Electron Spin Resonance Studies of Ziegler-type Catalysts. Part I. Characterisation of a Vanadium–Aluminium Complex obtained on mixing Dichlorobis(η-cyclopentadienyl)vanadium with Ethylaluminium Dichloride

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Mixtures of dichlorobis(η-cyclopentadienyl)vanadium and ethylaluminium dichloride have been examined in methylene dichloride–heptane at Al : V ratios of $\geqslant 7 : 1$. This system catalyses polymerisation of ethylene to give a polymer with good characteristics. Three species which exhibit e.s.r. spectra are present in this catalyst system, and one of these has been studied in detail by e.s.r. (room and glass temperature) and u.v. spectroscopy. The results show that this species, $[\mathrm{Cl(cp)_2V(\mu\text{-}Cl)_2AlCl_2}]$ (which is not catalytically active), has a trigonal-bipyramidal structure.

In recent years there has been a large number of studies of Ziegler–Natta catalysts,[1-11] and a vast amount of kinetic data has been obtained for polymerisation reactions catalysed by these systems. Unfortunately, the heterogeneous nature of these catalysts makes it difficult to investigate the nature of the active site (or sites) on the surfaces or edges of the crystal lattice. More recently, therefore, efforts have been directed mainly at structure elucidation of the catalytically active species in homo-

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geneous systems.[12-37] These soluble systems are far more amenable to study, since they eliminate the complications of particle size and surface properties of the catalyst, and, in addition, enable kinetic and spectroscopic measurements to be made more easily.

If the transition metal of the catalyst has an unpaired electron the system can be monitored by electron spin resonance spectroscopy (e.s.r.) and there have been several reports [8-18] of work in this field. These studies, however, have involved either heterogeneous systems [8-11] or the examination of products of catalyst deactivation in soluble titanium systems.[12-14,16,17] (These deactivation products are Ti^{III} species having a d^1 electronic configuration, whereas the catalysts from which they are derived are d^0 and therefore are not detectable by e.s.r. spectroscopy.)

The work described in the present paper concerns an investigation of the system obtained on mixing dichlorobis(η-cyclopentadienyl)vanadium, in dichloromethane as solvent, with ethylaluminium dichloride in heptane as solvent. In this case, we expect (by analogy with the mechanism proposed by Olivé [16] for the corresponding titanium system) that the catalyst species involves vanadium(IV) (having a d^1 electronic configuration), and can therefore be monitored by e.s.r. spectroscopy which provides a sensitive method of following changes in the environment of the vanadium.

EXPERIMENTAL

Materials.—Dichloromethane (B.D.H., redistilled) was heated under reflux over P_2O_5 in a stream of dry dinitrogen, and then distilled under dry dinitrogen into sealed ampoules (b.p. 39 °C). These were transferred to a high-vacuum system, where the dichloromethane was degassed by pumping at −78 °C, warming to room temperature, and pumping again at −78°C; this process was repeated until all the dissolved gas had been removed. The dichloromethane was then distilled *in vacuo* and stored in sealed ampoules. Heptane (B.D.H.) was heated under reflux over sodium wire in a stream of dry dinitrogen, degassed under high vacuum, and then distilled and stored in sealed ampoules as above. Ethylaluminium dichloride (I.C.I. Ltd.) was obtained as a 1·63M solution in pentamethylheptane under dinitrogen.* It was transferred under dry dinitrogen to a closed vacuum system, degassed by freezing to −196 °C, pumping, raising to room temperature, and repeating the cycle until no further gas bubbles were apparent on thawing. It was then diluted with dry heptane and stored under vacuum. Aluminium trichloride (B.D.H., fused or anhydrous) was crushed in a pestel and mortar in a dry dinitrogen atmosphere and then sublimed under vacuum immediately prior to use. Dichlorobis(η-cyclopentadienyl)vanadium (Alfa Inorganics) was recrystallised from dichloromethane, and solutions made up in dichloromethane on the high-vacuum apparatus. Pyridine (B.D.H.) was distilled under dry dinitrogen, and then *in vacuo*, and finally stored in sealed ampoules. Ethylene (I.C.I.) was used as supplied.

Procedure.—E.s.r. spectra were obtained on a Varian Associates E-3 spectrometer fitted with a Varian E-4557-9 temperature controller. U.v.–visible spectra were obtained on Pye–Unicam SP 800 or Beckman DK-2 spectrophotometers. Computer-simulated spectra were calculated from empirically determined hyperfine and linewidth parameters, on an I.C.L. System 4-70 computer with 256 kbytes main store. The spectra were plotted on a Calcomp drum plotter.

Preparation of catalyst system, $[(cp)_2VCl_2]$–$EtAlCl_2$. All operations were carried out under high-vacuum, using greaseless joints and taps with poly(tetrafluoroethylene) sleeves and O rings. Figure 1 shows the apparatus used for preparation of the catalyst and for the e.s.r. study. A measured amount of $[(cp)_2VCl_2]$ (cp = η-cyclopentadienyl) in dichloromethane was run into the reaction vessel (A) with stirring. A measured amount of ethylaluminium dichloride solution in heptane was then introduced to give the desired Al : V ratio. A sample was taken from the stirred solution through tap (B) into the sample tube, which was then sealed at tap (C) and transferred to the e.s.r. spectrometer. Several samples could be taken from the one mixture by adding new sample tubes at joint (D) and evacuating the dead space. In this way the change in the nature of the catalyst with time could be examined.

Polymerisation experiments. A solution of catalyst was prepared in the reaction vessel as above, and ethylene admitted to this vessel, from a reservoir containing a fixed amount of the gas, through a pressure-limiting valve. The pressure in the reaction vessel was maintained at 1 atm and the uptake of ethylene was monitored by observing the drop

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* 1M = 1 mol dm^{-3}.

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in pressure in the reservoir. Samples of the reaction mixture could be removed for e.s.r. examination through tap (B).

$[(cp)_2VCl_2]$–$AlCl_3$ *System.* Aluminium trichloride was sublimed *in vacuo* into a reaction vessel to form an even film. A $[(cp)_2VCl_2]$ solution in CH_2Cl_2 was then run in and shaken to cause reaction with the aluminium trichloride. The resultant mixture was filtered in to an e.s.r. sample tube and a u.v. cell.

Effect of pyridine. Pyridine was added to the above system, and also to the $[(cp)_2VCl_2]$–$EtAlCl_2$ system after it had been standing for 2 weeks. A slightly less than stoicheiometric amount was added first, followed by a large excess.

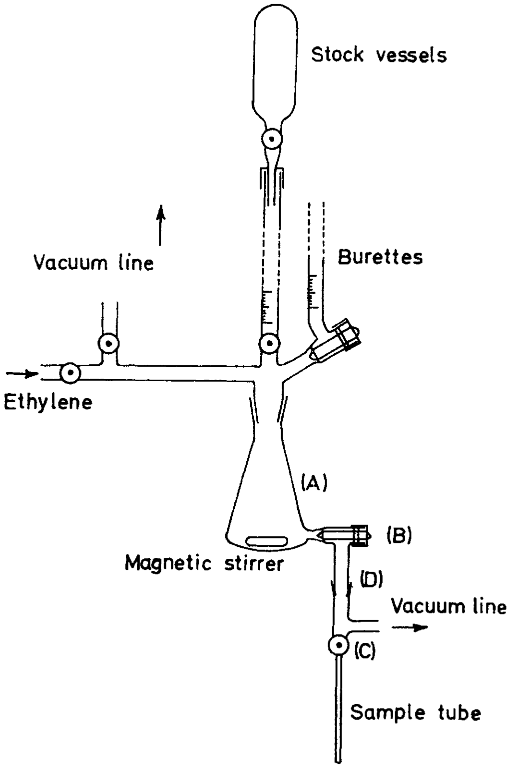

FIGURE 1 Apparatus for preparation of the catalyst and e.s.r. study

All these operations were carried out in the high-vacuum apparatus.

RESULTS AND DISCUSSION

Catalyst System $[(cp)_2VCl_2]$–$EtAlCl_2$.—When a heptane solution of $EtAlCl_2$ (10 cm^3 of 0·25 mol l^{-1}) and a dichloromethane solution of $[(cp)_2VCl_2]$ (30 cm^3 of 10^{-2} mol l^{-1}) were mixed at Al : V ratios of 7 : 1 and greater, the resulting system gave an e.s.r. spectrum; Figure 2(*a*) is a typical spectrum which was taken 4 h after mixing. This complicated spectrum showed the presence of more than one vanadium species. On leaving the sample to stand for up to 2 weeks, the spectrum changed to that of a single species [Figure 3(*a*)]. This species was stable with time and exhibited hyperfine interaction of 0·63 mT due to one aluminium nucleus, which showed that a stable complex had been formed containing one vanadium and one aluminium atom.

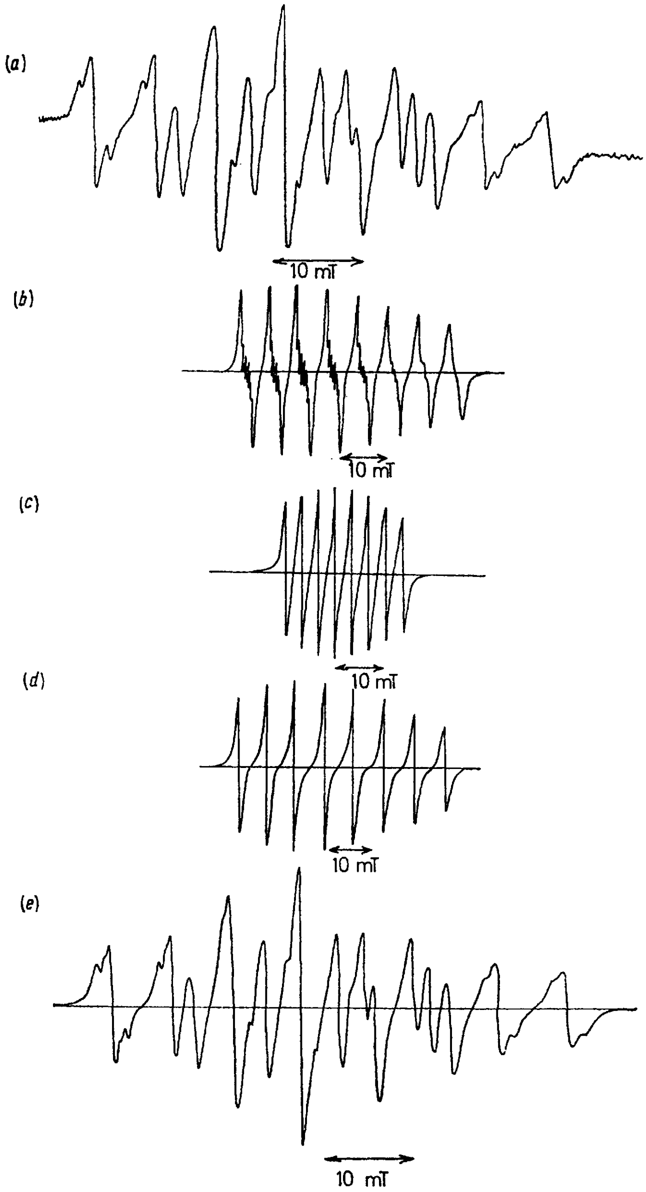

FIGURE 2 (*a*), E.s.r. spectrum at room temperature obtained by mixing a heptane solution of $EtAlCl_2$ with a dichloromethane solution of $[(cp)_2VCl_2]$ at an Al : V molar ratio of 7 : 1 and allowing the mixture to stand for 4 h; (*b*)—(*d*), computer-simulated spectra of vanadium species (I)—(III) which when added together in the proportions 26, 40, and 34% respectively give spectrum (*e*); (*e*), computer-simulated spectrum of (*a*)

The complicated e.s.r. spectrum, shown in Figure 2(*a*), was analysed by a trial and error procedure. A computer program was used to simulate the e.s.r. spectra and Figure 2(*e*) shows such a simulation. It can be seen that the spectra in Figure 2(*a*) and (*e*) are identical and can be superimposed over each other. The simulated spectrum consisted of three vanadium species as shown in Figure 2(*b*), (*c*), and (*d*), the relative amounts for this particular time of standing being: 26 [species (I)]; 40 [(II)]; and 34% [(III)]. E.s.r. parameters of the three species are given in Table 1. Comparison of Figures 2(*b*) and 3(*a*) shows that the species responsible for the e.s.r. spectrum in Figure 3(*a*) is (I). It can be seen that the vanadium linewidths for species (II) and (III) are similar and greater than that for (I). This suggests that there could be aluminium splitting in species (II) and (III) hidden under the vanadium lines. When species (II) and (III) were simulated using the linewidth parameters of (I) and varying aluminium splitting, a good fit was obtained using a value of 0·1 mT for the aluminium splitting.

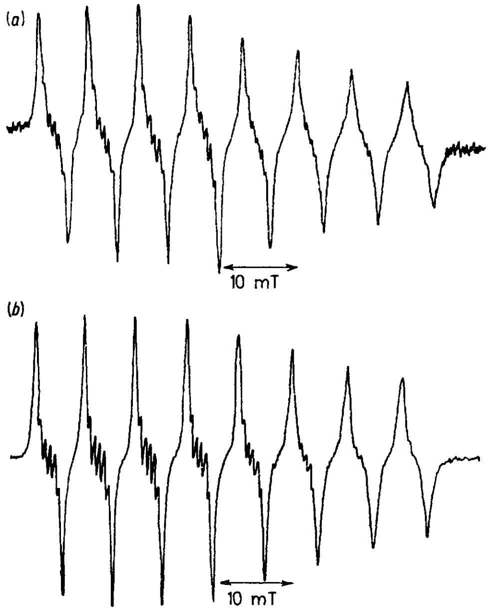

FIGURE 3 E.s.r. spectra obtained by (*a*) allowing the mixture giving the spectrum shown in Figure 2(*a*) to stand at room temperature for 2 weeks [species (I)]; (*b*) passing a dichloromethane solution of [(cp)$_2$VCl$_2$] over a film of aluminium trichloride at room temperature

Olivé [16,17] found, while studying the titanium complex, that if one of the terminal chlorine atoms on aluminium was replaced by an alkyl group, *e.g.* Et, the aluminium splitting decreased from 0·69 to *ca.* 0·30 mT, *i.e.* the unpaired electron density decreased on the aluminium atom. By analogy with Olivé's work, it is possible, therefore, that species (II) and (III) could have an alkyl group attached to the aluminium atom. In Table 1 we also give for comparison the e.s.r. parameters for [(cp)$_2$VCl$_2$]. It is clearly seen that the mixed solutions do not contain any [(cp)$_2$VCl$_2$].

TABLE 1

E.s.r. parameters

Species	Splitting constants/mT			Linewidth parameters [a]/mT		
	$a(^{51}V)$	$a(^{27}Al)$	g_{iso}	A_1	A_2	A_3
(I)	7·390	0·630	1·968	0·10438	−0·00720	0·00200
(II)	4·140	Not detected [b]	1·982	0·14530	−0·00200	0·00200
(III)	7·380	Not detected [b]	1·969	0·14530	−0·00640	0·00290
[(cp)$_2$VCl$_2$]	7·410		1·986	0·08346	−0·00377	0·00120

[a] Parameters A_1, A_2, and A_3 are those used in the expression $1/T_2 = \pi 3^{\frac{1}{2}}(A_1 + A_2M_I + A_3M_I^2)$ for the relaxation time T_2 (R. N. Rogers and G. E. Pake, *J. Chem. Phys.*, 1960, **33**, 1107). [b] Possibly present, but hidden by linewidth.

Effect of time of ageing. The intensity of species (I) was very small initially but increased with time until it reached a steady maximum after 2 weeks. The intensity of species (II) also increased initially, reaching a maximum in *ca.* 4 h; thereafter, it decayed slowly until at *ca.* 24 h ageing only 50% of the maximum intensity remained, and after 2 weeks it had disappeared completely. Species (III) had maximum intensity immediately after mixing and this decayed to zero over *ca.* 2 weeks.

Polymerisation experiments. If, after preparing the catalyst by mixing the [(cp)$_2$VCl$_2$] and EtAlCl$_2$ solutions, ethylene was immediately introduced, polymerisation occurred and the polyethylene formed rapidly crystallised out of the reaction medium (dichloromethane–heptane, *ca.* 3 : 1 by volume). A typical polymer obtained in this way had a high m.p. of 139 °C, a molecular weight of *ca.* 300 000, no detectable unsaturation in the i.r. region, and a linearity of approximately one Me group per 1 000 carbon atoms, that is a polymer with good characteristics. When polymerisation ceased (in the presence of ethylene), the only species detected by e.s.r. was (I). Polymerisation usually continued for between 30 and 60 min, after which time no further uptake of ethylene was detected.

Study of Species (I).—*Preparation.* When a dichloromethane solution of [(cp)$_2$VCl$_2$] was passed over a freshly sublimed film of aluminium trichloride and the resulting solution filtered into an e.s.r. tube, an e.s.r. spectrum was obtained which was identical in every respect [see Figure 3(*b*)] with that obtained at the end of polymerisation [species (I), Figure 3(*a*)]. Therefore species (I) can be synthesised without contamination by the other two species. Species (I) prepared in this way was tested for catalytic activity; it would not catalyse the polymerisation of ethylene. This is in agreement with the noncatalytic activity of species (I) formed by ageing of the catalyst mixture [(cp)$_2$VCl$_2$]–EtAlCl$_2$ (see above). Our results are in contrast to the early work of Abakumov *et al.*[38] using benzene solutions. They found, on treating [(cp)$_2$VCl$_2$] with EtAlCl$_2$ or AlCl$_3$ in benzene, that the e.s.r. spectra obtained were similar in *g* value and vanadium hyperfine splitting to the spectrum obtained from pure [(cp)$_2$VCl$_2$] in benzene. No aluminium hyperfine splitting was detected, although they found that the

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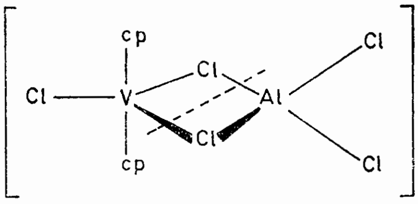
linewidths of the spectra obtained from the mixtures were greater than those of the $[(cp)_2VCl_2]$ spectrum.

Structure of species (I). The vanadium unpaired electron showed interaction with the aluminium nucleus (spin $I = 5/2$) giving six lines on each of the eight vanadium lines (Figure 3). Thus there is only one aluminium nucleus present in the complex. (If two aluminium nuclei were present one would expect to observe 11 lines on each of the eight vanadium lines in the e.s.r. spectrum.) On addition of pyridine to the solution of species (I) formed (*a*) from ageing the catalyst mixture or (*b*) by adding $[(cp)_2VCl_2]$ to $AlCl_3$, the lime green colour of $[(cp)_2VCl_2]$ returned immediately and the e.s.r. spectrum of the solution corresponded in every way to that of $[(cp)_2VCl_2]$. If pyridine was added in a less than an equivalent amount, a mixture of $[(cp)_2VCl_2]$ and species (I) resulted. This regeneration of $[(cp)_2VCl_2]$ from species (I) by pyridine indicates that the cp rings must be attached to the vanadium at all times and are not displaced on addition of $AlCl_3$ or $EtAlCl_2$. (It has been reported that cp rings are not even displaced by metal alkyls.[25]) It can also be inferred that there is no alkyl group attached to the vanadium atom. Pyridine does not complex with the vanadium since this would be observed by e.s.r. as another species and of course $[(cp)_2VCl_2]$ would not be regenerated. It would appear therefore that the action of pyridine is confined to removal of the aluminium trichloride fragment from the complex. {We found that pyridine did not react with $[(cp)_2VCl_2]$.} The terminal ligands on the aluminium atom must be only chlorine since species (I) could be obtained with no aluminium alkyl present. This was confirmed by the splitting constant for the aluminium nucleus of 0·63 mT, which compares well with that of 0·69 mT reported by Olivé [16,17] for a similar titanium complex, $[(cp)_2Ti(\mu\text{-}Cl)_2AlCl_2]$.



(A)

These results are consistent with structure (A) for species (I). The dashed line shows the cleavage that occurs on addition of pyridine. It is possible with the aid of the isotropic coupling constant [39] of the free aluminium atom (98·3 mT) to estimate the density of the unpaired spin ρ_{Al} at the Al nucleus. An Al hyperfine splitting of 0·63 mT would give a value for ρ_{Al} of $(0{\cdot}63/98{\cdot}3) \times 100 = 0{\cdot}64\%$. This is to be compared with a value of 0·7% found by Olivé [17] for the Al spin density in the complex $[(cp)_2Ti(\mu\text{-}Cl)_2AlCl_2]$.

Electronic absorption spectra. The structure of species (I) written above shows a five-co-ordinate V^{IV} atom with a probable trigonal-bipyramidal configuration. Because of mixed ligands and possible Jahn–Teller distortions, the molecule will have low symmetry, but it is possible for such a molecule to approximate to D_{3h} symmetry. The *d* orbitals of a d^1 system with D_{3h} symmetry are split into three levels, $^2E''$ (d_{xz},d_{yz}), $^2E'$ $(d_{xy},d_{x^2-y^2})$, and $^2A_1'$ (d_{z^2}).[40] In our case, because of the low symmetry, the energy levels will probably be singly and not doubly degenerate, but we believe that the effect of this degeneracy will be small and so two ligand-field transitions are predicted: $\nu_1(^2E''\rightarrow{}^2E')$ and $\nu_2(^2E''\rightarrow{}^2A_1')$. The electronic absorption spectra of species (I) showed two such *d–d* bands, one at *ca.* 630 and one at *ca.* 950 nm (ε *ca.* 50 l mol^{-1} cm^{-1}) which was very weak and broad. In addition there was an intense charge-transfer band at *ca.* 560 nm.

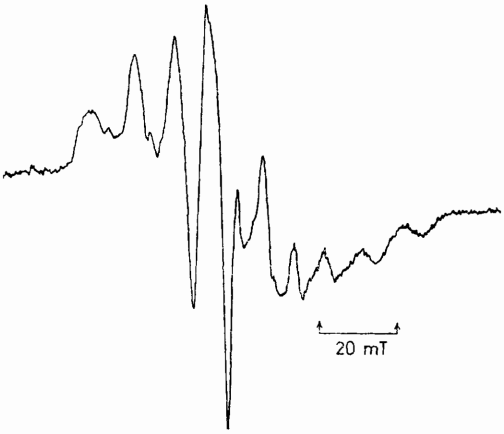


FIGURE 4 E.s.r. spectrum of the system giving the spectrum shown in Figure 3(*b*) when cooled to −140 °C

TABLE 2

Analysis of the e.s.r. spectrum at room temperature and −140 °C obtained (*a*) on passing a dichloromethane solution of $[(cp)_2VCl_2]$ over aluminium trichloride, (*b*) on mixing a dichloromethane solution of $[(cp)_2VCl_2]$ with a heptane solution of $EtAlCl_2$ and allowing to stand for 2 weeks

	g Values			^{51}V Splitting constants/mT			a_{iso} (^{27}Al)/
	$g_{\parallel}$	$g_{\perp}$	g_{iso} *	$a_{\parallel}$	$a_{\perp}$	a_{iso} *	mT
(*a*)	1·946	1·975	1·968	12·06	9·64	7·39	0·63
(*b*)	1·946		1·968	12·06		7·39	0·63

For (*b*), $g_{\perp}$ and $a_{\perp}$ could not be accurately obtained. *g* Values are accurate to ±0·002.

* Measured at room temperature.

Glass-temperature spectra. On cooling species (I) to *ca.* −140 °C, a rigid matrix e.s.r. spectrum appeared (Figure 4) and values of $g_{\parallel}$, $g_{\perp}$, $a_{\parallel}$, and $a_{\perp}$ were obtained (Table 2). It is known [41] that deviations of the *g* value from 2·0023 are inversely proportional to the energy separation between the orbital containing the unpaired electron and that with which it may mix by spin–orbit coupling. Therefore for the case of a single electron in a

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non-degenerate orbital equations (1) and (2) obtain,

$$g_{\parallel} = g_0 \pm (n\lambda/\Delta_1) \qquad (1)$$

$$g_{\perp} = g_0 \pm (n\lambda/\Delta_2) \qquad (2)$$

where $g_0 = 2{\cdot}0023$, λ is the spin–orbit coupling constant, and Δ is the energy separation between the orbital containing the unpaired electron and that with which it mixes by spin–orbit coupling. For D_{3h} symmetry in a d^1 system equations (3) and (4) may be written. The

$$g_{\parallel} = g_0 - (6\lambda/\Delta E)(d_{z^2} \leftarrow d_{xz}, d_{yz}) \qquad (3)$$

$$g_{\perp} = g_0 - (2\lambda/\Delta E)(d_{xy}, d_{x^2-y^2} \leftarrow d_{xz}, d_{yz}) \qquad (4)$$

coefficient n may be deduced from the ' magic pentagon.'[41] Substituting values for $g_{\parallel}$ and $g_{\perp}$ in the above equations and using a spin–orbit coupling constant of 140 cm^{-1} (similar to that used by other workers),[42,43] the transitions occur at $\nu_2(d_{z^2} \leftarrow d_{xy}, d_{yz}) = 670$ and ν_1 $(d_{xy}, d_{x^2-y^2} \leftarrow d_{xz}, d_{yz}) = 975$ nm, in reasonable agreement with maxima in the electronic absorption spectrum at 630 and 950 nm respectively. If we approximate the symmetry of this vanadium complex to D_{3h}, therefore, the data from the electronic and e.s.r. spectra can be fitted to a five-co-ordinate $\mathrm{V^{IV}}$ atom with a trigonal-bipyramidal configuration.

Conclusions.—On mixing CH_2Cl_2 solutions of $[(cp)_2VCl_2]$ with heptane solutions of $EtAlCl_2$ a complex e.s.r. spectrum was observed which contained three species, one of which is $[Cl(cp)_2V(\mu\text{-}Cl)_2AlCl_2]$ in which the configuration around the vanadium atom is trigonal bipyramidal. The fact that this complex is bipyramidal means that no solvent molecule is associated with the vanadium atom. In addition it was found that pyridine attacks this complex at the aluminium and not the vanadium atom. These two results may be related to the fact that the complex does not act as a catalyst for polymerisation of ethylene. In such a polymerisation process, of course, the olefin has to be located in an octahedral system.

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