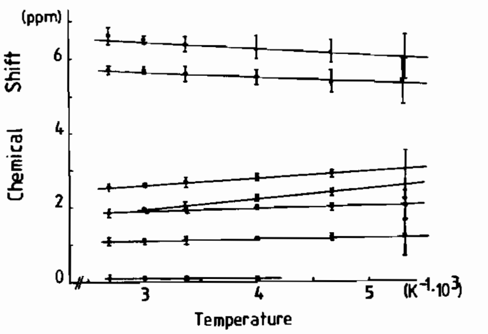
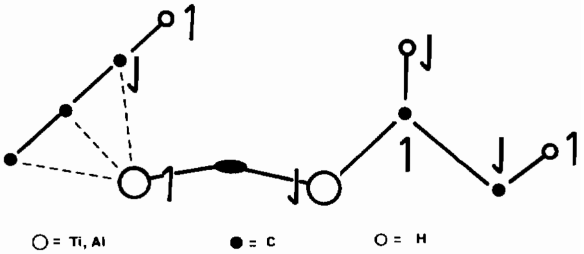


Fig. 2. Proton NMR shifts for III *vs.* the inverse temperature. Each curve follows the assignment given in Table II. For simplicity the average values of the methylene and methyl resonances were used. The hydride proton shift is not shown on the Figure.

Also, for the ethyl groups the paramagnetic shifts are to high fields for the methylene protons and to low fields for the methyl protons. Conversely, the carbon shifts follow an opposite trend. Assuming the isotropic shift is dominated by contact interaction the spin coupling sign can be found from the direction of the paramagnetic shifts [24]. Scheme 1 represents the relative spin directions found by NMR at the different atoms for I and II. The spin directions at Ti and Al atoms have been placed to coincide with the contact scheme. Moreover, the inverse spin direction between the two metals is consistent with a three center Ti–X–Al bond (only 2 electrons) in the bridge.



Scheme 1.

Since the Shilov type hydride $Cp_2TiX'_2AlEt_2$, X'_2 = HCl or H_2, could not be isolated, the reaction of Cp_2TiCl and $HAlEt_2$ was followed by proton NMR. Figure 3 shows a spectrum in toluene-d_8 after 24 h. Spectra B and C were recorded for the reaction at room temperature after several days.

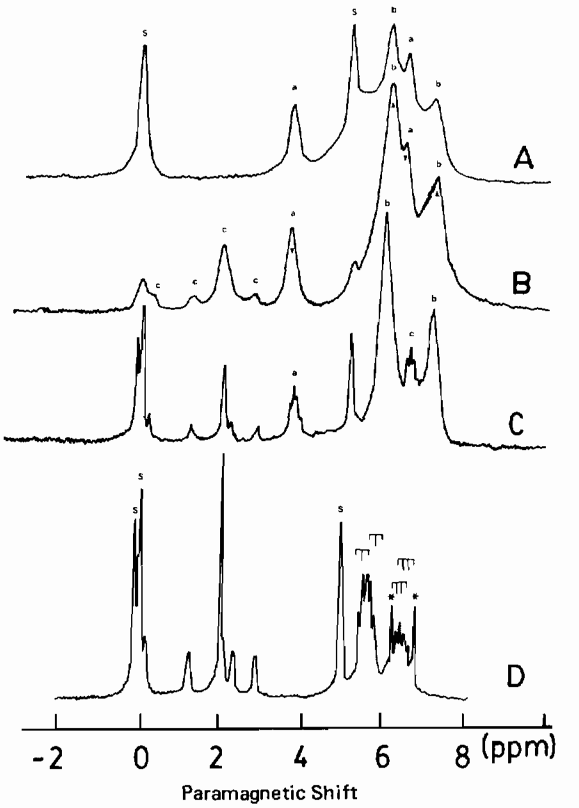


Fig. 3. Proton NMR spectra (90 MHz) showing the changes observed in the reaction mixture of **III**. A, spectrum taken after 24 h; B, spectrum taken after 8 days; C, spectrum taken after 18 days; D, spectrum of the isolated hydride **III**. All spectra were taken in toluene-d$_8$ (5–20% v/v) and at 333 K, s = solvent, * = impurity.

The room temperature EPR spectrum of **III** in toluene solvent is shown in Fig. 4. The spectrum was interpreted in terms of two magnetically distinct and non-coupled paramagnetic centers. The doublet signal has a line spacing of 5 Gauss centered at $g = 1.982$. This resonance is depicted by the a splitting. Superimposed on this, is a sextet pattern made-up of four lines at low field of the former doublet plus two more mixed-in and equally spaced by 3 Gauss. This is shown by the b splitting centered at $g = 1.985$. The observed intensities coincide with the 1:2:2:2:2:1 ratio calculated for spin coupling between one proton and a ^{27}Al ($I = 5/2$, 100%) metal atom. The EPR spectrum for a polycrystalline sample is given in Fig. 4. The spectrum of the solid product is made up of a featureless sine shaped base line and a much weaker singlet resonance at $g = 1.987$.

Discussion

NMR has in the past proven to be an efficient spectroscopic method for studying the structure of paramagnetic organometallic metallocenes. The NMR theory of paramagnetic molecules has been exposed by DeBoer and Van Willigen [24] and a few reviews on its application to paramagnetic metallocenes have been published [25–27].

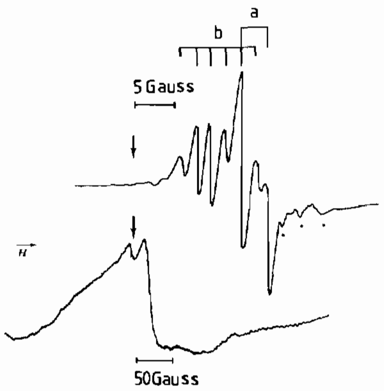


Fig. 4. Room temperature EPR spectrum (9.3 GHz) of **III** in toluene solution (upper) and as polycrystalline solid (lower). The arrow indicates the DPPH resonance position, * = impurity.

The study of **I** and **II** *in situ* from reaction mixtures can pose some problems. Under normal conditions β-unsaturated alkyl complexes such as $(\eta^5\text{-}C_5H_5)_2TiCl_2AlX_2$ are known to yield significant amounts of mono and dihydride titanocene–aluminum complexes in solution [3]. The products are also exchanging with free aluminum alkyls, molecular hydrogen or olefine molecules in the solution [3, 9–11]. Hence, the spectroscopic data was recorded from samples prepared from the isolated products.

The NMR isotropic shift can be expressed as the sum of the contact (Fermi) and pseudo-contact (dipolar) spin interactions with the nucleus. For **I** and **II** the later interaction can be assumed to be negligible (<1 ppm) because of the small molecular anisotropic g differences and the large distances separating the nuclei and the titanium paramagnetic center. Hence, from the isotropic shift expression, $\Delta H/H$(iso), given in eqn. (1) the hyperfine coupling constant (A_h, in Gauss) can be calculated for a given temperature (T) and the total molecular spin (S) [23, 25–27].

$$\Delta H/H(\text{iso}) = -A_h \frac{g^2\beta^2}{g_N\beta_N} \frac{S(S+1)}{3kT} \qquad (1)$$

This equation predicts that the isotropic shifts will follow the Curie law: $\Delta H/H \propto T^{-1}$ and the A_h value can be gathered with precision, and independently of the diamagnetic reference compound, from the slope of the $\Delta H/H$ *versus* T^{-1} plot.

NMR Spectra of I and II

The NMR spectra taken in solution are consistent with the 'dumb-bell' like solid state structures. The

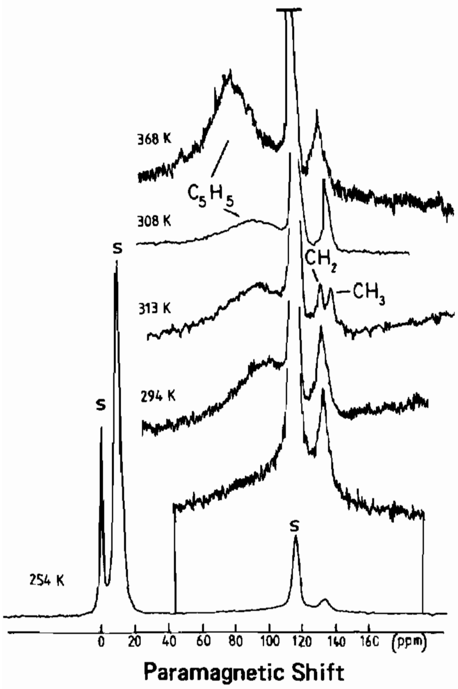


Fig. 5. Carbon NMR spectra (20 MHz) of I at selected temperatures taken in toluene-d_8, s = solvent.

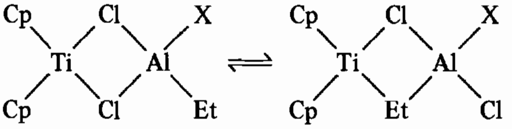
proton and carbon spectra show a single ring resonance and two signals attributable to the ethyl ligands. The proton and carbon ring resonances are in the general frequency area previously reported for other titanium(III) metallocenes [28]. The relative CH_2/CH_3 proton assignment is based on the stronger intensity for the latter. For the carbon resonances this assignment could not be made from the spectral characteristics alone. The assignment was made by predicting the spin at the carbons from the proton spectrum and a narrow band width expected for the terminal methyl resonance. Also, there is only one assignment which can account for the reverse directions observed for the temperature dependence of the shifts as discussed further.

Thermal decomposition of the samples during the NMR experiments was not significant. In experiments where the solutions were heated for several hours near 373 K, two weak signals near 6 and 7 ppm were observed in the spectra. These resonances are believed to be due to the same transient species discussed in the next section for the hydride reaction mixture.

For the methylene and methyl protons, the $\Delta H/H$ *versus* T^{-1} curves intercept each other at $T^{-1} = 0$ as shown in Fig. 1. For I this occurs at the origin of the graph as expected from the Curie law. The 1 ppm chemical shift for II at the origin could be due to stronger molecular association in the more halogen rich reference compounds $(AlCl_2Et)_2$. Hence, these observations tend to corroborate the choice of diamagnetic references and assignments used in this work.

At 20 MHz, the carbon spectra of I and II showed resolved resonances due to the ethyl ligand only over a narrow temperature range, *ca.* 300 to 315 K, in toluene or benzene. For instance in benzene only one strong resonance was located at 137 ppm for II at 300 K. The spectra in Fig. 5 shows this for complex I between 254 and 368 K. At a field strength of 101 MHz, the spectra were better resolved above 300 K but not at lower temperatures. For instance, at 333 K two partially resolved ($W_{1/2}$ = 240 Hz) peaks of almost equal intensities were at 133.3 and 133.9 ppm. Hence, for the ethyl carbon the A_h couplings given in Table III were calculated from the resolved spectrum taken near 307 K. The Curie curves in both cases could not be drawn because the shift difference over the 186 to 373 K temperature range is only 4 ppm ($W_{1/2}$ = *ca.* 100 MHz).

The physico-chemical properties of Lewis acids of the type Al_2X_6 are mainly due to the intramolecular ligand exchange going on between the two metals. Similarly, for I and II the single most important molecular process occurring is certainly the bridge-terminal scrambling of the ethyl and chloride ligand [1, 22]:



(2)

X = Et (I), Cl (II); Cp = C_5H_5)

The single carbon resonance observed at low temperatures can be explained by a slower rate for this exchange and concomitant broadening of the resonances. Then the less affected methyl carbon would be the only detected signal for the ethyl group. This explanation also coincides with the negative coupling value found (Table III) for this resonance at 187 K which best fits the CH_3 assignments in both compounds.

The observed overlap of the carbon resonances above 310 K is coincidental due to the lower field of the methyl carbon relative to the methylene carbon resonances in the spectra. This situation is the reverse of that observed for the free diamagnetic ligands [29]. Hence, as the temperature is raised the decrease in isotropic shifts causes both resonances to cross-over each other.

Based on the contact spin delocalization scheme, Ti–CH_2 bonding should cause up- and downfield contribution at the carbon and proton atoms, respectively. In our experiments we observed the opposite. Hence, the spin density must be transmitted via the aluminum metal as indicated in Scheme 1. Also, the linear Curie law behavior found for the ethyl protons indicates that this structure should be dominant for any rapid exchange. The 2-3 fold smaller absolute values of the proton and carbon A_h couplings at the methylene compared to methyl groups is indicative of a contribution from the ethyl-bridge in the structure of these complexes. Usually, the metal bonded carbon is expected to have the largest spin density [26, 27].

Though a more elaborate study is warranted to completely understand the molecular dynamics of the complexes below 295 K, preliminary results indicate that the spectra are exchange averaged for a rapid bridge-terminal ethyl process.

NMR and EPR Spectra of III

The room temperature proton shifts for **III** are given in Table II together with those of three other hydrides having μ-(η^1:η^5-C_5H_4) or μ-(η^5:η^5-$C_{10}H_8$) structures. A spectrum is also shown in Fig. 3 (minus the hydride resonance). The assignments of the resonances was made on the basis of the following comparisons and relative signal integrations. Complex **III** has in the 0.11 to 2.71 ppm region, a narrow intense plus four less intense resonances (see spectrum D, Fig. 3) at frequencies similar to those reported for the C_5H_5 and C_5H_4 resonances, respectively, of $[(C_5H_5)(C_5H_4)Ti(H)Al(C_2H_5)_2]_2$ and $[(C_5H_5)Ti]_2(H)[H_2Al(C_2H_5)_2]$. The high-field position of the 13.77 ppm signal is typical of a hydridic proton and is quite close to the values reported for the Ti–H–Al bridge-proton in $[(C_5H_5)(C_5H_4)Ti(H)Al(C_2H_5)_2]_2$ and $[(C_5H_4)TiHAl(C_2H_5)_2]_2(C_{10}H_8)$. In this respect, the –5 ppm difference observed with $[(C_5H_5)Ti]_2(H)(H_2Al(C_2H_5)_2)$ could be due to the lower temperature (225 K) at which the latter NMR experiment was carried out. Finally, four resonances in the 5 to 7 ppm region are assigned to the ethyl ligands. The relative CH_2/CH_3 proton assignments was made based on the signal integrations and proton–proton couplings (see Fig. 3). For the resonances assigned to the methylene group, the relative intensities measured are near 1:4:6:4:1, calculated for two chemically distinct and overlapping quadruplets: 1:(3:1):(3:3):(1:3):1. Similarly, the intensities at a higher field assigned to the methyl group are near 1:2:2:2:1, predicted for two chemically distinct but overlapping triplets: 1:2:(1:1):2:1. Also, the 8 Hz proton–proton coupling is identical to that observed in the aluminum alkyl ligands.

In order to better understand the magnetic properties of the isolated hydride complex, variable temperature NMR spectra were recorded. The proton shifts are represented as a function of the inverse temperature in Fig. 2. From these curves it can be seen that the ethyl resonances and two cyclopentadiene ring resonances are temperature dependent but do not follow the Curie law. The ethyl and cyclopentadienyl curves are parallel with negative and positive slopes respectively. Also, the band widths of these resonances are very small. All these results are opposite to those found for **I** and **II**.

The poor solubility of **III** and the broad hydride signal made its detection difficult. No temperature dependence was observed at 373 K for this resonance. The chemical shift values of **III** are comparable to those reported for similar diamagnetic hydrides. Moreover, the temperature dependence of the shifts does not follow the Curie law. For these reasons we believe that **III** is diamagnetic.

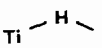
In one experiment the hydride reaction was followed by NMR. Spectra were taken over several days. The progression of the reaction is illustrated in Fig. 3. Spectrum A was taken 24 h after the $(\eta^5\text{-}C_5H_5)_2TiCl$ and $HAl(C_2H_5)_2$ reaction was started. The cyclopentadienyl ring and the ethyl group resonances were surveyed. Hence, spectrum A shows four resonances in addition to the solvent (marked s). Spectrum B is typical of the intermediate spectra recorded a few days in the reaction at room temperature. It shows, two of the four original resonances (marked b) were relatively stronger compared to the remaining other two signals (marked a), and new resonances grew-in as the reaction progressed (marked c). The narrower band widths were characteristic of the new c resonances. Spectrum C is the last of the series taken before the hydride was isolated as described in 'Experimental'. This spectrum shows clearly that the set of c resonances matches with the isolated titanium hydride **III**, spectrum D. This was further substantiated by the presence of a hydride resonance at 13.5 ppm for the reaction mixture. The a resonances coincide with the ethyl protons of $HAl(C_2H_5)_2$ given in Table III. The small difference observed and the broad band widths can be attributed to molecular association in solution and to paramagnetism.

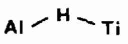
This experiment shows that the hydride isolated is not the initially formed product (b) present at 5.81 and 6.83 ppm. The isolated reaction product **III** is derived from b. We believe the transient species is a dimetallic hydrido-bridge monomer structurally identical to **I** and **II** and previously characterized by EPR [8].

The EPR solution spectra of **III** shown in Fig. 4 is typical of two magnetically non-equivalent and non-coupled spin centers. The spectra are different from those reported for the dimetallic Shilov type complexes. Hence, the reproducible EPR spectra is due to partial dissociation in solution to give two neutral paramagnetic molecules. The sextet/doublet intensity ratio for the room temperature spectra recorded for samples from different preparations and following repeated recrystallization, were invariable within experimental error (e.g. measured variations from 8:10 to 13:10) and can be assumed to be 1:1. Weak signals present at $g = 1.978$, 1.973 and 1.967, due to impurities, varied in intensity.

Structural Features of III

A survey of the literature shows that most stable titanocene–aluminum compounds are polymeric solids [33]. In these structures the metal–metal bond distances are sufficiently short to allow Ti–Ti (2.910–3.195 Å) bonding and in at least two cases, Ti–Al (2.782 and 2.792 Å) bonding. In general, the titanium units are held together by Ti–H–Ti, Ti–C(ring)–Al and Ti–H–Al bridges shown below [17–20]:





The more important fragments observed in the electron impact mass spectra of **III** are given in Table I. Of particular interest is the large abundance of aluminum and titanium metal fragments corresponding to deprotonated metal–C_5H_4 moieties, e.g. *m/z* 91, 112, 120, 147, 149, 211, and 212 (relative intensity = 14%). Also, the titanium–cyclopentadienyl fragments at *m/z* ± 2 and *m/z* ± 2 for *m/z* 213 and 148 (*i.e.* $[C_{10}H_{10}TiCl]^+$ and $[C_{10}H_{10}Ti]^+$) are much more intense than expected for the titanium or chlorine natural isotopic abundances. These peaks were not observed in the spectra of the titanocene monochloride starting compound or its dichloride analogue taken under identical experimental conditions. Identical results have been reported by Brintzinger and Bercaw and are presumably due to elimination of neutral dihydrogen from the molecular ions of dititanium hydrides and chlorides [31]. These results are indicative of the structures discussed in the preceding paragraph.

Examination of the IR results (KBr) (see 'Experimental') shows vibration modes attributable to the π-coordinated cyclopentadienyl ligand at 800, 1010, 1445, and 3100 cm^{-1} [30]. One broad (100 cm^{-1}) absorption, observed centered at 1700 cm^{-1}, and a second broad absorption, ranging from 500 to 950 cm^{-1}, were of medium intensity in the spectrum. The other absorptions observed between 3300 and 900 cm^{-1} in toluene solution and for the KBr wafers coincided with the frequencies usually attributed to the hydrocarbon moiety in titanocene complexes. However, one strong band present in the spectrum at 1227 cm^{-1} with two medium shoulders at higher frequencies, 1260 and 1237 cm^{-1}, could be due to Ti–H–Al stretching modes in the molecule as reported for other dimetallic hydrides [16, 31, 32]. Since these absorptions are also in the range of aliphatic C–C stretchings and C–H deformations, confirmation of the hydride structure using IR spectroscopy is not definitve without a deuterium isotope study.

The absence of a significant EPR signal at $g = 1.978$ for **III** excludes the possibility of having isolated a mixture of the titanium(III) monochloride starting material. The presence in the mass spectra of $[(C_5H_5)_2TiCl]^+$ (*m/z* 213) and $[(C_5H_5)_2Ti]^+$ (*m/z* 178) fragments can be explained by a titanocene unit structure similar to that proposed by Brintzinger and Bercaw for the $[(C_5H_5)(C_5H_4)TiX]_2$, X = H and Cl, complexes [31].

Unfortunately, the high sensitivity of the compound to traces of oxygen and water did not allow us to carry out reproducible molecular weight determination experiments. Hence, the hydride belongs to the μ-(η^1:η^5-C_5H_4) class of hydrides. Given the stoichiometric formula $C_{44}H_{50}Cl_4AlTi_4$ that best fits the microanalytical results it is still impossible to determine the structural formula of this hydride.

Acknowledgements

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