Electron Spin Resonance Spectra of Methyl-substituted Titanocene(III) Halides†

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Electron spin resonance spectra of [Ti($C_5H_{5-n}Me_n$)$_2$X] (n = 0, 1, 3, 4 or 5; X = Cl, Br or I) have been recorded in toluene and 2-methyltetrahydrofuran (mthf) solution at 77 and 295 K. Anisotropic spectra in frozen glasses were satisfactorily simulated and the parameters interpreted in terms of a generalised molecular orbital energy diagram. The monomeric species were characterised by a highly asymmetric g tensor, the lowest component being strongly dependent on the number of methyl groups (n) and the nature of the halide ligand; it moved to a lower value on going from Cl to I and with an increase in n. The ESR spectra revealed that compounds with n = 3–5 were monomeric in toluene whereas those with n = 0 or 1 were dimers. The latter compounds dissociated in mthf with the co-ordination of the solvent molecule. Mixtures of [Ti($C_5H_2Me_3$)$_2$Cl] or [Ti($C_5H_2Me_3$)$_2$Br] with their co-ordinated solvates were found in mthf at room temperature while [Ti($C_5H_2Me_3$)$_2$I] and all the C_5HMe_4 and C_5Me_5 compounds remained unsolvated. At 77 K the monomer–solvate equilibria were shifted so that all the $C_5H_2Me_3$ compounds formed only solvates, the C_5HMe_4 compounds were only partly solvated and the C_5Me_5 compounds remained unsolvated.

The early transition metals readily form complexes with cyclopentadienyl and substituted cyclopentadienyl ligands. We have made a particular study of those involving titanium and have found that their properties and reactivity are affected significantly by the number of methyl substituents in the cyclopentadienyl rings. Thus the ESR parameters (g_{iso} and linewidth) of the family [($C_5H_{5-n}Me_n$)$TiAl_2Cl_{8-x}Et_x$] changed directly with the number of methyl groups on the cyclopentadienyl ligands. As steric hindrance is absent in these complexes, then the change in ESR parameters must be due to an electron-donation effect of the methyl substituents.[1]

However, in the [($C_5H_{5-n}Me_n$)$_2TiAlCl_{4-x}Et_x$] (x = 0–2)[2] and [($C_5H_{5-n}Me_n$)$_2TiAlH_4$][3] complexes, deviations from the dependences of ESR parameters and reactivity upon the number of Me groups occurred for the C_5Me_5 derivatives. In the photoelectron spectra of the [Ti($C_5H_{5-n}Me_n$)$_2Cl_2$] compounds the shifts in the ionisation energies of the lowest-energy bands for [Ti(C_5Me_5)$_2Cl_2$] were considerably higher than expected from the average increments per methyl group found for the [Ti($C_5H_{5-n}Me_n$)$_2Cl_2$] (n = 0–4) series.[4] The thermal decomposition of the [Ti($C_5H_{5-n}Me_n$)$_2Me_2$] compounds afforded different products for the n = 0–3 compounds compared with the C_5HMe_4 and C_5Me_5 compounds.[5]

In the [Ti($C_5H_{5-n}Me_n$)$_2$Cl] series different solid-state structures were found for the C_5H_5 and C_5Me_5 compounds, the former forming a dimer with a (μ-Cl)$_2$ bridge[6] and the latter a monomer.[7] In solution, [Ti(C_5H_5)$_2$X] (X = Cl, Br or I) are all dimeric in benzene[8] but in polar solvents, *e.g.* tetrahydrofuran (thf), they are monomeric and have a molecule of solvent co-ordinated.[9] The compounds [Ti(C_5Me_5)$_2$X] (X = Cl, Br or I) are all monomeric in hydrocarbon solvents.[7] Despite the power of ESR spectroscopy, parameters are only known for solutions of [Ti(C_5H_5)$_2$X] and [Ti(C_5Me_5)$_2$X] (X = Cl, Br or I) (Table 1).

In this paper we report a detailed ESR study of a large series of [Ti($C_5H_{5-n}Me_n$)$_2$X] (X = Cl, Br or I) compounds in toluene and 2-methyltetrahydrofuran (mthf) solvents obtained at 77 and 295 K. The results have been rationalised in terms of the molecular orbital energy-level schemes of Lauher and Hoffmann.[11]

Experimental

General.—All manipulations with titanocene monohalides and solvents were performed under high-vacuum conditions. A high-vacuum line with metal valves and glass devices equipped with magnetically breakable seals and ESR sample tubes were used to handle all sample solutions. All solvents were dried by refluxing over $LiAlH_4$ and by storing as solutions of green dimeric titanocene, μ-(η^5:η^5-bicyclopenta-2,4-dien-1-ylidene)-di-μ-hydrido-bis(cyclopentadienyltitanium).[10]

Chemicals.—The C_5H_5, C_5H_4Me, $C_5H_2Me_3$ (1,2,3-trimethyl), and C_5HMe_4 titanocene chlorides and bromides were prepared by reduction of corresponding titanocene dihalides with aluminium powder in thf as described for non-methylated derivatives.[8] The C_5H_5 and C_5H_4Me compounds were purified by extracting solid products with diethyl ether and by sublimation of the residue *in vacuo*. The $C_5H_2Me_3$ and C_5HMe_4 compounds were extracted from the solid products with minimum amounts of hexane. The latter compounds were also prepared in the absence of thf by reduction of the dihalides with $LiAlH_4$ in boiling toluene; the reaction was stopped when the solution turned blue. The compounds [Ti(C_5Me_5)$_2$Cl] and [Ti(C_5Me_5)$_2$Br] were prepared by reducing the dihalide compounds with 1.2 equivalents of isopropyl Grignard reagent in diethyl ether. After evaporation of the ether, the residue was extracted with hexane and the products were recrystallised from hexane. The compound [Ti(C_5H_5)$_2$I] was obtained by reduction of [Ti(C_5H_5)$_2I_2$] with aluminium powder in thf; [Ti($C_5H_2Me_3$)$_2$I], [Ti(C_5HMe_4)$_2$I] and [Ti(C_5Me_5)$_2$I] were obtained by the exchange reaction of the corresponding titanocene monochlorides with LiI in ether.[7] The solid products were extracted in hexane. The solutions of all the titanocene monohalides were prepared by removal of hexane or thf on a vacuum line followed by distillation of toluene or mthf under

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† *Non-SI units employed:* eV ≈ 1.60×10^{-19} J, G = 10^{-4} T.

Table 1 ESR parameters of $[Ti(C_5H_5)_2X]$ and $[Ti(C_5Me_5)_2X]$ (X = Cl, Br or I) compounds in solution

Compound	Solvent	g_{iso}	Linewidth ΔH/G	Hyperfine coupling/G	Ref.
$[\{Ti(C_5H_5)_2Cl\}_2]$	Toluene	1.977	92		10
$[Ti(C_5H_5)_2Cl]$	thf	1.976	2		9
$[Ti(C_5H_5)_2Br]$	thf	1.988		2.1 (Br)	9
$[Ti(C_5H_5)_2I]$	thf	2.008		5.1 (I)	9
$[Ti(C_5Me_5)_2Cl]$	Pentane	1.956	60		7
$[Ti(C_5Me_5)_2Br]$	Pentane	1.953	65		7
$[Ti(C_5Me_5)_2I]$	Pentane	1.939	80		7

cooling with liquid nitrogen. Special care was taken in the sealing of ampoules containing diethyl ether, thf or mthf. It was carried out only when the solvents were properly cooled by liquid nitrogen, otherwise pyrolysis of their vapours generated compounds which reacted with the $[Ti(C_5H_{5-n}Me_n)_2X]$ compounds. The products of the latter reactions gave ESR spectra very similar to those of the $[Ti(C_5H_{5-n}Me_n)_2X]$·mthf adducts, both in fluid solution and in frozen glass. The purity of all the $[Ti(C_5H_{5-n}Me_n)_2X]$ compounds was assayed by mass spectrometry (direct inlet, dosing under argon).

Spectra.—The ESR spectra were recorded on an ERS-220 X-band spectrometer (Central Institute for Production of Scientific Instruments, Academy of Sciences of GDR). The magnetic field was calibrated with a proton magnetometer MJ-110 R (Radipan, Poznan, Poland). The g values were referred to the signal of Mn^{2+} ($M_I = -\frac{1}{2}$ line) as standard at $g = 1.9860$. Samples were measured at room temperature, at 77 K and at controlled temperatures within this range using a variable-temperature unit (STT-3). Samples of the solutions were sealed in bulbs equipped with an ESR quartz sample tube (Spectrosil).

Results and Discussion

Toluene Solution.—No ESR spectra could be obtained for $[Ti(C_5H_5)_2X]$ and $[Ti(C_5H_4Me)_2X]$ (X = Cl, Br or I) in toluene solution at 77 K. This is because these compounds exist in a monomer–dimer equilibrium in non-co-ordinating solvents at room temperature, but dimerise in frozen solution to form an antiferromagnetically coupled pair.[12] A broad asymmetric single line and a low-intensity narrow signal were observed at 295 K for the chloro and bromo derivatives indicating the triplet state of the dimer and partial dissociation in solution. The existence of the dimer triplet–singlet equilibrium has been established from the temperature dependence of the magnetic susceptibility for $[Ti(C_5H_5)_2X]$ in benzene.[8]

In the case of $[Ti(C_5Me_5)_2X]$, $[Ti(C_5HMe_4)_2X]$ and $[Ti(C_5H_2Me_3)_2X]$ (X = Cl, Br or I) in toluene well resolved spectra were observed at 77 K. For X = Cl the spectrum consisted of three g features with no resolved hyperfine splitting. For X = Br and I there was hyperfine splitting on the two g features at lower fields. Spectra are shown in Fig. 1.

Clear trends are observed in the g value of the feature at highest field: it increases as the number of methyl substituents decreases, and decreases as the halide changes from Cl to I. Furthermore, the hyperfine coupling on the two highest g features gets slightly larger as the number of methyl substituents decreases. These trends are readily explained in terms of the generalised energy-level diagrams (Fig. 2) originally proposed by Lauher and Hoffmann,[11] and also on structural considerations.

Fig. 2 shows the lowest unfilled orbitals, including the one which contains the unpaired electron ($1a_1$) for the bent $M(C_5H_5)_2$ fragment. To be consistent with the notation used by Lauher and Hoffmann,[11] we assume an idealised eclipsed form so that the symmetry of the fragment, and of $[M(C_5H_5)_2X]$, is C_{2v}. In this point group the z axis lies along the M–X bond, and the y axis lies in the plane between the two rings. Hückel calculations for this fragment show that the orbitals can be described by the

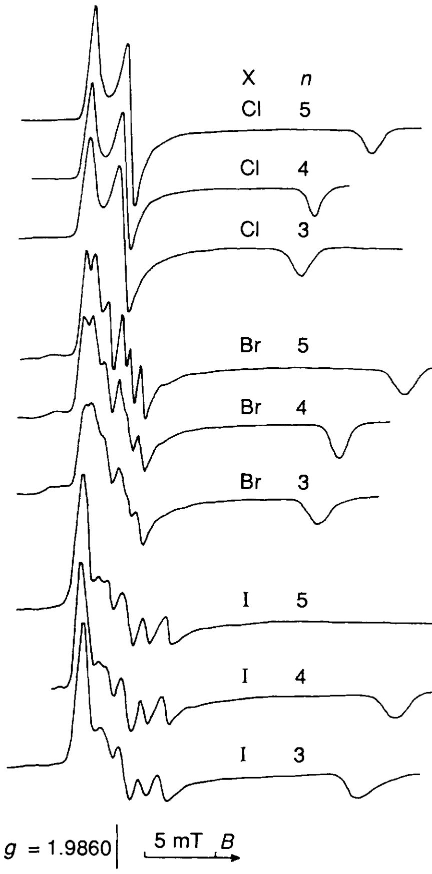

Fig. 1 The ESR spectra of $[Ti(C_5H_{5-n}Me_n)_2X]$ in toluene at 77 K

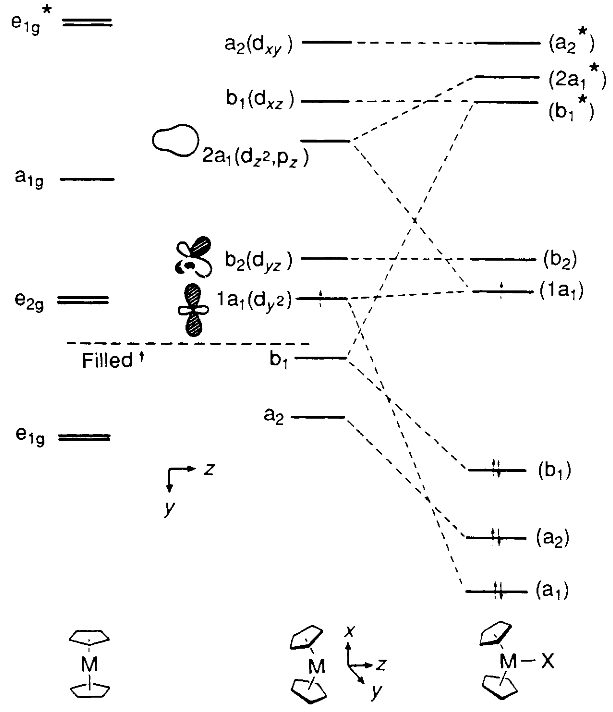

Fig. 2 Schematic molecular orbital energy-level diagram showing the relative energies of orbitals in the bent $Ti(C_5H_5)_2$ fragment and $[Ti(C_5H_5)_2X]$

Table 2 ESR parameters for methyl-substituted titanocene halides

Compound	Solvent	g_{iso}	Linewidth $\Delta H/G$	g_{av} [a]	g_z [b]	g_y [b]	g_x		Hyperfine coupling/G
							No solvent adduct	Solvent adduct	
$[Ti(C_5Me_5)_2Cl]$	Toluene	1.957	34	1.956	1.999	1.984	1.889	—	
	mthf	1.956	39	1.957	1.999	1.984	1.888	—	
$[Ti(C_5HMe_4)_2Cl]$	Toluene	1.964	12	1.965	2.000	1.985	1.910	—	
	mthf	1.964	12	1.964 [c]	2.000	1.984	1.909	1.954	
$[Ti(C_5H_2Me_3)_2Cl]$	Toluene	1.965	13	1.967	2.001	1.986	1.915	—	
	mthf	1.979 1.965	3.5 13	1.979	2.001	1.983	—	1.954	
$[Ti(C_5H_4Me)_2Cl]$	mthf	1.979	5	1.980	2.001	1.983	—	1.954	$a(Ti) = 12.0$
$[Ti(C_5H_5)_2Cl]$	mthf	1.979	5	1.981	2.001	1.982	—	1.959	$a(Ti) = 12.0$
$[Ti(C_5Me_5)_2Br]$	Toluene	1.951	39	(1.952) [d]	*e*	*e*	1.874	—	
	mthf	1.951	40	*e*	*e*	*e*	1.874	—	
$[Ti(C_5HMe_4)_2Br]$	Toluene	1.960	23	(1.961)	*e*	*e*	1.900	—	
	mthf	1.960	23	*e*	*e*	*e*	1.898	—	
$[Ti(C_5H_2Me_3)_2Br]$	Toluene	1.962	23	(1.963)	*e*	*e*	1.908	—	
	mthf	1.961 1.987	23 —	*e*	*e*	*e*	—	1.962	$a_{iso}(Br) = 3.0$
$[Ti(C_5H_4Me)_2Br]$	mthf	1.989	—	*e*	*e*	*e*	—	1.963	$a_{iso}(Br) = 2.3$ $a_{iso}(Ti) = 12$
$[Ti(C_5H_5)_2Br]$	mthf	1.988	—	*e*	*e*	*e*	—	1.963	$a_{iso}(Br) = 1.8$ $a_{iso}(Ti) = 12$
$[Ti(C_5Me_5)_2I]$	Toluene	1.940	63	(1.942)	*e*	*e*	1.842	—	
	mthf	1.940	64	*e*	*e*	*e*	1.836	—	
$[Ti(C_5HMe_4)_2I]$	Toluene	1.951	39	(1.953)	*e*	*e*	1.877	—	
	mthf	1.951	37	*e*	*e*	*e*	1.873	—	
$[Ti(C_5H_2Me_3)_2I]$	Toluene	1.954	38	(1.957)	*e*	*e*	1.889	—	
	mthf	1.954	39	*e*	*e*	*e*	—	—	
$[Ti(C_5H_5)_2I]$	mthf	2.008	—	*e*	*e*	*e*	—	—	$a_{iso}(I) = 5.0$ $a_{iso}(Ti) = 12$

[a] Average of g_z, g_y and g_x. [b] Assignment of g_z and g_y can be interchanged. [c] Where there are two g_x peaks, g_{av} is calculated using the g_x (no solvent adduct) value. [d] Values in parentheses are calculated for adopted values of $g_z = 2.000$ and $g_y = 1.983$. [e] Value cannot be determined accurately because of overlapping lines.

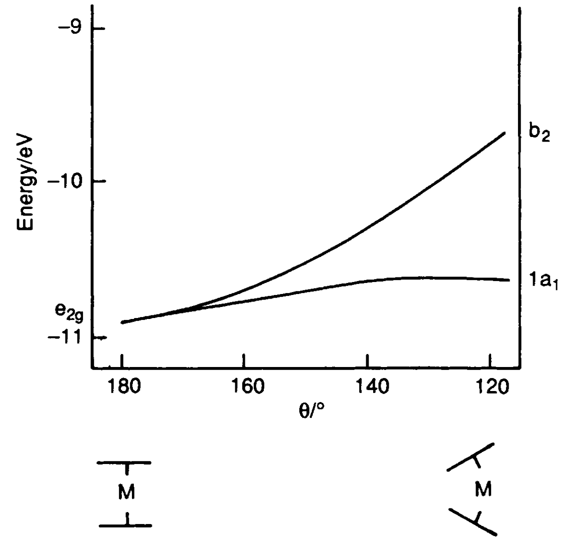

Fig. 3 Influence of bending of the C_5H_5 rings upon the $1a_1$ and b_2 energy levels in $[M(C_5H_5)_2X]$

shapes given for the three of particular relevance. The ground-state $1a_1$ orbital is composed of 51% $d_{x^2-y^2}$, 30% d_{z^2}, 1% s and 18% C_5H_5. This makes it strongly resemble a 'd_{z^2}' orbital but lined up along the *y* axis, and so we can informally call it a d_{y^2} orbital. The b_2 orbital resembles a d_{yz} orbital, and the $2a_1$ orbital looks like a combination of d_{z^2} and p_z, strongly pointing along the *z* axis with the larger end of the lobe directed towards the incoming ligand X.

It is known from photoelectron spectroscopy that the energy of the $1a_1$ orbital is almost unaffected upon bringing up a ligand along the *z* axis.[13] The energy of the b_2 orbital will however be influenced by π back bonding between the empty $b_2(d_{yz})$ metal orbital and the filled p_y orbital of the ligand. It will be stabilised in the order I > Br > Cl > CH_3 {g_x for $[Ti(C_5Me_5)_2Me]$ is known to be 1.895[14]}. Also, the $2a_1$ orbital will rise sharply in energy because of the direct interaction with the ligand lone pair. This $2a_1$ orbital becomes strongly antibonding and is labelled $2a_1$*. The corresponding bonding orbital is labelled $1a_1$. Lauher and Hoffmann[11] calculate that for the mythical d^0 complex $[Ti(C_5H_5)_2H]^+$ the hydrogen atom would not lie on the two-fold axis but at an angle of about 65° from it, and in a d^1 hydride complex the angle would be about 35° from the two-fold axis. In the d^1 structures known with ligating Cl, the latter atom is always on the two-fold axis, presumably for steric reasons.[7,15–17]

Symmetry considerations allow us to predict that the ground-state electron will only mix by spin–orbit coupling with a b_2 orbital upon rotation about the *x* axis (g_x). Likewise, g_y is associated with the b_1 orbital and g_z with the a_2 orbital. Since the closest orbital to the unpaired electron is the b_2, then g_x will deviate strongly from 2 and be <2; g_y and g_z will both be close to 2 and may be >2 or <2 depending upon whether mixing is predominantly with empty or filled levels. We can now assign the high-field *g* values to g_x in Fig. 1.

The large variation of g_x with X (Fig. 1) is readily explained by the variation in energy of the b_2 level. Since the π bonding between Ti and Cl, Br and I varies as I > Br > Cl, then the b_2 level will be lowered accordingly. This brings it closer to the $1a_1$ level and significantly affects g_x, making it smaller (the closer they are, the larger will be the deviation of g_x from the free-spin value). The values of g_x are summarised in Table 2.

There is a clear trend of g_x increasing as the number of methyl substituents decreases for each halide. This is probably best

Table 3 Angles (CE)–Ti–(CE) θ in some $[Ti(C_5H_{5-n}Me_n)_2Cl]$ and relevant $[Ti(C_5H_{5-n}Me_n)_2Cl_2]$ complexes (CE = centroid of the cyclopentadienyl ring)

	$[Ti(C_5H_{5-n}Me_n)_2Cl]$		$[Ti(C_5H_{5-n}Me_n)_2Cl_2]$	
Ligand	θ/°	Ref.	θ/°	Ref.
C_5Me_5	143.6	7	137.4	18
C_5HMe_4	139.1	15	133.4	17
C_5H_5	131.2–133.4 *	6	130.97	16

* For the two structures of the dimeric compound $[\{Ti(C_5H_5)_2Cl\}_2]$.

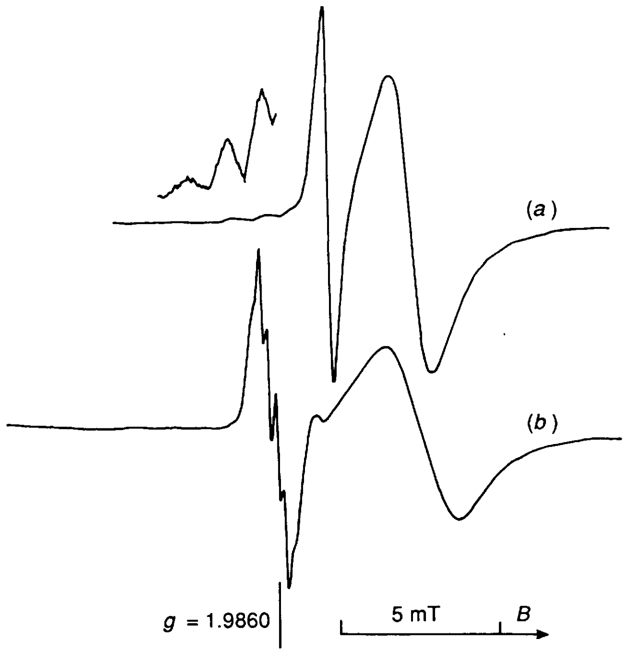

Fig. 4 The ESR spectra of (*a*) $[Ti(C_5H_2Me_3)_2Cl]$ and (*b*) $[Ti(C_5H_2Me_3)Br]$ in mthf at 295 K

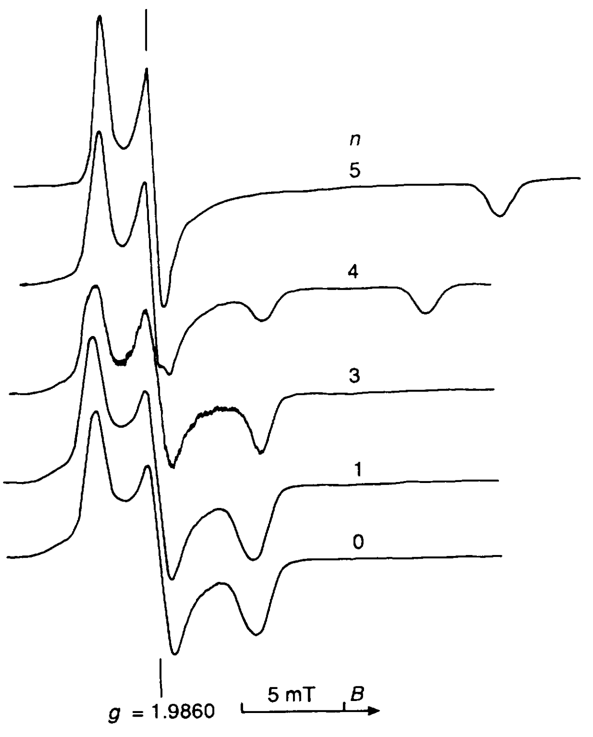

Fig. 5 The ESR spectra of $[Ti(C_5H_{5-n}Me_n)_2Cl]$ in mthf at 77 K

explained by the effect the number of substituents has upon the angle between the two cyclopentadienyl rings. If θ is the angle between the normals from the metal to the C_5H_5 rings, then Lauher and Hoffmann[11] have shown that the energy level b_2 rises markedly as θ decreases (more bending) (Fig. 3). There is also a smaller increase in the energy of the $1a_1$ orbital as shown by photoelectron spectroscopy,[13] but ESR spectroscopy only is concerned with the difference in energy of the two levels. The crystal structures of important $[Ti(C_5H_{5-n}Me_n)_2Cl]$ and relevant $[Ti(C_5H_{5-n}Me_n)_2Cl_2]$ complexes are known and their angles are listed in Table 3. Although the series of $[Ti(C_5H_{5-n}Me_n)_2Cl]$ complexes is not complete the θ angles of $[Ti(C_5H_{5-n}Me_n)_2Cl_2]$ complexes show that the largest difference in θ occurs between $[Ti(C_5Me_5)_2Cl]$ and $[Ti(C_5HMe_4)_2Cl]$. This is because the staggered C_5HMe_4 rings are 'hinged' together at ring carbon atoms bearing hydrogen atoms.[15,17] Two other structures of titanocene chlorides, $[Ti(C_5H_3Bu^t_2\text{-}1,3)_2Cl]$ (θ = 134.8°)[19] and $[Ti(C_5HPh_4)_2Cl]$ (θ = 136°),[20] contain bulky ligands which may substantially influence the value of θ.

There seems to be no significant variation in the steric influence caused by the halides upon the tilting of the cyclopentadienyl rings. Calculation of the cone angle at the titanium using typical Ti–X (X = halide) distances show that it is 91, 90 and 94 ± 2° for Cl, Br and I respectively.

One striking difference between the bromide and iodide complexes on one hand and the chloride on the other is the presence of hyperfine couplings on the two low-field *g* features. The hyperfine coupling arises from the halide ligands. Unpaired spin density reaches the ligand through a variety of mechanisms. There would be a small amount of direct delocalisation and dipolar coupling through the $1a_1$ orbital, together with a significant amount of polarisation through bonding molecular orbitals. Because of the small magnitude of the magnetic moment of the chlorine nucleus, coupling to chlorine will be small and lost within the linewidth. The coupling observed in the bromide and iodide complexes arises from the g_y and g_z features, each with an expected large quadrupole interaction. We have not been able to simulate to our satisfaction the resulting envelope of overlapping spectra.

Methyltetrahydrofuran Solution.—Fluid solution. For $[Ti(C_5H_2Me_3)_2X]$ (X = Cl or Br) in mthf the ESR spectrum at 295 K consisted of two well separated isotropic lines (Fig. 4). In the case of the chloride complex the line at $g = 1.979$ was much narrower than that at $g = 1.965$ and also exhibited well resolved hyperfine splitting to Ti. For the bromide complex the line at lower field ($g = 1.987$) exhibited four partially resolved hyperfine lines due to Br, superimposed on a slightly broader line, together with poorly resolved coupling to Ti. Samuel and Vedel,[9] working with $[Ti(C_5H_5)_2X]$ (X = Cl, Br or I) in thf, attribute these superimposed pair of lines to $[Ti(C_5H_5)_2Br(thf)]$ and $[Ti(C_5H_5)_2Br(H_2O)]$. The broad line at higher field ($g = 1.961$) for the bromide compound showed no hyperfine splitting. We believe the two well separated isotropic lines arise from an equilibrium between the complex with and without a mthf molecule co-ordinated as an adduct, having the higher and lower *g* value respectively. Supporting evidence for this comes from the frozen-solution spectra. None of the other complexes exhibited such pairs of lines. The C_5HMe_4 and C_5Me_5 complexes gave only the broad lines whose *g* values and linewidths were very close to those of lines obtained in toluene solutions (see Table 2). This implies that the low-*g*-value lines are due to non-solvated species. In the case of $[Ti(C_5H_4Me)_2Br]$ and $[Ti(C_5H_5)_2Br]$, hyperfine coupling to Br and Ti was observed, and with $[Ti(C_5H_5)_2I]$ coupling to I and Ti was seen. In these, and the other cases where only one line was seen, the *g* values were very similar to those found in thf solutions[9] (*cf.* Tables 1 and 2).

Frozen solution. The frozen-solution ESR spectra of these complexes in mthf varied depending upon the halide and the

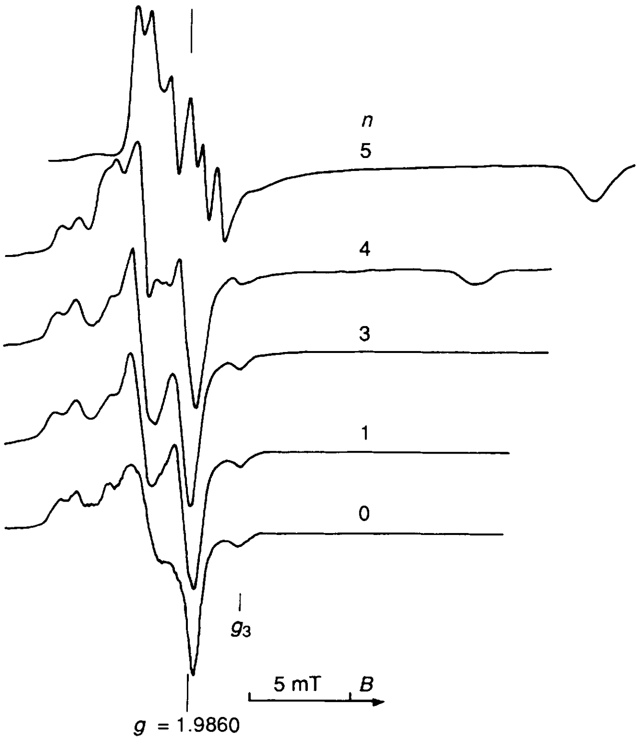

Fig. 6 The ESR spectra of $[\mathrm{Ti(C_5H_{5-n}Me_n)_2Br}]$ in mthf at 77 K

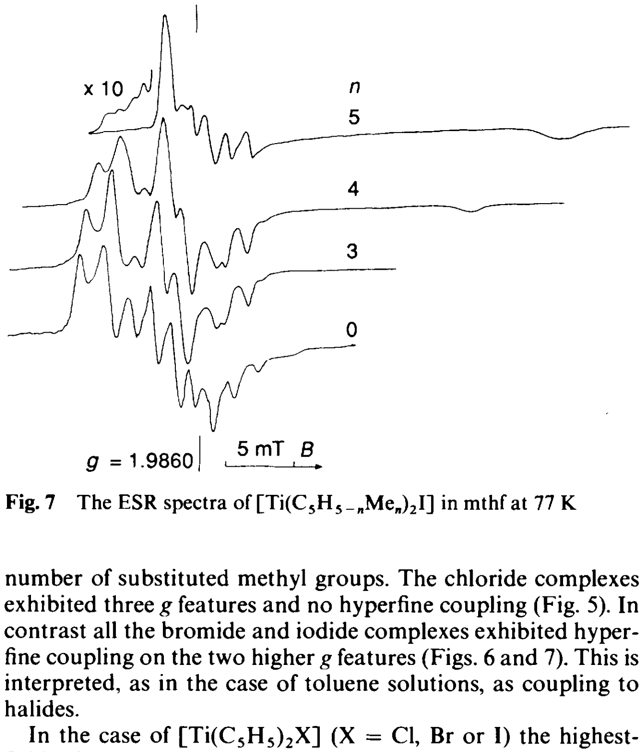

Fig. 7 The ESR spectra of $[\mathrm{Ti(C_5H_{5-n}Me_n)_2I}]$ in mthf at 77 K

number of substituted methyl groups. The chloride complexes exhibited three *g* features and no hyperfine coupling (Fig. 5). In contrast all the bromide and iodide complexes exhibited hyperfine coupling on the two higher *g* features (Figs. 6 and 7). This is interpreted, as in the case of toluene solutions, as coupling to halides.

In the case of $[\mathrm{Ti(C_5H_5)_2X}]$ (X = Cl, Br or I) the highest-field *g* feature was almost the same as in toluene solution. For $[\mathrm{Ti(C_5H_2Me_3)_2X}]$ (X = Cl or Br), $[\mathrm{Ti(C_5H_4Me)_2X}]$ and $[\mathrm{Ti(C_5H_5)_2X}]$ (X = Cl or Br) this high-field *g* feature was shifted much closer to $g = 2$. In the case of X = I it is lost under the high-field lines close to $g = 2$. For $[\mathrm{Ti(C_5HMe_4)_2X}]$ (X = Cl or Br) two similar shaped high-field *g* features are visible, one close to that found in toluene solution and another much closer to 2, whilst in the case of X = I only one high-field *g* feature is seen, close to that in toluene solution. The pair of high-field *g* features arises from a trapped equilibrium between a complex with and without a co-ordinated mthf solvent molecule in the same way as the $[\mathrm{Ti(C_5H_2Me_3)_2X}]$ (X = Cl or Br) at 295 K are in equilibrium (Fig. 4). These complexes with *g* around 1.95–1.96 are adducts with mthf, and those with a much lower *g* are without co-ordinated solvent. The presence of the $[\mathrm{Ti(C_5HMe_4)_2I}]$ adduct with mthf follows from the similar features of the low-field part of the spectrum with those observed for the less methylated complexes.

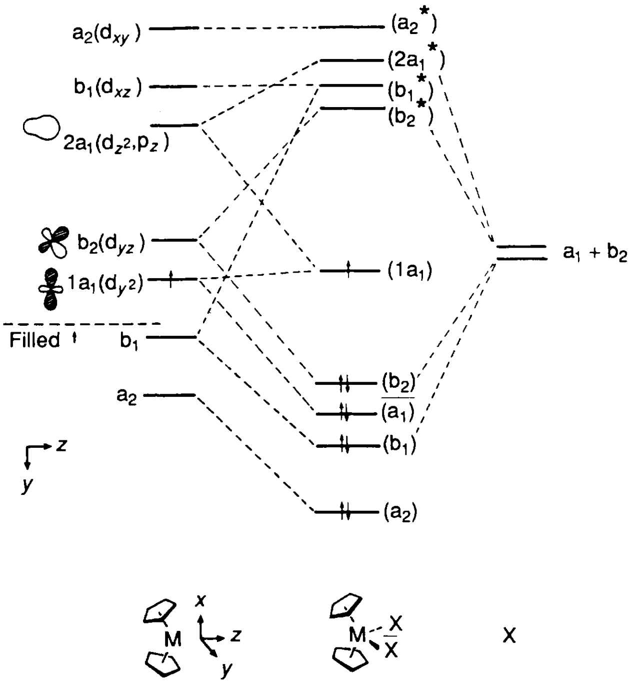

Fig. 8 Schematic molecular orbital energy-level diagram showing the relative energies of orbitals in the bent $\mathrm{Ti(C_5H_5)_2}$ fragment and in $[\mathrm{Ti(C_5H_5)_2X_2}]$

That the complexes with the most methyl groups cannot form complexes with mthf co-ordinated is due, we believe, to the strong inductive effect of the methyls making these complexes only weak Lewis acids and not capable of binding to the basic mthf. The $[\mathrm{Ti(C_5H_2Me_3)_2X}]$ (X = Cl or Br) complexes represent a borderline case where both a complex with and without co-ordinated mthf solvent are in equilibrium at room temperature. However, $[\mathrm{Ti(C_5H_2Me_3)I}]$ does not co-ordinate mthf. At lower temperatures the equilibria are shifted so that only complexes with co-ordinated mthf are observed for all $[\mathrm{Ti(C_5H_2Me_3)_2X}]$ at 77 K.

The molecular orbital energy levels for complexes of the type $[\mathrm{Ti(C_5H_5)_2X_2}]$ have also been described by Lauher and Hoffmann.[11] Fig. 8 shows a generalised energy-level diagram which highlights the effect upon the levels of the $\mathrm{Ti(C_5H_5)_2}$ fragment of having two ligands X co-ordinating. The main difference between $[\mathrm{Ti(C_5H_5)_2X}]$ and $[\mathrm{Ti(C_5H_5)_2X_2}]$ is that two groups X co-ordinate at *ca.* 85° apart {the most stable angle calculated for $[\mathrm{Ti(C_5H_5)_2H_2}]$[11]}. Then, the lone-pair orbitals on each X will interact directly with the lobes of b_2 (d_{yz}), and minimally with $1a_1$ (d_{y^2}). It follows that the energy of $1a_1$ is unaltered, but that b_2 splits into a bonding (b_2) and antibonding (b_2^*) pair. The $2a_1$ orbital still is active in bonding and forms a bonding (a_1) and antibonding ($2a_1^*$) pair as in $[\mathrm{Ti(C_5H_5)_2X}]$. Since g_x depends on the relative magnitudes of the separations $b_2^* - 1a_1$ and $1a_1 - b_2$, which are similar in energy, and especially on the energy gap $b_2^* - 1a_1$ which is much larger than the corresponding energy gap in $[\mathrm{Ti(C_5H_5)_2X}]$, then g_x will be much closer to 2 for $[\mathrm{Ti(C_5H_5)_2X_2}]$ than for $[\mathrm{Ti(C_5H_5)_2Cl}]$. This accounts for the major change in the spectra of complexes with and without co-ordinated solvent.

The other trends in *g* values of compounds in mthf solution, *e.g.* with the number of methyl groups and with halide, are much less significant when a solvent molecule is co-ordinated than without co-ordination as in the toluene solutions.

As described above for the toluene complexes, hyperfine coupling to chlorine is not observed, but to bromine and iodine is quite well resolved. Unfortunately, the hyperfine parameters could not be extracted satisfactorily.

Unambiguous interpretation of the *g* tensor is not possible without a full single-crystal study since the directions of the *g* tensors and also the halogen hyperfine tensors are both unknown, and will probably be different from each other.

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