Electron Spin Resonance Studies of Ziegler-type Catalysts. Part 2.[1] Identification and Spectra of some Dialkyldi(η-cyclopentadienyl)vanadium(IV) Complexes

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E.s.r. evidence has been obtained for the formation of $[VEt_2(cp)_2]$ on reaction of ethyl-lithium with $[VCl_2(cp)_2]$ (cp = η-cyclopentadienyl), and for $[V(CH_2SiMe_3)_2(cp)_2]$ from the reaction of trimethylsilylmethyl-lithium, or the corresponding Grignard reagent, with $[VCl_2(cp)_2]$. The results have also been examined by a theoretical treatment. The $A_{iso.}$ and $g_{iso.}$ values for $[VEt_2(cp)_2]$ and $[V(CH_2SiMe_3)_2(cp)_2]$ are 6.24 mT and 1.995 and 6.45 mT and 1.990 respectively.

In Part 1[1] of this series the catalytic system obtained by mixing $[VCl_2(cp)_2]$ (cp = η-cyclopentadienyl) with $AlEtCl_2$ was found to contain three paramagnetic species with splitting constants $A(^{51}V) = 7.39$, 4.14, and 7.38 mT for species (I), (II), and (III) respectively. Experiments were described which established that species (I) was a non-catalytic 1 : 1 complex between $[VCl_2(cp)_2]$ and $AlCl_3$. Treatment of this complex with pyridine ruptured the bridge between V and Al and gave a product with $A(^{51}V) = 7.41$ mT showing that $[VCl_2(cp)_2]$ had been formed.

In order to identify species (II) and (III) we need to make them in a pure state by forming complexes of $[VL_2(cp)_2]$ (L is a ligand) with different aluminium alkyls, and then to split the bridge between the vanadium and aluminium by the addition of pyridine. Identification of the vanadium compound so produced will establish the nature and positions of the ligands, L, in the complex. We have begun this process of identification by preparing and identifying the complex $[VEt_2(cp)_2]$ in solution. The complex $[V(CH_2SiMe_3)_2(cp)_2]$ has also been prepared and identified in solution, and is included in this paper for comparison.

EXPERIMENTAL

Materials.—All the solvents were thoroughly dried and outgassed before use. The reactions and manipulations were carried out under an atmosphere of dry nitrogen. Ethyl-lithium was prepared in the usual manner from ethyl chloride (B.D.H.) and lithium powder (Koch–Light Ltd.), recrystallised from toluene, and stored as a 1 mol dm^{-3} solution in toluene. Trimethylsilylmethyl-lithium and trimethylsilylmethylmagnesium chloride were prepared in the usual manner from (chloromethyl)trimethylsilane (Phase Separation Ltd.). Dichlorobis(η-cyclopentadienyl)-vanadium was prepared by the method of Wilkinson and Birmingham.[2]

Procedure.—Electron spin resonance spectra were recorded on a Varian E-109 spectrometer fitted with a Varian E-4557 variable-temperature control unit. Computer-simulated spectra were calculated from the empirically determined values, correct to second order, using the equations of Pilbrow and Winfield.[3]

RESULTS

$[VEt_2(cp)_2]$. Ethyl-lithium (10 mmol) in toluene was added dropwise to a slurry of $[VCl_2(cp)_2]$ (4 mmol) in toluene at −30 °C, stirred for several hours, then brought to 0 °C and the solvent removed *in vacuo*. The resulting black solid was extracted several times with pentane giving a dark green solution. The solvent was removed *in vacuo* at −30 °C in the absence of light to give a green-brown residue which was again extracted with pentane to give a dark green solution in which lithium and chlorine could not be detected by chemical analysis.

$[V(CH_2SiMe_3)_2(cp)_2]$. Trimethylsilylmethyl-lithium or the corresponding Grignard reagent was added dropwise to a stirred solution of $[VCl_2(cp)_2]$ in methylene dichloride at −30 °C. The solution was warmed to room temperature and filtered through Kieselguhr or grade B alumina. The solvent was stripped off *in vacuo*, and the solid redissolved in hexane to give a deep green solution which steadily darkened on exposure to light and was very unstable to air and moisture. On concentrating the solution and cooling to −78 °C, a number of green needle-like crystals were deposited which decomposed slowly at room temperature. Analysis of the solution by atomic-absorption spectroscopy gave a V : Si ratio of 1 : 2.2. Chemical analysis gave 0.05% residual Li (or, when the Grignard reagent was used, 0.5% Mg and <1% Cl) by weight of the total vanadium.

Reaction of $[VEt_2(cp)_2]$ and $[V(CH_2SiMe_3)_2(cp)_2]$ with HCl gave systems having e.s.r. spectral parameters identical with those for $[VCl_2(cp)_2]$.

DISCUSSION

$[VEt_2(cp)_2]$.—A toluene solution of $[VEt_2(cp)_2]$ at room temperature gave an eight-line e.s.r. spectrum having $A_{iso.}(^{51}V) = 6.24$ mT and $g_{iso.} = 1.995$ (Table). Examination of each of these lines showed that there was a further splitting (illustrated for line 4 in Figure 1). The second derivative of the fourth line [Figure 1(*a*)] shows a distortion of the line shape corresponding to an intensity ratio of 4 : 6 : 4 with the two outer lines flattening the edges of the spectrum. These outer lines become apparent on examination of the fifth derivative spectrum [Figure 1(*b*)] which on computer simulation shows structure corresponding to an intensity ratio of 1 : 4 : 6 : 4 : 1, indicating interaction between the odd electron on the vanadium and the four equivalent

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[1] Part 1, A. G. Evans, J. C. Evans, and E. H. Moon, *J.C.S. Dalton*, 1974, 2390.

[2] G. Wilkinson and J. M. Birmingham, *J. Amer. Chem. Soc.*, 1954, **76**, 4281.

[3] J. R. Pilbrow and M. E. Winfield, *Mol. Phys.*, 1973, **25**, 1073.

protons of the two methylene groups. In order to confirm this analysis, derivatives were mixed according to the method of Glarum[4] to give the sharpened first-derivative spectrum [Figure 1(*c*)]. A value of 0.30 mT is obtained for this proton hyperfine coupling. The line broadening which inhibits observation of superhyperfine structure in the first derivative is due to interaction between these protons and the non-equivalent, and presumably unrestricted, rotatory methyl protons from the ethyl groups. The fact that the apparent lines on the wings (marked by arrows) of the fifth-derivative spectrum are features of the differentiation and not spectral lines is confirmed by a comparison of Figure 1(*b*) and (*c*). Figure 2 shows the frozen-solution spectrum at 77 K from which the parameters listed in the Table were calculated. The simulated spectrum using these parameters gave a good fit [Figure 2(*c*)] to the observed spectrum.

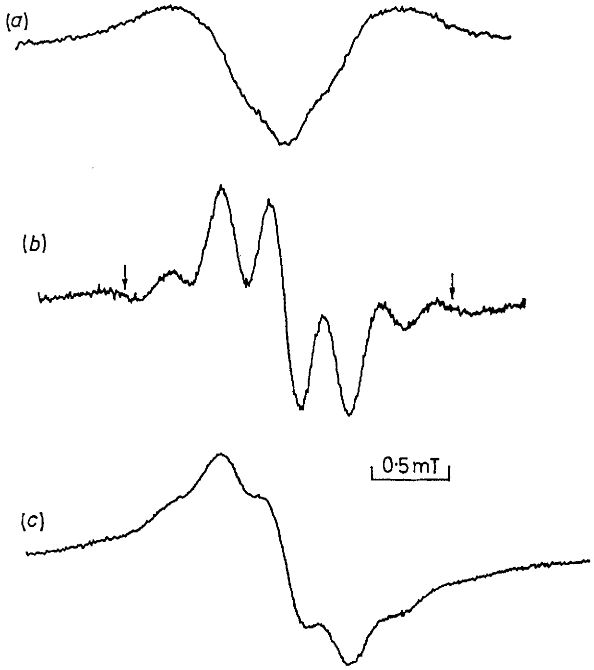

FIGURE 1 E.s.r. spectrum of solution of $[VEt_2(cp)_2]$ at room temperature. The following are shown for line 4: (*a*) second-derivative spectrum; (*b*) fifth-derivative spectrum; and (*c*) sharpened first-derivative spectrum

	$[VCl_2(cp)_2]$ [7]	$[VEt_2(cp)_2]$	$[V(CH_2SiMe_3)_2(cp)_2]$
T_x/mT	−7.92	−6.70	−6.60
T_y/mT	−12.52	−10.80	−11.45
T_z/mT	−1.63	−1.39	−1.206
g_x	1.986	1.977	1.997
g_y	1.971	2.000	1.999
g_z	2.000	1.993	1.999
a	−0.976	−0.972	−0.966
b	0.215	0.232	0.256
a^2/b^2	20.5	17.4	14.1
10^4P/cm^{-1}	99.5	89.2	96.05
K/mT	7.17	6.18	6.31
$\langle r^{-3}\rangle$/pm	0.0113	0.0101	0.0108
χ	−2.15	−1.85	−1.89
$A_{iso.}$/mT	7.35	6.24	6.45
$g_{iso.}$	1.988	1.995	1.990
λ(from P)/cm^{-1}	34	24	30

$[V(CH_2SiMe_3)_2(cp)_2]$.—A toluene solution of $[V(CH_2SiMe_3)_2(cp)_2]$ at room temperature gave an eight-line e.s.r. spectrum having $A_{iso.}(^{51}V) = 6.45$ mT and $g_{iso.} = 1.990$ (Table). Examination of each of these lines showed that there was further splitting (illustrated for line 4 in Figure 3). The second derivative of the fourth line [Figure 3(*a*)] shows a 1 : 4 : 6 : 4 : 1 structure confirming that four equivalent protons from the two methylene groups are interacting with the odd electron on the vanadium. This is clearly shown by the fifth-derivative spectrum which is completely resolved [Figure 3(*b*)]. For comparison, we again show the spectrum of the sharpened first derivative [Figure 3(*c*)].

Proton hyperfine splitting is greater here than with $[VEt_2(cp)_2]$ due to greater delocalisation of the unpaired electron on to the trimethylsilyl methylene ligands. A frozen-solution spectrum (Figure 4) gave the parameters listed in the Table.

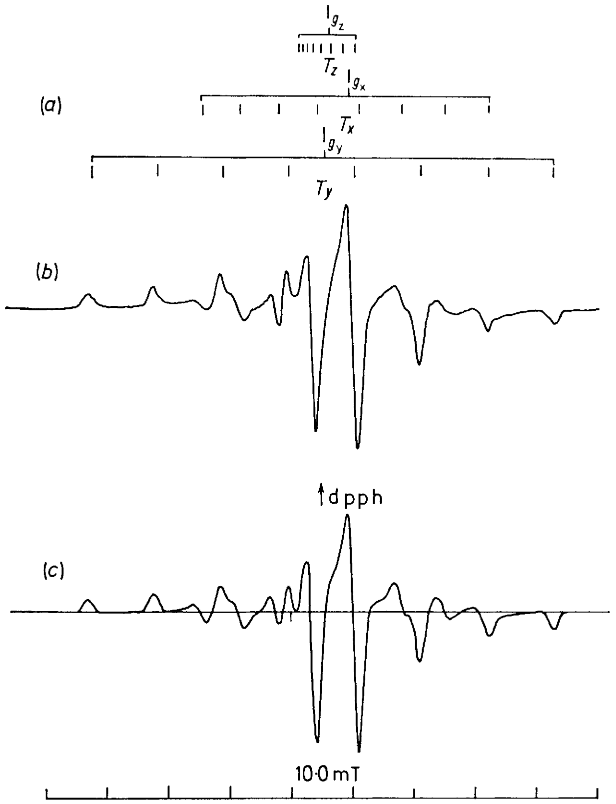

FIGURE 2 E.s.r. spectrum of a frozen solution of $[VEt_2(cp)_2]$ at 77 K: (*a*) stick spectrum; (*b*) experimental first-derivative spectrum; and (*c*) computer-simulated first-derivative spectrum. dpph = Diphenylpicrylhydrazyl

Theoretical Treatment.—Examination of the spectral parameters of frozen solutions of both species shows that they are similar in nature to other $[VL_2(cp)_2]$ complexes

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[4] S. H. Glarum, *Rev. Sci. Instr.*, 1965, **36**, 771.

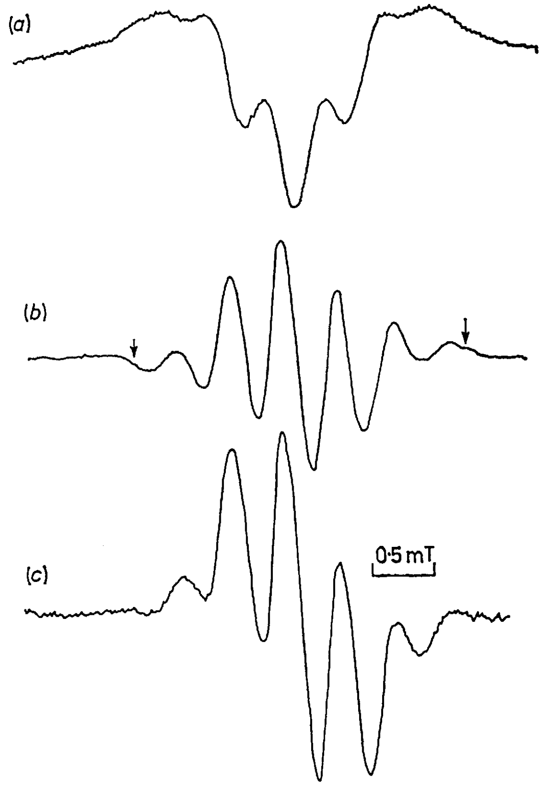

FIGURE 3 E.s.r. spectrum of a solution of [V(CH$_2$SiMe$_3$)$_2$(cp)$_2$] at room temperature. Details as in Figure 1

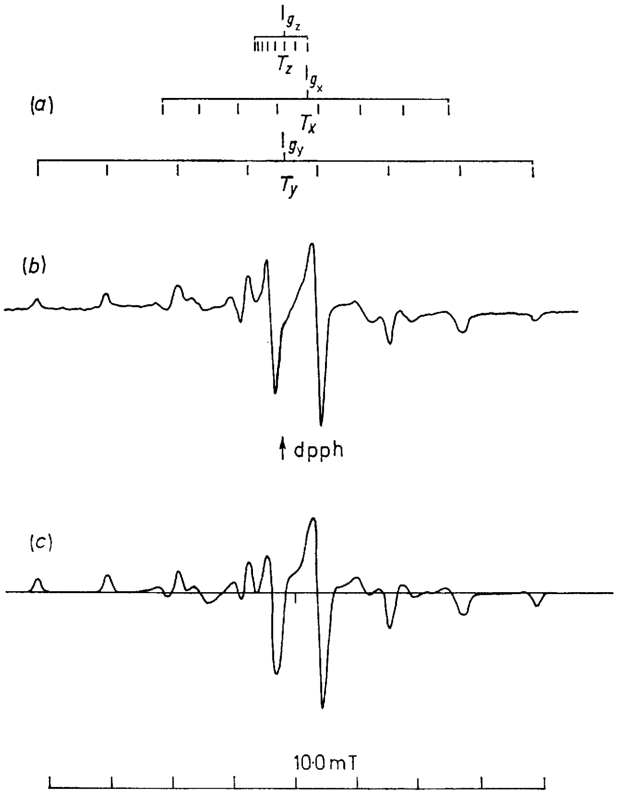

FIGURE 4 E.s.r. spectrum of a frozen solution of [V(CH$_2$SiMe$_3$)$_2$(cp)$_2$] at 77 K. Details as in Figure 2

of C_{2v} symmetry.[5-7] Thus the same axial reference frame can be assumed as was determined by Petersen and Dahl from single-crystal e.s.r. spectra and X-ray data.[5,6]

From our spectra we have obtained initial values of T_y, and g_y and T_x and g_x, where $T_j = A_{\text{iso.}} + A_{j,\text{aniso.}}$. From these values, using equations (1) and (2), initial

$$3\,A_{\text{iso.}} = T_x + T_y + T_z \qquad (1)$$

$$3\,g_{\text{iso.}} = g_x + g_y + g_z \qquad (2)$$

values of T_z and g_z were determined. Using these six parameters the computed spectrum was obtained, and this was in good agreement with the experimental one. The standard iterative process was used to make a fine adjustment to achieve the best fit and the final values obtained for the six parameters are given in the Table. The simulation was very sensitive to changes in g_z and T_z which means that the final values obtained for these parameters are extremely good, despite the fact that they are not resolved in the experimental spectrum. On the basis of a crystal-field treatment, the unpaired electron is in an A_1 ground state, and the relative orbital character gives an electronic ground state of $|\psi\rangle_0 = a|d_{z^2}\rangle + b|d_{x^2-y^2}\rangle$ where $a^2 + b^2 = 1$. The frozen-solution spectral data can, therefore, be treated using the expressions (3)—(10) derived from second-order perturbation theory by McGarvey.[8]

$$T_x = -K + P[\alpha_x - (g_0 - g_x)] \qquad (3)$$

$$T_y = -K + P[\alpha_y - (g_0 - g_y)] \qquad (4)$$

$$T_z = -K + P[\alpha_z - (g_0 - g_z)] \qquad (5)$$

$$\alpha_x = \frac{-2}{7}(a^2 - b^2) - \frac{4 \times 3^{\frac{1}{2}}ab}{7}\left[1 - \frac{(g_0 - g_z)}{8b^2}\right] - \frac{3^{\frac{1}{2}}}{14}\,\frac{(a + b \times 3^{\frac{1}{2}})(g_0 - g_y)}{(a \times 3^{\frac{1}{2}} - b)} \qquad (6)$$

$$\alpha_y = \frac{-2}{7}(a^2 - b^2) + \frac{4 \times 3^{\frac{1}{2}}ab}{7}\left[1 - \frac{(g_0 - g_z)}{8b^2}\right] - \frac{3^{\frac{1}{2}}}{14}\,\frac{(a - b \times 3^{\frac{1}{2}})(g_0 - g_x)}{(a \times 3^{\frac{1}{2}} + b)} \qquad (7)$$

$$\alpha_z = \frac{4}{7}(a^2 - b^2) + \frac{3^{\frac{1}{2}}}{14}\left[\frac{(a + b \times 3^{\frac{1}{2}})\,(g_0 - g_y)}{(a \times 3^{\frac{1}{2}} - b)} + \frac{(a - b \times 3^{\frac{1}{2}})(g_0 - g_x)}{(a \times 3^{\frac{1}{2}} + b)}\right] \qquad (8)$$

$$P = g_0 g_n{}^{51}\,\beta\beta_n \langle r^{-3} \rangle \qquad (9)$$

$$K = -g_0 g_n{}^{51}\beta\beta_n \frac{2}{3}\,\chi \qquad (10)$$

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[5] J. L. Petersen and L. F. Dahl, *J. Amer. Chem. Soc.*, 1975, **97**, 6416.

[6] J. L. Petersen and L. F. Dahl, *J. Amer. Chem. Soc.*, 1975, **97**, 6422.

[7] C. P. Stewart and A. L. Porte, *J.C.S. Dalton*, 1973, 722.

[8] B. R. McGarvey in 'Electron Spin Resonance of Metal Complexes,' ed. Teh. F. Yen, Plenum, New York, 1969.

The coefficients a and b for the three species are given in the Table. It is seen that they are of the same order for each species, and similar to the values for [$VCl_2(cp)_2$], which has C_{2v} symmetry. This means that the unpaired electron of the vanadium resides in an A_1 ground state, largely composed of $3d_{z^2}$ with a small amount of $3d_{x^2-y^2}$ character, in the ratio of *ca.* 17 : 1 for [$VEt_2(cp)_2$] and 14 : 1 for [$V(CH_2SiMe_3)_2(cp)_2$]. The corresponding ratio for [$VCl_2(cp)_2$] is 20 : 1. Thus, as the organic nature of the ligands on the vanadium increases so does the $d_{x^2-y^2}$ contribution to the ground state of the unpaired electron.

Comparison of the calculated P values with those obtained from Hartree–Fock $\langle r^{-3}\rangle$ values[9] shows that the effective nuclear charge on the vanadium changes from *ca.* +1.0 for [$VCl_2(cp)_2$] to +0.5 for [$VEt_2(cp)_2$]. The corresponding value for [$V(CH_2SiMe_3)_2(cp)_2$] is +0.8. This decrease in effective nuclear charge indicates an increase in covalency as chlorine atoms are replaced by alkyl groups, as one would expect.

The values of K, the spin-polarisation component, compare well with $A_{\text{iso.}}$ which is to be expected, since $A_{\text{iso.}} = -K + (g_{\text{iso.}} - 2.002\,3)P$ and $g_{\text{iso.}} \simeq 2$ in all three cases.[9] A negative value of χ is to be expected. A decrease in the negative value of χ indicates a small increase in the 4s character of the unpaired electron from 1.3% in [$VCl_2(cp)_2$] to 1.9% in [$VEt_2(cp)_2$]. The corresponding value for the complex [$V(CH_2SiMe_3)_2(cp)_2$] is also 1.9%.

The u.v. spectra of solutions of these complexes show similar transitions to those observed for other [$VL_2(cp)_2$] complexes having C_{2v} symmetry.[7] Typical of such complexes are the d–d transitions at 13 800, 18 180, and 22 200 cm^{-1} found for [$VEt_2(cp)_2$]. The g values given in the Table are close to 2.002, which indicates considerable delocalisation of charge on to the ligands. This is confirmed by the observation of ligand hyperfine splitting. Thus the application of equations (11)—(13)[5] to obtain the u.v. transitions is not justified.

$$g_x = g_0 - \frac{\lambda(a + b \times 3^{\frac{1}{2}})^2}{E_{yz}} \tag{11}$$

$$g_y = g_0 - \frac{\lambda(a - b \times 3^{\frac{1}{2}})^2}{E_{xz}} \tag{12}$$

$$g_z = g_0 - \frac{b^2\lambda}{E_{xy}} \tag{13}$$

Until a more sophisticated treatment is available, we cannot relate our e.s.r. results to the u.v. spectral data.

Another explanation for our inability to explain the u.v. transitions in terms of the e.s.r. data might be that the g and T axes are non-coincident. This cannot be so, because the relative line intensities which we obtain theoretically using a simulation based on coincident g and T tensors agree with the experimental relative line intensities. From the work of Golding and Tennant[10] we deduce that, if the axes were non-coincident, the use of such a simulation would not give relative line intensities in agreement with the experimental results. In order to confirm this we attempted to simulate to second order the powder spectrum of [$VS_5(cp)_2$],[5] and found that the relative intensities could not be simulated from an expression assuming coincidence. However, for our complexes, simulation of the spectra gives a good fit, and this suggests that the g and T axes are coincident and that the symmetry does not deviate significantly from C_{2v}.

Because the above equations do not apply for the present complexes, the spin–orbit coupling, λ, can only be estimated indirectly from the effective nuclear charge.[5,11] The values determined in this way (Table) for our two complexes are significantly less than that for [$VCl_2(cp)_2$].

Alternative Method of producing [$VEt_2(cp)_2$].—Addition of excess of triethylaluminium to [$VCl_2(cp)_2$] in tetrahydrofuran gives two species initially, one of which {probably [$VCl(Et)(cp)_2$]} is predominant. The concentration of the second species increases with time at the expense of the first until, depending on the concentration of $AlEt_3$, the second species ($A_{\text{iso.}}$ 6.24 mT and $g_{\text{iso.}}$ 1.995), is observed as a single species. These values show that this species is [$VEt_2(cp)_2$]. A spectrum of the frozen solution of this second species at 77 K (Figure 2) gave the parameters listed in the Table for [$VEt_2(cp)_2$].

Infrared Spectra.—The i.r. spectrum of [$V(CH_2SiMe_3)_2(cp)_2$] in hexane showed bands characteristic of the trimethylsilylmethyl and cyclopentadienyl ligands. There is a strong doublet between 1 240 and 1 260 cm^{-1} which is characteristic of a symmetric deformation of the Me–Si bond which in $SiMe_3$ groups has two components of equal intensity. There are also strong bands in the 750—900 cm^{-1} region, probably due to methyl rocking vibrations coupled with Si–C stretches. Absorptions occur at 840 and 770 cm^{-1} which are characteristic of the $SiMe_3$ group. A strong broad band occurs at *ca.* 490 cm^{-1} probably due to metal–carbon modes. The i.r. spectrum gives strong evidence that the trimethylsilylmethyl groups are σ-bonded to the metal centre. The i.r. spectrum of [$VEt_2(cp)_2$] in pentane shows similarly characteristic cyclopentadienyl bands at *ca.* 2 700, 1 260, 1 020, and 815 cm^{-1}.

Conclusions.—From these results we conclude that we have prepared [$VEt_2(cp)_2$] and [$V(CH_2SiMe_3)_2(cp)_2$] in solution. These complexes display surprising stability in solution. They can be handled for considerable periods at room temperature without decomposition, and can be kept almost indefinitely at −40 °C; [$V(CH_2SiMe_3)_2(cp)_2$] has been kept for 1 year at 0 °C.

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[9] B. R. McGarvey, *J. Phys. Chem.*, 1967, **71**, 51.

[10] R. M. Golding and W. C. Tennant, *Mol. Phys.*, 1973, **25**, 1163.

[11] T. M. Dunn, *Trans. Faraday Soc.*, 1961, **57**, 1441.

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