Bis(η-cyclopentadienyl)vanadium(III) Derivatives as Models in Insertion Reactions [1]

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Reaction of carbon monoxide with benzyl- or methyl-bis(η-cyclopentadienyl)vanadium(III), $[V(cp)_2X]$, gives acyl derivatives, $[V(cp)_2(CO)(COX)]$, while under the same conditions $[V(cp)_2Ph]$ yields, *via* phenyl migration to a cyclopentadienyl ligand, dicarbonyl(η-5-phenylcyclopenta-1,3-diene)(η-cyclopentadienyl)vanadium(I), which forms carbonyl(η-cyclopentadienyl)(η-phenylcyclopentadienyl)vanadium(II). Carbon monoxide promotes the insertion of $SnCl_2$ into the V–Cl bond of $[V(cp)_2Cl]$, and carbonylbis(η-cyclopentadienyl)(trichlorostannio)-vanadium(III) is obtained. Insertions of CS_2 into the V–SR bond of $[V(cp)_2(SR)]$ give bis(η-cyclopentadienyl)-(trithiocarbonato)vanadium(III) complexes, which can be oxidised to the corresponding vanadium(IV) derivatives.

MUCH of the recent interest in insertion reactions stems from the emphasis placed on the development of homogeneous catalysis. In addition, many insertion reactions have been used successfully in organic and organometallic syntheses.[2] The chemistry of bis(η-cyclopentadienyl)vanadium(III) complexes, $[V(cp)_2X]$ (I; X = alkyl, aryl, halogeno, or thiolato), provides an opportunity to investigate the factors affecting insertion reactions. One of the main results of this study is the synthesis of hitherto unknown derivatives of bis(η-cyclopentadienyl)vanadium together with useful insights into the general aspects of insertion reactions. Part of this work has been briefly communicated.[3]

RESULTS AND DISCUSSION

Reactions with Carbon Monoxide.—The reactions of bis(η-cyclopentadienyl)vanadium(III) derivatives, $[V(cp)_2X]$, (I), with carbon monoxide are dependent on the nature of X. The complexes (I; X = I, SMe, or SPh), dissolved in toluene, absorbed CO reversibly at atmospheric pressure and room temperature. The

$$\underset{\text{(I)}}{[V(cp)_2X]} + CO \xrightleftharpoons{\text{toluene}} \underset{\text{(II)}}{[V(cp)_2(CO)X]} \qquad (1)$$

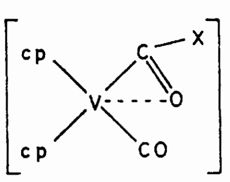
$X = I$,[4] $\nu(CO)$ at 1 953 cm^{-1}
$X = SMe$,[5] $\nu(CO)$ at 1 940 cm^{-1}
$X = SPh$,[5] $\nu(CO)$ at 1 943 cm^{-1}

results can be easily accommodated in terms of a tendency for an open-shell (16-electron) to change into a closed-shell (18-electron) configuration.[6] The high spin state of the 16-electron configurations and the high oxidation number may explain the incomplete addition of CO. The electron-pairing energy hinders the tendency towards the closed-shell configuration. The *cis*-VX(Y) systems, such as (II) (Y = CO, *etc.*), provide very good models for studying the relation between the nature of X and Y in insertion reactions. Complexes (II) are not converted into the corresponding insertion products, the ability of CO to insert into a metal–halogen or –sulphur bond being poor.

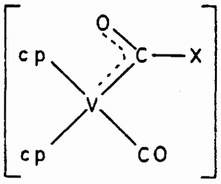
Reaction of carbon monoxide with (I; X = Me or CH_2Ph)[7] in heptane or toluene, at room temperature

$$\text{(I)} + CO \longrightarrow \text{(II)} \longrightarrow \underset{\text{(III)}\ X\,=\,Me\ \text{or}\ CH_2Ph}{[V(cp)_2(CO)(COX)]} \qquad (2)$$

and atmospheric pressure, gave green-maroon crystals of the acyl complexes (III) on cooling the solution to −80 °C. Complexes (III) are soluble in aromatic solvents, sensitive to air, and reasonably thermally stable. The molecular weights in benzene (Table 1) and the i.r. spectra (Table 2) justify the formulations given. The i.r. spectra showed a rather low frequency for the carbonyl CO. This is not unexpected for neutral d^2 complexes, the nucleophilic properties of which are well known for titanium(II)[8] and molybdenum(IV) cyclopentadienyl derivatives.[9] The low ν(CO) (acyl) frequencies may arise from intramolecular interaction between the metal and the acyl group, as indicated in (A) or (B).[10] Diamagnetism in (III) is suggested by the sharpness of the n.m.r. peaks. Of the bis(η-cyclopentadienyl)vanadium(III) derivatives reported in this paper, complexes (III) are the only ones which do not lose CO even under drastic conditions. In this case the open-shell 16-electron configuration does not seem to be energetically accessible.



(A)



(B)

The tendency towards co-ordination of carbon monoxide by the $[V(cp)_2X]$ complexes, reaction (1), enables us to describe the formation of the acyl derivatives (III) as proceeding *via* an alkylcarbonyl intermediate, (II), although no experimental evidence is available for the existence of such a species.

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[1] Abstracted from the thesis by S. Del Nero, University of Pisa, 1975.

[2] A. Woijcicki, *Adv. Organometallic Chem.*, 1973, **11**, 87; 1974, **12**, 31.

[3] G. Fachinetti and C. Floriani, *J.C.S. Chem. Comm.*, 1974, 516.

[4] F. Calderazzo, G. Fachinetti, and C. Floriani, *J. Amer. Chem. Soc.*, 1974, **96**, 3695.

[5] G. Fachinetti and C. Floriani, *J.C.S. Dalton*, 1974, 2433.

[6] C. A. Tolman, *Chem. Soc. Rev.*, 1972, **1**, 337.

[7] H. J. de Liefde Mejier, M. J. Janssen, and G. H. J. Van Der Kerk, *Rec. Trav. chim.*, 1961, **80**, 831.

[8] C. Floriani and G. Fachinetti, *J.C.S. Dalton*, 1973, 1954.

[9] M. L. H. Green, J. A. McCleverty, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 1961, 4854.

[10] M. L. H. Green, 'Organometallic Compounds,' Methuen, London, 1968, vol. 2, pp. 94 and 215.

TABLE 1

Analytical and magnetic data

Complex	Colour	Analysis [a](%) C	H	S	$\mu_{eff.}$ [b] B.M.	M [a,c]
$[V(cp)_2(CO)(COMe)]$ (III; X = Me)	Green-maroon	61.1 (61.9)	5.1 (5.2)		d.[d]	263 (252)
$[V(cp)_2(CO)(COCH_2Ph)]$ (III; X = CH_2Ph)	Green-maroon	69.4 (69.5)	5.0 (5.2)		d.[d]	338 (328)
$[V(cp)(C_5H_5Ph)(CO)_2]$ (IV)	Red	68.6 (68.8)	5.3 (4.8)		d.[d]	
$[V(cp)(C_5H_4Ph)(CO)]$ (V)	Green	71.6 (71.6)	5.4 (4.9)		1.87 (291)	278 (285)
$[V(cp)(C_5H_4Ph)(CO)_2][I_3]$ (VI)	Orange-maroon	31.6 (31.1)	2.3 (2.0)	55.1 (54.9) [e]	d.[d]	
$[V(cp)_2(CO)(SnCl_3)]$ (VII)	Deep violet	30.6 (30.4)	2.3 (2.4)	24.4 (24.6) [e]	d.[d]	
$[V(cp)_2(CO)_2][SnCl_3]$ (VIII)	Yellow-orange	31.2 (31.2)	2.1 (2.1)	23.1 (23.0) [e]	d.[d]	
$[V(cp)_2(S_2CSCH_2Ph)]$ (IX; R = CH_2Ph)	Deep blue	57.1 (56.9)	4.7 (4.5)	24.8 (25.3)	d.[f]	372 (380)
$[V(cp)_2(S_2CSEt)]$ (IX; R = Et)	Deep blue	48.7 (49.0)	4.6 (4.7)	32.1 (30.2)	d.[f]	304 (318)
$[V(cp)_2(S_2CSMe)]$ (IX; R = Me)	Deep blue	47.5 (47.4)	4.5 (4.3)	32.1 (31.6)	d.[f]	304 (304)
$[V(cp)_2(S_2CSPr^i)]$ (IX; R = Pr^i)	Blue-maroon	50.4 (50.6)	4.85 (5.1)	28.7 (28.9)	d.[f]	313 (332)
$[V(cp)_2(S_2CNEt_2)]$ (X)	Violet	54.4 (54.7)	6.3 (6.1)	19.4 (19.4)	d.[d]	316 (329)
$[V(cp)_2(S_2CSEt)][I_3]$ (XI)	Violet-maroon	22.4 (22.3)	2.4 (2.1)	13.3 (13.7)	1.75 (290)	
$[V(cp)_2(S_2CNEt_2)][I_3]$ (XII)	Violet-maroon	26.0 (25.4)	2.9 (2.8)	9.2 (9.0)	1.77 (289)	

[a] Calculated values are given in parentheses. [b] Expressed per metal atom. [c] By cryoscopy in benzene. [d] Diamagnetic, from the sharpness of the n.m.r. peaks. [e] Halogen. [f] Diamagnetic, from the magnetic-susceptibility determinations (solid state).

TABLE 2

Spectroscopic data

Complex	^1H N.m.r. Chemical shift (τ) and solvent	Relative intensity (n H)	Assignment	I.r. (cm^{-1})
(III; X = Me)	7.44 (s) C_6D_6	3	Me	ν(CO) (thf) 1 904s
	5.63 (s)	10	η-C_5H_5	ν(CO) (acyl) 1 605m—s
(III; X = CH_2Ph)	5.86 (s) C_6D_6	2	CH_2	ν(CO) (thf) 1 903s
	5.67 (s)	10	η-C_5H_5	ν(CO) (acyl) (thf) 1 615m—s
	2.80 (m)	5	Ph	
(IV)	6.47 (m) C_6D_6	2	η^4-C_5H_5	ν(CO) (thf) 1 861s, 1 929s
	5.80 (s)	5	η^5-C_5H_5	ν(CH) (Nujol) 2 750m
	5.24 (m)	2	η^4-C_5H_5	
	4.90 (m)	1	η^4-C_5H_5	
	2.65 (m)	5	η^4-C_5H_5Ph	
(VI)	4.15 (s) $(CD_3)_2CO$	5	η^5-C_5H_5	ν(CO) (Nujol) 2 000s, 2 040s
	3.93 (m)	2	η^5-C_5H_4Ph	
	3.36 (m)	2	η^5-C_5H_4Ph	
	2.43 (m)	5	Ph	
(VII)	4.60 (s) $(CD_3)_2CO$		η^5-C_5H_5	ν(CO) (Nujol) 1 950s
(VIII)	4.10 (s) $(CD_3)_2CO$		η^5-C_5H_5	ν(CO) (Nujol) 1 985s, 2 040s
(IX; R = CH_2Ph)	5.54 (s) C_6D_6 [a]	2	CH_2	ν(CS) (region) 918m—s, 930ms
	2.90 (br, m)	5	Ph	
	1.95 (br, s)	10	η^5-C_5H_5	
(IX; R = Et)	8.76 (v) $[^2H_8]$thf [a]	3	Me	ν(CS) (region) 935 s, 980m—s
	6.73 (q)	2	CH_2	
	2.10 (br, s)	10	η^5-C_5H_5	
	8.78 (v) $[^2H_8]$thf [b]	3	Me	
	7.00 (q)	2	CH_2	
	4.36 (br, s)	10	η^5-C_5H_5	
	8.78 (v) $[^2H_8]$thf [c]	3	Me	
	7.00 (q)	2	CH_2	
	4.5 (s)	10	η^5-C_5H_5	
(IX; R = Me)	7.54 (s) C_6D_6 [a]	3	Me	
	2.35 (br, s)	10	η^5-C_5H_5	
(IX; R = Pr^i)	8.87 (d) C_6D_6 [a]	6	Me	ν(CS) (region) 920s, 930 (sh), 985m—s
	6.14 (m)	1	CH	
	3.4 (br, s)	10	η^5-C_5H_5	
(X)	8.85 (v) C_6D_6 [a]	6	Me	
	6.67 (q)	4	CH_2	
	4.96 (s)	10	η^5-C_5H_5	

[a] 20 °C. [b] −35 °C. [c] −50 °C.

The reaction of (I; X = Ph)[11] with CO illustrates an important competing process to CO insertion, namely CO-induced aryl migration.[12] In toluene at 16 °C, 2 mol of CO per vanadium atom were absorbed, giving the red crystalline solid (IV) which is thermally unstable. The formulation of (IV) is based on the analytical data (Table 1) and on the i.r. and n.m.r. spectra (Table 2). Diamagnetism is evident from the sharpness of the n.m.r. peaks. The low frequencies of the two CO bands agree with the low oxidation state (+I) of vanadium. The C–H stretching at 2 750 cm^{-1}, together with the n.m.r. values, strongly suggests that one of the

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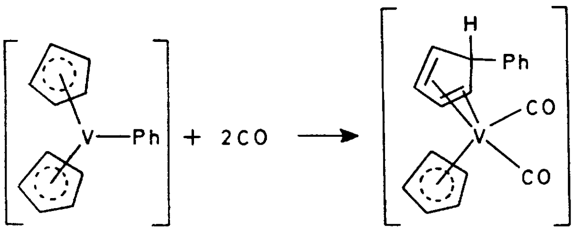
[11] H. J. de Liefde Meijer, M. J. Janssen, and G. H. J. Van Der Kerk, *Chem. and Ind.*, 1960, 119.

[12] P. S. Braterman and R. J. Cross, *Chem. Soc. Rev.*, 1973, 2, 271.

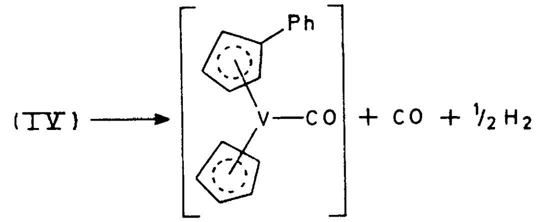
original cyclopentadienyl rings is now present as a diolefin as a consequence of phenyl migration to it. This i.r. band, normally characteristic of *exo*-C–H, seems to indicate the presence of an *endo*-phenylcyclopentadiene ligand in (IV).[13] Complexes similar to (IV) can be obtained from $[V(cp)(CO)_4]$ *via* carbon monoxide substitution by diolefins.[14] Complex (IV) can be regarded as arising from direct intramolecular attack of the phenyl group on the cyclopentadienyl ligand induced by the incoming CO. This is supported by the i.r. spectrum of the toluene or tetrahydrofuran (thf) solutions recorded during the CO insertion.



(3)

(IV)

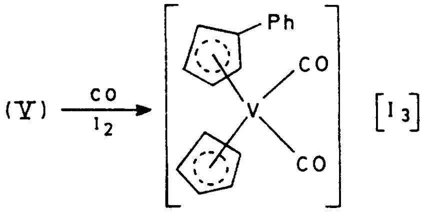
Carbonylation of a thf or toluene solution of (I; X = Ph) with CO at atmospheric pressure and at temperatures not higher than 16 °C gave rise to three strong bands at 1 861, 1 905, and 1 929 cm^{-1} in the carbonyl region and no band in the acyl region, with the 1 905 cm^{-1} band disappearing at the end of the carbonylation. The 1 905 cm^{-1} band can reasonably be attributed to species (II; X = Ph), as a precursor to (IV). The formation of (IV) *via* an acyl intermediate similar to (III) seems to be excluded by the absence of an acyl band in conjunction with the 1 905 cm^{-1} band during the carbonylation. Reaction (3) seems a rare example of a CO-induced alkyl migration to an accepting group different from carbon monoxide. Only a few related examples have been reported for molybdenum alkylcyclopentadienyl derivatives.[15,16]



(4)

(V)

Complex (IV), both in the solid state and in toluene solution at 25—30 °C, rapidly evolves carbon monoxide (1 mol per mol) and molecular hydrogen (1 mol per 2 mol vanadium) to give a maroon-green solution from which (V) can be obtained as green crystals on addition of heptane and cooling. Complex (V) melts at *ca.* 46 °C, is monomeric in benzene (*M* 278), exhibits ν(CO) at 1 893 cm^{-1} (in heptane), and has a magnetic moment (1.87 B.M. at 291 K) * corresponding to one unpaired electron. The C–H cleavage in reaction (4) may be envisaged as either an intermolecular metal-assisted process or a reaction which does not proceed *via* a metal hydride species. A monocarbonyl similar to (V) can be obtained on mild carbonylation of $[V(cp)_2]$.[4] The stable 17-electron configuration seems general for vanadium in low oxidation states, *e.g.* $[V(CO)_6]$,[17] $[V(cp)_2(CO)]$,[4] and $[V(cp)(C_5H_4Ph)(CO)]$. On treating a toluene solution of (V) with excess of I_2 in an atmosphere of carbon monoxide a maroon-orange crystalline solid (VI) was obtained. Complex (VI) is soluble only in polar solvents such as acetone. The analytical results and spectroscopic data are consistent with the formulation given. The most characteristic properties are the diamagnetism, suggested by the sharpness of the n.m.r. peaks, and the two CO bands (Nujol) at 2 000 and 2 040 cm^{-1} in the carbonyl region. Similar results were obtained in the iodine oxidation of $[V(cp)_2(CO)]$ giving $[V(cp)_2(CO)_2][I_3]$.[18] In all cases the reactions seem to go *via* intermediate formation of highly unsaturated 16-electron $[V(cp)_2]^+$ or $[V(cp)_2(CO)]^+$.[18]



(5)

(VI)

Under mild conditions (room temperature and aromatic solvents) no reactions were observed between (I; X = Me, CH_2Ph, and Ph) and CS_2 and CO_2.

Reactions with Tin Dichloride.—The reactions of tin(II) chloride with low-valent transition-metal complexes containing metal–chlorine bonds usually result in formation of complexes containing covalently bound $SnCl_3^-$ ligands.[19]

No reaction of (I; X = Cl) was observed with $SnCl_2$ in the solution or in a toluene suspension under a nitrogen atmosphere. However, in the presence of CO at atmospheric pressure, either in thf or in toluene, a red-violet solution was obtained from which $[V(cp)_2(CO)(SnCl_3)]$, (VII), crystallised out as a red-violet solid (Tables 1 and 2). *In vacuo*, complex (VII) loses CO and

$$[V(cp)_2Cl] + SnCl_2 \underset{-CO}{\overset{+CO}{\rightleftharpoons}} [V(cp)_2(CO)(SnCl_3)] \quad (6)$$

(VII)

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* 1 B.M. ≈ 9.27 × 10^{-24} A m^2.

[13] D. A. White, *Organometallic Chem. Rev.*, 1968, **A3**, 497.

[14] E. O. Fischer, H. P. Kögler, and P. Kuzel, *Chem. Ber.*, 1960, **93**, 3006.

[15] F. W. S. Benfield and M. L. H. Green, *J.C.S. Dalton*, 1974, 1324.

[16] J. A. McCleverty and G. Wilkinson, *J. Chem. Soc.*, 1963, 4096.

[17] R. Ercoli, F. Calderazzo, and A. Alberola, *J. Amer. Chem. Soc.*, 1960, **82**, 2966.

[18] G. Fachinetti, S. Del Nero, and C. Floriani, unpublished work.

[19] J. F. Young, *Adv. Inorg. Chem. Radiochem.*, 1968, **11**, 91.

can be reconverted into the starting materials. This reversibility can be followed either by the change in colour [(I; X = Cl) is blue and (VII) is red-violet] or, in toluene, by the disappearance (under CO atmosphere) and appearance *in vacuo* of the white suspension of $SnCl_2$. The insertion of the ' carbenoid ' $SnCl_2$ into the vanadium–chlorine bond may be explained by the tendency for Cl to migrate preferably to a ligand such as $SnCl_2$.[19] Under the same conditions, $SnCl_2$ also reacted with (I; X = I and SR), although no reproducible products were obtained.

Very long reaction times for (6) in thf solution resulted in heterolytic cleavage of the V–Sn bond giving (VIII) (Tables 1 and 2). Reaction (7) is not reversible. The

$$\text{(VII)} \xrightarrow[\text{thf}]{\text{CO}} \underset{\text{(VIII)}}{[V(cp)_2(CO)_2][SnCl_3]} \qquad (7)$$

formation of a covalent or ionic complex will depend on a number of factors such as the electronic configuration of the transition metal and the nature of the other ligands present. For (I; X = I or SR), ionic complex formation seems to predominate.

Reactions with Carbon Disulphide.—Insertion of CS_2 into metal–sulphur bonds leads to the formation of metal trithiocarbonates.[20] However, examples of such complexes are scarce and poorly characterised. These have been stated to be unstable or to decompose into the metal mercaptide and CS_2. Here we describe the preparation and properties of some quite stable trithiocarbonato-complexes obtained by insertion of CS_2 into a V–S bond.

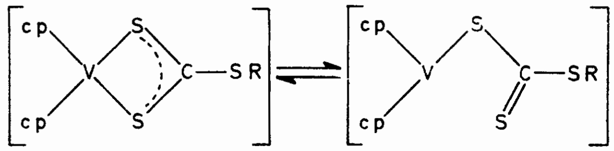
Reaction between (I; X = SR) [15] and CS_2 in toluene solution took place very rapidly giving a blue solution from which, on addition of heptane and cooling, alkyl trithiocarbonates, $[V(cp)_2(S_2CSR)]$, (IX), were obtained.

$$\text{(I)} + CS_2 \longrightarrow \underset{\text{(IX)}}{[V(cp)_2(S_2CSR)]} \qquad (8)$$

$$R = CH_2Ph,\ Et,\ Me,\ \text{or}\ Pr^i$$

The colour of the complexes in the solid state ranges from blue (R = Me, CH_2Ph, or Et) to blue-maroon (R = Pr^i). All solutions have a deep blue colour. We did not observe a reaction when R = Ph. The analytical data (Table 1) and i.r. spectra agree with the formulation given.

The most striking difference between the spectra (solid state) of complexes (I) and (IX) is the appearance of a strong band near 950 cm^{-1} in the latter series (Table 2). This band position appears to be only slightly sensitive to the nature of R and was always accompanied by one or two other bands of lesser intensity. The main band is probably associated with a C–S stretching mode of a chelated system since both the location and intensity of the band can be reconciled with such a group.[21] The monomeric nature was confirmed by cryoscopy in benzene (Table 1). Insight into the structure of the trithiocarbonates comes from the n.m.r. spectra (Table 2). A ' normal ' ^1H n.m.r. spectrum for the diamagnetic complexes was observed only at −50 °C; at room temperature, however, although the chemical shift and pattern were practically identical to those observed at −50 °C for the R substituent, a strongly shifted broad band was observed for the cyclopentadienyl protons (Table 2). This may be interpreted as being due to equilibrium (9) in solution.



(9)

(C) (D)

The observed paramagnetism for structure (D) containing unidentate trithiocarbonate agrees with that expected.[22] Solution paramagnetic-susceptibility measurements by n.m.r.[23] showed decreasing paramagnetism with decreasing temperature, a completely diamagnetic solution being obtained at −50 °C. Decreasing temperature promotes the tendency [reaction (1)] of V^{III} to be four-co-ordinate (18-electron configuration),[4,5] *i.e.* for the metal to change from a high-spin structure (D) to the diamagnetic configuration (C). A further shift to (C) is produced in reaction (9) by the chelate effect. Together with the i.r. spectra (Nujol), the diamagnetism (Table 1) suggests the chelate structure (C) for the trithiocarbonato-complexes in the solid state.

We do not agree with the general statement that the complexes are unstable.[24] The complexes are only unstable to oxidation by oxygen, to which all these complexes are very sensitive. In order to study further the stability of this type of complex we prepared bis(η-cyclopentadienyl)(diethyldithiocarbamato)vanadium(III), $[V(cp)_2(S_2CNEt_2)]$, (X), from reaction (10) in thf.

$$[V(cp)_2Cl] + Na[S_2CNEt_2] \xrightarrow{\text{thf}} \underset{\text{(X)}}{[V(cp)_2(S_2CNEt_2)]} + NaCl \qquad (10)$$

The complex was obtained from the thf solution, on addition of heptane and cooling, as violet crystals which were quite sensitive to oxygen. The i.r. spectrum, molecular weight, and analytical data (Table 1) correspond to the formulation reported. The expected diamagnetism can be deduced from the n.m.r. spectrum which was typical of a diamagnetic substance (room temperature). No unidentate–bidentate equilibrium for

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[20] I. S. Butler and A. E. Fenster, *J. Organometallic Chem.*, 1974, **66**, 161 and references therein.

[21] R. Bruce and G. R. Knox, *J. Organometallic Chem.*, 1966, **6**, 67.

[22] D. R. Eaton, ' Physical Methods in Advanced Inorganic Chemistry,' eds. H. A. O. Hill and P. Day, Interscience, London, 1968, p. 514.

[23] J. Löliger and R. Scheffold, *J. Chem. Educ.*, 1972, 646.

[24] A. M. Bond, A. T. Casey, and J. R. Thacheray, *J.C.S. Dalton*, 1974, 773 and references therein.

the sulphur-containing ligand was observed in this case at room temperature.

One-electron oxidation by I_2 in thf of the trithiocarbonato- and carbamato-complexes led to corresponding vanadium(IV) derivatives, (XI) and (XII) [reactions (11) and (12)], as crystalline maroon solids on addition of benzene or Et_2O. The tri-iodides are apparently formed *via* the corresponding, less soluble, monoiodides which were obtained on using the stoicheiometric amount of I_2. The i.r. spectra, magnetic moments, and analytical results (Table 1) agree with the proposed structures. The ' chelate ' co-ordination of the CS_2 unit can be understood in terms of the molecular model proposed for bent bis(cyclopentadienyl) derivatives.[25] In this case, with only one unpaired electron on the metal atom, no factor hinders the four-co-ordination at vanadium.[24]

$$(\text{IX};\ R = \text{Et}) + \tfrac{3}{2}I_2 \longrightarrow \underset{(\text{XI})}{[V(cp)_2(S_2CSEt)][I_3]} \qquad (11)$$

$$(\text{X}) + \tfrac{3}{2}I_2 \longrightarrow \underset{(\text{XII})}{[V(cp)_2(S_2CNEt_2)][I_3]} \qquad (12)$$

EXPERIMENTAL

Unless otherwise stated, all the reactions described here were carried out under an atmosphere of purified nitrogen; solvents were purified by standard methods. Benzyl-, methyl-,[7] and phenyl-bis(η-cyclopentadienyl)vanadium(III),[11] and iodo- and chloro-bis(η-cyclopentadienyl)vanadium(III),[7] were prepared as previously described. Carbon monoxide, tin dichloride, and carbon disulphide were dried and purified by the standard methods.

I.r. spectra were measured with a Perkin-Elmer 337 spectrometer and n.m.r. spectra with a T-60 Varian spectrometer. Magnetic-susceptibility measurements were made with a Gouy balance.

Some of the typical reactions are described in detail, the preparation of the other complexes being carried out under similar conditions.

Preparations.— *Acetylcarbonylbis*(η-*cyclopentadienyl*)-*vanadium*(III), (III; R = Me). A toluene solution (50 cm^3) of the complex $[V(cp)_2Me]$, (I; X = Me) (1.5 g, 7.65 mmol), was treated with purified carbon monoxide at atmospheric pressure and room temperature for 3—4 h. On addition of heptane (100 cm^3) and cooling to -80 °C, green-maroon *crystals* of (III; R = Me) were obtained (*ca.* 50%). Absorption measurements in toluene solution gave CO: V = 1.87 : 1.

Carbonylbis(η-*cyclopentadienyl*)*phenylacetylvanadium*(III), (III; R = CH_2Ph). A toluene solution (20 cm^3) of complex (I; X = CH_2Ph) (1.2 g, 4.4 mmol) was treated with purified carbon monoxide at atmospheric pressure and room temperature for 1 h. On addition of heptane (50 cm^3) and cooling to -80 °C, deep green-maroon *crystals* of (III; R = CH_2Ph) were obtained (*ca.* 62%). The complex is soluble in all hydrocarbons, and very sensitive to oxygen and moisture. Absorption measurements in toluene solution gave CO: V = 2.04 : 1.

Dicarbonyl(η-*cyclopentadienyl*)(η-5-*phenylcyclopenta*-1,3-*diene*)*vanadium*(I), (IV). A toluene solution (20 cm^3) of complex (I; X = Ph) (1.2 g, 4.65 mmol) was treated with carbon monoxide at atmospheric pressure and below 16 °C. After 2 h the deep green starting solution had become deep red. On addition of cold heptane (100 cm^3), saturated with CO, and cooling to -80 °C, a deep red crystalline *solid*, (IV), was obtained. The solid was filtered in a CO atmosphere and dried *in vacuo* at 0 °C (*ca.* 80%). The complex was stable when kept at -80 °C. Both in the solid state and in solution, at greater than 25 °C, the complex decomposes rapidly. Absorption measurements in toluene solution gave CO : V = 2.03 : 1.

Carbonyl(η-*cyclopentadienyl*)(η-*phenylcyclopentadienyl*)-*vanadium*(II), (V). A heptane (50 cm^3) solution of complex (I; X = Ph) (1.1 g, 4.26 mmol) was treated with CO at atmospheric pressure and 16 °C. After 5 min, red crystals began to separate. After 2 h the CO supply was shut off, and the reaction vessel was connected to a container for gas analysis. Gas was evolved on warming the reaction vessel at 25—30 °C, during which time the red suspension disappeared and a deep green solution was obtained. On cooling to -80 °C, deep green *crystals* of (V) were obtained (*ca.* 74%), m.p. 46—47 °C. Gas-chromatographic analysis gave 2.34% of H_2 and 4.44% of CO.

Dicarbonyl(η-*cyclopentadienyl*)(η-*phenylcyclopentadienyl*)-*vanadium*(III) *tri-iodide*, (VI). A toluene solution (30 cm^3) of complex (V) (0.5 g, 1.75 mmol) was treated with a toluene solution of I_2 (excess) under an atmosphere of carbon monoxide. Rapid absorption of CO was observed, and an orange-maroon *solid* (*ca.* 80%) separated from the solution.

Carbonylbis(η-*cyclopentadienyl*)*trichlorostanniovanadium*-(III), (VII). A toluene (80 cm^3) solution of (I; X = Cl) (0.45 g, 2.08 mmol) was treated with a suspension of $SnCl_2$ (0.400 g, 2.10 mmol), and kept for 2 d under an atmosphere of CO. The white $SnCl_2$ disappeared and red-violet *solid* (VII) was formed. It was collected and washed with toluene (*ca.* 80%). Complex (VII) is not sensitive to oxygen in the solid state, slightly soluble in hydrocarbons, and soluble in thf or acetone.

Dicarbonylbis(η-*cyclopentadienyl*)*vanadium*(III) *trichlorostannate*, (VIII). A thf solution (50 cm^3) of (VII) (1.23 g, 2.83 mmol) was kept under CO for 8 d, after which a orange-yellow crystalline *solid* was obtained from the solution. Addition of benzene caused further formation of the product (*ca.* 61%). The complex is soluble in acetone.

Bis(η-*cyclopentadienyl*)(S-*methyl trithiocarbonato*)*vanadium*(III), (IX; R = Me). A toluene solution (30 cm^3) of (I; X = SMe) (0.6 g, 2.63 mmol) was treated at room temperature with CS_2 (3 cm^3). The solution changed immediately from green to deep blue and was concentrated under reduced pressure, treated with heptane (100 cm^3), and cooled to -60 °C. The resulting deep blue *crystals* of (IX; R = Me) were collected, washed with heptane, and dried (*ca.* 56%). The other complexes (IX) were similarly prepared from the corresponding complex (I) and carbon disulphide.

Bis(η-*cyclopentadienyl*)(*diethyldithiocarbamato*)*vanadium*-(III), (X). A thf solution (50 cm^3) of (I; X = Cl) (1.1 g, 5.1 mmol) was treated with $Na[S_2CNEt_2]\cdot 3OH_2$ (1.15 g, 5.1 mmol); a violet suspension immediately formed, from which NaCl was filtered off. The filtered solution was concentrated to 10 cm^3, heptane (100 cm^3) added, and slightly cooled (-10 °C) and gave a small quantity of a maroon solid. The latter was filtered off and the solution

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[25] J. L. Petersen and L. F. Dahl, *J. Amer. Chem. Soc.*, 1974, **96**, 2248 and references therein.

cooled to −80 °C. The resulting violet *crystals* of (X) were filtered off and washed with heptane (*ca.* 53.5%).

Bis(η-cyclopentadienyl)(S-*ethyl trithiocarbonato)vanadium*(IV) *tri-iodide*, (XI). A thf solution (25 cm^3) of I_2 (0.92 g, 3.62 mmol) was slowly added to a thf solution (25 cm^3) containing complex (IX; R = Et) (0.76 g, 2.39 mmol). At the end of the addition the suspension gave a yellow-maroon solution, from which, after concentration and addition of diethyl ether (150 cm^3), (XI) was obtained as a violet-maroon *solid* (*ca.* 78%). I.r. (in Nujol) (C–S region): 945s and 975m cm^{-1}.

Bis(η-cyclopentadienyl)(diethyldithiocarbamato)vanadium(IV) *tri-iodide*, (XII). To a thf solution (20 cm^3) of I_2 (0.4 g, 1.57 mmol) was added complex (X) (0.33 g, 1.0 mmol). A yellow-orange solution was immediately formed from which, on addition of benzene (100 cm^3), violet-maroon *crystals* of (XII) were obtained. These were collected, washed with benzene, and dried (*ca.* 82%). The complex is soluble only in acetone, and is not air sensitive.

We thank S.N.A.M. Progetti (Milan) for support, Dr. G. Dell'Amico for some magnetic-susceptibility measurements, Dr. C. Veracini for some n.m.r. spectra, and the referees for their suggestions.

[5/620 *Received*, 3*rd April*, 1975]