

Co-ordinative Addition Reactions to Bis(η -cyclopentadienyl)vanadium(II) and to the Bis(η -cyclopentadienyl)vanadium(III) Cation: Carbonyl, Iso-cyanide, Olefin, and Phosphine Derivatives

By Giuseppe Fachinetti, Stefano Del Nero, and Carlo Floriani,* Istituto di Chimica Generale ed Inorganica, Università di Pisa, 56100 Pisa, Italy

The co-ordinative addition of π -acid ligands to $[V(cp)_2]$ ($cp = \eta$ -cyclopentadienyl) gives the new vanadium complexes, $[V(cp)_2L]$ ($L = CO, 2,2'$ -bipyridyl, CS_2 , or activated olefins). Reduction of $[V(cp)_2(CO)]$ under mild conditions gives $[V(cp)(CO)_4]$. The generation and co-ordination ability of the titanocene-like $[V(cp)_2]^+$ is explored. It is a quite reactive species toward ligands (L) such as CO, phosphines, and RNC, giving $[V(cp)_2L_2][BPh_4]$ complexes. An unusual carbonylation of an aqueous solution of $[V(cp)_2]^+$ gives $[V(cp)_2(CO)_2]^+$.

THE chemistry of biscyclopentadienyl derivatives of the early transition metals has recently attracted much interest. This stems from the possibility that the derivatives can be considered as useful models of the role of the metal centres in such reactions of general interest as co-ordination, oxidative addition, and insertion.¹⁻⁶ Many interesting reactions of the highly reactive, sometimes elusive, species $[Ti(cp)_2]$, $[Mo(cp)_2]$, and $[W(cp)_2]$ have been reported ($cp = \eta$ -cyclopentadienyl).⁷ The d^2 biscyclopentadienyls, $[Ti(cp)_2]$,⁸ $[Ti(cp)_2(CO)_2]$,⁵ $[Mo(cp)_2H_2]$,⁹ $[W(cp)_2H_2]$, and $[V(cp)_2X]$ ^{6,10} are

¹ J. E. Bercaw, *J. Amer. Chem. Soc.*, 1974, **96**, 5087.

² J. X. Dermott and G. M. Whitesides, *J. Amer. Chem. Soc.*, 1974, **96**, 947.

³ C. A. Bertelo and J. Schwartz, *J. Amer. Chem. Soc.*, 1975, **97**, 228 and refs. therein.

⁴ J. A. Labinger, J. Schwartz, and J. M. Townsend, *J. Amer. Chem. Soc.*, 1974, **96**, 4009.

⁵ G. Fachinetti and C. Floriani, *J.C.S. Dalton*, 1974, 2433 and refs. therein.

⁶ G. Fachinetti, S. Del Nero, and C. Floriani, *J.C.S. Dalton*, 1976, 203.

of particular interest. The existence of the $[Ti(cp)_2]$ -like d^2 species $[V(cp)_2]^+$ has been proposed,¹¹ but its reactivity was completely unexplored. In this paper the generation and isolation of $[V(cp)_2]^+$ are reported and its reactivity is compared with that of other d^2 biscyclopentadienyl systems. Part of this work has been briefly communicated.¹²

RESULTS AND DISCUSSIONS

Co-ordinative and Oxidative Additions to $[V(cp)_2]$.—Bis(η -cyclopentadienyl)vanadium(II), $[V(cp)_2]$ (I), is a quite reactive species with an open-shell configuration

⁷ J. L. Thomas, *J. Amer. Chem. Soc.*, 1973, **95**, 1838.

⁸ J. E. Bercaw, R. H. Marvich, L. G. Bell, and H. H. Brintzinger, *J. Amer. Chem. Soc.*, 1972, **94**, 1219.

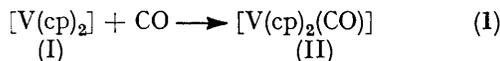
⁹ A. Nakamura and S. Otsuka, *J. Amer. Chem. Soc.*, 1973, **95**, 7262.

¹⁰ F. Calderazzo, G. Fachinetti, and C. Floriani, *J. Amer. Chem. Soc.*, 1974, **96**, 3695.

¹¹ G. Wilkinson and J. M. Birmingham, *J. Amer. Chem. Soc.*, 1954, **76**, 4281.

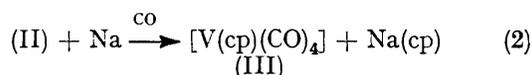
¹² G. Fachinetti and C. Floriani, *J.C.S. Chem. Comm.*, 1975, 578.

(15 electrons) which may be easily converted into the closed-shell 17-electron configuration usual for vanadium. The reaction ¹⁰ with CO [equation (1)] may suggest a π -



basic behaviour, and this is further supported by the failure to observe reactions with more 'basic' ligands such as PPh_3 , PEt_3 , or pyridine.

Attempts to transform (II) into the hypothetical 18-electron species, $[\text{V}(\text{cp})_2(\text{CO})]^-$, by reaction with sodium (one equivalent per vanadium) in tetrahydrofuran (thf) in the presence of CO at atmospheric pressure, gave tetracarbonyl(η -cyclopentadienyl)vanadium(I), $[\text{V}(\text{cp})_2(\text{CO})_4]$, (III) [equation (2)]. Reaction (2) can be carried

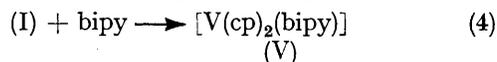


out at room temperature and is certainly the best route to (III) ¹³ which can be obtained in very high yield (ca. 75%).

Complex (I) may be considered, through its ability to co-ordinate different inorganic and organic molecules (e.g. CO,¹⁰ acetylenes,¹⁴ and azobenzene¹⁵), as a good model for studying molecular activation. The reaction between

with the reported data in CS_2 solution. Since two potential nucleophilic centres (C and S) are present, (IV) seems to be a good model for studying the reactivity of co-ordinated carbon disulphide.¹⁷

The π -extended system of the ligand 2,2'-bipyridyl (bipy) may explain the occurrence of reaction (4) compared with the negative results obtained with pyridine, phosphines, and 1,2-bis(diphenylphosphino)ethane. Re-



action (4) was carried out in heptane, from which (V) (Table) was obtained as black crystals on cooling the solution to -70°C . The solid-state formulation of (V) arises from the analytical and magnetic data, although these do not establish whether bipy is uni- or bi-dentate. The molecular-weight determinations in benzene seem to indicate a high degree of ligand dissociation in solution.

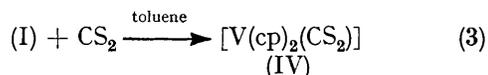
One of the problems not yet fully understood in the chemistry of vanadium is the existence of π -olefin complexes, which are possible intermediates in the polymerisation of olefins. Olefins with no strongly electron attracting groups, e.g. *trans*-stilbene, norbornadiene, and 1,4-diphenylbutadiene, lack reactivity towards (I). Typical activated olefins such as diethyl fumarate (defu) and diethyl maleate (dema) readily react at room

Analytical, i.r., and magnetic data

Complex	Analysis (%) ^a			$\mu_{\text{eff.}}^b/\text{B.M.}$ (T/K)	I.r. data (cm^{-1})
	C	H	N and others		
$[\text{V}(\text{cp})_2(\text{CS}_2)]$ (IV)	50.8 (51.4)	3.75 (3.9)	S 24.1 (24.9)	1.85 (289)	$\nu(\text{CS})$ in CS_2 1 140s
$[\text{V}(\text{cp})_2(\text{bipy})]$ (V)	71.05 (71.2)	5.35 (5.3)	8.0 (8.3)	1.83 (289)	
$[\text{V}(\text{cp})_2(\text{defu})]$ (VI)	61.3 (61.2)	6.2 (6.2)		1.82 (289)	$\nu(\text{CO})$ in Nujol, 1 650m—s, 1 675m—s
$[\text{V}(\text{cp})_2(\text{dema})]$ (VI)	61.4 (61.2)	6.2 (6.2)			$\nu(\text{CO})$ in thf 1 680
$[\text{V}(\text{cp})_2(\text{OCMe}_2)][\text{BPh}_4]$ (IX)	80.0 (79.5)	6.7 (6.4)		2.93 (292)	$\nu(\text{CO})$ in Nujol 1 660
$[\text{V}(\text{cp})_2(\text{py})][\text{BPh}_4]$ (X)	81.3 (81.0)	6.1 (6.0)	2.6 (2.4)	2.6 (291)	
$[\text{V}(\text{cp})_2(\text{CNC}_6\text{H}_{11})_2][\text{BPh}_4]$ (XII)	80.7 (80.2)	7.00 (7.25)			$\nu(\text{CN})$ in Nujol 2 120s, 2 150s
$[\text{V}(\text{cp})_2(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)][\text{BPh}_4]$ (XII)	79.5 (80.5)	6.25 (6.0)	P 6.5 (6.0)	<i>d</i>	
$[\text{V}(\text{cp})_2(\text{CO})(\text{py})][\text{BPh}_4]$ (XIII)	78.7 (79.1)	5.75 (5.75)	2.40 (2.3)		$\nu(\text{CO})$ in Nujol 1 930s
$[\text{V}(\text{cp})_2(\text{CO})(\text{PEt}_3)][\text{BPh}_4]$ (XIII)	76.05 (75.85)	6.95 (6.50)	P 4.80 (5.00)		$\nu(\text{CN})$ in thf 1 950s
$[\text{V}(\text{cp})_2(\text{CNC}_6\text{H}_{11})_2]\text{Cl}$ (XIV)	65.8 (66.3)	7.65 (7.35)	6.30 (6.45)		$\nu(\text{CN})$ in Nujol 2 130s, 2 160s
$[\text{V}(\text{cp})_2(\text{CNC}_6\text{H}_{11})_2]\text{I}$ (XIV)	54.9 (54.75)	5.90 (6.10)	5.55 (5.30)		$\nu(\text{CN})$ in Nujol 2 130s, 2 160s
$[\text{V}(\text{cp})_2(\text{CO})(\text{PBu}^n_3)][\text{BPh}_4]$ (XIII)	77.0 (77.4)	7.9 (7.7)			$\nu(\text{CO})$ in thf 1 950s

^a Calculated values are given in parentheses. ^b Results expressed per metal atom. ^c Not determined. ^d Diamagnetic.

(I) and a stoichiometric quantity of carbon disulphide in toluene resulted in the preparation, in almost quantitative yield, of $[\text{V}(\text{cp})_2(\text{CS}_2)]$, (IV), as a maroon crystal-



line solid very sensitive to oxidation. The existence of (IV) in CS_2 solution was already inferred from i.r. and e.s.r. spectra, but no isolable product was reported.¹⁶ The i.r. spectrum [$\nu(\text{CS}_2)$ (Nujol) 1 125 cm^{-1}] and magnetic moment (μ 1.85 B.M., 289 K) * in the solid state agree

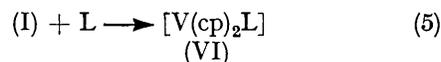
* 1 B.M. $\approx 9.27 \times 10^{-24}$ A m², 1 atm = 101 325 Pa.

¹³ R. B. King, *Organometallic Synth.*, 1965, **1**, 105.

¹⁴ R. Tsumura and N. Hagihara, *Bull. Chem. Soc. Japan*, 1966, **38**, 861.

¹⁵ G. Fachinetti, G. Fochi, and C. Floriani, *J. Organometallic Chem.*, 1973, **57**, C51.

temperature. The reaction of (I) in toluene solution, with either defu or dema, afforded the same adduct (VI) [equation (5)], which was isolated as a green-maroon

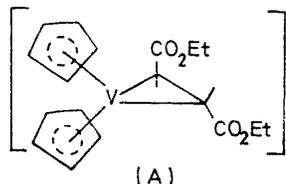


microcrystalline solid, insoluble in heptane and slightly soluble in toluene. The adduct is paramagnetic with one unpaired electron (Table), in agreement with a formal oxidation state of IV for the vanadium. The i.r. spectrum showed only one carbonylic band in solution at 1 680 cm^{-1} . Two bands were observed at 1 675m—s and 1 650m—s cm^{-1} (Nujol), probably due to solid-state

¹⁶ M. C. Baird, G. Hartwell, and G. Wilkinson, *J. Chem. Soc. (A)*, 1967, 2037.

¹⁷ G. W. A. Fowles, L. S. Pu, and D. A. Rice, *J. Organometallic Chem.*, 1973, **54**, C17.

effects. The i.r. spectral evidence shows that the CO groups are probably not directly involved in the co-ordination; in fact the absorptions due to these groups showed a shift to lower wavenumber of only 45 cm^{-1} with respect to the free ligand. When these groups participate directly in the bonding the shifts are much higher.¹⁸ A monomeric structure, (A), seems reasonable for (VI), although its low solubility prevented molecular-weight determinations in solution.



Some useful stereochemical information on (VI) can be obtained from its decomposition. Oxidation of (VI) in solution with dry oxygen gave only defu in quantitative yield. This result is support for the proposed *trans* arrangement of the CO_2Et groups in the olefinic complex. The reaction of (VI) with proton donors such as hydrochloric acid decomposed the complex with liberation of diethyl succinate and $[\text{V}(\text{cp})_2\text{Cl}_2]$. That reaction (5) gives only one olefinic complex, both with defu and dema, seems to indicate isomerisation takes place on bonding to vanadium.

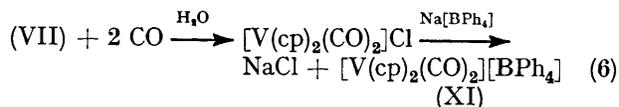
The high reactivity of (I) towards various small molecules such as CO, olefins, acetylenes, and azobenzene makes it a versatile substrate for complex formation.

Generation and Reactivity of the Bis(η -cyclopentadienyl)-vanadium(III) Cation.—Previous studies on $[\text{Ti}(\text{cp})_2]$ and other titanium species suggest that $[\text{V}(\text{cp})_2]^+$ will be coordinatively unsaturated and highly reactive.^{1,8} The presence of $[\text{V}(\text{cp})_2]^+$ in aqueous solution was inferred from magnetic measurements which showed two unpaired electrons per vanadium atom,¹¹ *i.e.* the electronic configuration of the unsolvated $[\text{V}(\text{cp})_2]^+$ species.¹⁹ The best genuine source of $[\text{V}(\text{cp})_2]^+$ is the aqueous solution $[\text{V}(\text{cp})_2\text{Cl}]$, (VII).

Addition of $\text{Na}[\text{BPh}_4]$ to a cold aqueous solution of (VII) gave a blue-violet precipitate, (VIII), which was slightly soluble in thf when well dried and well soluble when containing a certain amount of water. In spite of many attempts, we never obtained a material analysing correctly for $[\text{V}(\text{cp})_2][\text{BPh}_4]$. This seems to be attributable to the instability of the unsaturated 14-electron configuration of $[\text{V}(\text{cp})_2]^+$.²⁰ Recrystallisation of (VIII) from acetone gave deep-blue crystals of $[\text{V}(\text{cp})_2(\text{OCMe}_2)]-[\text{BPh}_4]$, (IX) (Table). Reaction of (VII) in thf in the presence of pyridine and $\text{Na}[\text{BPh}_4]$ gave blue-green crystals of $[\text{V}(\text{cp})_2(\text{py})][\text{BPh}_4]$, (X) (Table). These results suggest that the magnetic moment reported for $[\text{V}(\text{cp})_2]^+$ in aqueous solution⁹ can be attributed to the

solvated monoaqua-species $[\text{V}(\text{cp})_2(\text{OH}_2)][\text{BPh}_4]$. The isolation of a monosolvated species, $[\text{V}(\text{cp})_2\text{L}]^+$ ($\text{L} = \text{acetone}$ or pyridine), agrees with the higher stability typical of the 16-electron configuration.²⁰

The reactivity of solvated $[\text{V}(\text{cp})_2]^+$ species is exemplified by the carbonylation of an aqueous solution of $[\text{V}(\text{cp})_2\text{Cl}]$. On treating a cold aqueous solution of (VII) with CO at atmospheric pressure a rapid absorption of the gas was observed, and the colour of the solution changed from blue to maroon. Addition of $\text{Na}[\text{BPh}_4]$ to the maroon solution gave the known dicarbonyl (XI).²¹

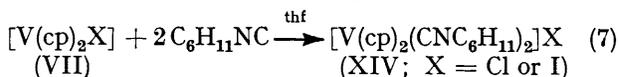


Reaction (6) is the best synthetic route to (XI) (yield *ca.* 70%). Tetrahydrofuran or acetone solutions of (VIII) and (IX) reacted with CO, $\text{C}_6\text{H}_{11}\text{NC}$, and $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$, giving $[\text{V}(\text{cp})_2\text{L}_2][\text{BPh}_4]$, (XI) and (XII) ($\text{L} = \text{C}_6\text{H}_{11}\text{NC}$ or $\text{L}_2 = \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$) (Table). Complex (XII; $\text{L}_2 = \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$) is diamagnetic in the solid state, but its slight solubility prevented n.m.r. measurements being made. N.m.r. spectrum of (XII; $\text{L} = \text{C}_6\text{H}_{11}\text{NC}$) in $(\text{CD}_3)_2\text{CO}$: τ 8.3 (20 H, m, C_6H_{11}), 6.0 (2 H, m, C_6H_{11}), 4.36 (10 H, s, cp), and 2.8 (20 H, m, BPh_4).

The high π basicity of $[\text{V}(\text{cp})_2]^+$ may be contrasted with the σ basicity of, for example, $[\text{Ti}(\text{cp})_2(\text{CO})_2]$ and $[\text{Mo}(\text{cp})_2\text{H}_2]$. The π basicity makes $[\text{V}(\text{cp})_2]^+$ a versatile metal complex in co-ordinating π -acid molecules.

On treating a thf solution of (VIII) or (IX) in the presence of PEt_3 , PBu^n_3 , or pyridine (L) with CO at atmospheric pressure the corresponding monocarbonyl species $[\text{V}(\text{cp})_2(\text{CO})\text{L}][\text{BPh}_4]$, (XIII), were obtained as crystalline, violet, diamagnetic solids (Table). N.m.r. spectra: in $[\text{H}_8]$ tetrahydrofuran, τ 3.0 (20 H, m, BPh_4), 5.1 (10 H, d, cp) [$J(\text{P},\text{cp})$ 2.0 Hz], and 9.0 (15 H, bm, Et) for $\text{L} = \text{PEt}_3$; in $(\text{CD}_3)_2\text{CO}$, τ 3.0 (20 H, bm, BPh_4), 4.75 (10 H, d, cp) [$J(\text{P},\text{cp})$ 2.0 Hz], and 9.0 (27 H, bm, Bu^n) for $\text{L} = \text{PBu}^n_3$.

An alternative synthetic route to di-isocyanide complexes may be the reaction between bis(η -cyclopentadienyl)halogenovanadium(III) with cyclohexyl isocyanide in thf solution, from which (XIV) precipitated as insoluble solids (Table). The diamagnetism of (XIV; $\text{X} = \text{Cl}$)



is evident from the sharpness of the peaks in the n.m.r. spectrum [in $(\text{CD}_3)_2\text{CO}$, τ 8.3 (20 H, bm, C_6H_{11}), 4.65 (10 H, s, cp), and 5.9 (2 H, bm, C_6H_{11})].

EXPERIMENTAL

Unless otherwise stated, all the reactions described were carried out under an atmosphere of purified nitrogen; solvents were purified by standard methods. Bis(η -cyclo-

¹⁸ H. P. Fritz and G. N. Schrauzer, *Chem. Ber.*, 1961, **94**, 650; R. B. King and A. Fronzaglia, *Inorg. Chem.*, 1966, **5**, 1837.

¹⁹ G. E. Coates, M. L. H. Green, and K. Wade, 'Organometallic Compounds,' Methuen, London, 1968, vol. 2, p. 103; K. D. Warren, *Inorg. Chem.*, 1974, **13**, 1317.

²⁰ C. A. Tolman, *Chem. Soc. Rev.*, 1972, **1**, 337.

²¹ F. Calderazzo and S. Bacciarelli, *Inorg. Chem.*, 1963, **2**, 721.

pentadienyl)vanadium(II), (I),²² and chloro- and iodo-bis(η -cyclopentadienyl)vanadium(III), (VII),²³ were prepared by essentially the same methods as described in the literature. All the other reagents were commercial products. I.r. spectra were measured with a Perkin-Elmer spectrophotometer and n.m.r. spectra with a T-60 Varian spectrometer. Magnetic susceptibility measurements were carried out with a Gouy balance.

Preparations.—*Tetracarbonyl(η -cyclopentadienyl)vanadium(I)*, (III). A thf solution (50 cm³) of (I) (1.73 g, 9.5 mmol) was kept under CO (1 atm) for 30 min at room temperature, and then treated with 1 equivalent of sodium sand (0.23 g, 10 mmol). The solution was maintained under CO for 12 h with stirring. The solution changed from green-maroon, [V(cp)₂(CO)], to deep yellow. The solution was evaporated to dryness, and the residue sublimed as an orange-yellow crystalline solid, [V(cp)(CO)₄] (ca. 75%).

(Carbon disulphide)bis(η -cyclopentadienyl)vanadium(IV), (IV). To a toluene solution (50 cm³) of (I) (1.45 g, 8.0 mmol), cooled to -80 °C, was added pure distilled CS₂ (0.5 cm³, 8.3 mmol). On slowly raising the temperature, the colour of the solution changed from violet through maroon to deep green. The maroon crystals of [V(cp)₂(CS₂)] which formed were collected and washed with cold toluene (ca. 78%).

(2,2'-Bipyridyl)bis(η -cyclopentadienyl)vanadium(II), (V). To a heptane solution (100 cm³) of (I) (0.95 g, 5.25 mmol), was added pure 2,2'-bipyridyl (1.0 g, 6.4 mmol) at room temperature. The colour of the solution changed at once from violet to black. On cooling the solution, black crystals of (V) were obtained, which were filtered off and washed with cold heptane (ca. 44%).

Bis(η -cyclopentadienyl)(diethyl maleate)vanadium(IV), (VI). To a thf solution (50 cm³) of (I) (1.1 g, 6.08 mmol) cooled to -80 °C, was slowly added a thf solution (50 cm³) of diethyl maleate (1.1 cm³, 6.82 mmol). On raising the temperature to that of the room, the colour changed from violet to deep maroon. After being allowed to stand at room temperature for 0.5 h, the solution was evaporated *in vacuo* to 20 cm³. On addition of heptane (100 cm³) and cooling to 0 °C, (VI) was obtained as deep maroon crystals (ca. 70%). A solution of (VI) (0.22 g, 0.62 mmol) in thf when treated with oxygen at room temperature gave diethyl fumarate (0.1 g, 0.58 mmol) as determined by g.l.c. The reaction between (I) and diethyl fumarate was carried out under similar conditions and gave the same product. Decomposition *via* oxidation gave an almost quantitative yield of diethyl fumarate. Treatment of complex (VI) (0.456 g, 1.29 mmol) in thf (25 ml) with dry HCl gave [V(cp)₂Cl₂] (0.29 g, 1.15 mmol), while the solution contained diethyl succinate (0.19 g, 1.09 mmol) (g.l.c.).

Acetonebis(η -cyclopentadienyl)vanadium(III) tetrakisphenylborate, (IX). An aqueous solution (250 cm³) of [V(cp)₂Cl] (3.0 g, 13.8 mmol) was treated with solid Na[BPh₄] (4.8 g, 14 mmol) and a violet precipitate immediately formed. The solid was washed with water (200 cm³) and recovered from thf (100 cm³). The deep-blue thf solution was evaporated to dryness, the residue was dissolved in acetone (70 cm³), and deep blue crystals of [V(cp)₂(OCMe₂)]₂[BPh₄], (IX) (ca. 70%), were obtained on cooling to -30 °C.

Bis(η -cyclopentadienyl)(pyridine)vanadium(III) tetrakisphenylborate, (X). A mixture of [V(cp)₂Cl] (1.0 g, 4.60 mmol) and Na[BPh₄] (1.58 g, 4.62 mmol) was dissolved in thf (100 cm³). Addition of pyridine (1.5 cm³) caused rapid formation of NaCl together with a blue solid. The suspension

was filtered when hot, in order to eliminate NaCl, and the resulting solution when cooled to 0 °C gave blue crystals of (X) (ca. 70%).

Dicarbonylbis(η -cyclopentadienyl)vanadium(III) tetrakisphenylborate, (XI). The complex [V(cp)₂Cl] (1.22 g, 5.64 mmol) was dissolved in cold water (20 cm³) and placed under CO. Rapid absorption of gas was observed and the colour of the solution changed from blue to maroon. At the end of the absorption, addition of Na[BPh₄] (2.1 g, 6.14 mmol) gave a maroon precipitate of [V(cp)₂(CO)₂]₂[BPh₄]. This was recrystallised from acetone (ca. 70%).

Alternatively, an acetone solution (30 cm³) of (IX) (1.20 g, 2.15 mmol) was kept under an atmosphere of CO. Rapid absorption of CO was observed, and the colour of the solution changed from blue to maroon. At the end of the gas absorption a yellow-maroon crystalline solid was formed. Addition of diethyl ether (100 cm³) caused further precipitation of (XI) (ca. 80%).

Bis(cyclohexyl isocyanide)bis(η -cyclopentadienyl)vanadium(III) tetrakisphenylborate, (XII). An acetone solution of (IX) (0.5 g, 0.895 mmol) was treated with C₆H₁₁NC (0.28 g, 2.57 mmol). The colour of the solution changed immediately from deep blue to maroon. On concentration and addition of toluene (50 cm³), (XII) was obtained as a maroon crystalline solid (ca. 75%). The solid can be recrystallised from tetrahydrofuran-toluene.

[1,2-Bis(diphenylphosphino)ethane]bis(η -cyclopentadienyl)vanadium(III) tetrakisphenylborate, (XII). A thf solution (50 cm³) of (IX) (0.670 g, 1 mmol) was treated with Ph₂PCH₂CH₂PPh₂ (0.5 g, 1.25 mmol) and the colour of the solution changed to deep green. On concentration and addition of OEt₂ (50 cm³), a green microcrystalline solid was obtained (ca. 60%).

*Carbonylbis(η -cyclopentadienyl)(tri-*n*-butylphosphine)vanadium(III) tetrakisphenylborate*, (XIII). A thf solution (50 cm³) of (IX) (0.7 g, 1.25 mmol) was treated with tri-*n*-butylphosphine (1.0 g, 4.96 mmol), the colour of the solution changing to violet. The solution was treated with CO (1 atm) and the colour changed to red-violet. On concentration, (XIII; L = PBu₃) was obtained as a deep red-violet crystalline solid (ca. 60%). Similarly, a thf solution of (X), treated with CO, gave red-violet crystalline (XIII; L = py) (ca. 30%).

Bis(cyclohexyl isocyanide)bis(η -cyclopentadienyl)vanadium(III) chloride, (XIV). On mixing a toluene solution (50 cm³) of [V(cp)₂Cl] (0.87 g, 4.02 mmol) with a toluene solution (20 cm³) of C₆H₁₁NC (1.2 ml, 9.80 mmol), a microcrystalline maroon precipitate was immediately obtained. This was filtered off and washed well with toluene (ca. 55%). The complex is practically insoluble in hydrocarbons, but is soluble in acetone.

Bis(cyclohexyl isocyanide)bis(η -cyclopentadienyl)vanadium(III) iodide, (XIV). To a toluene solution (20 cm³) of [V(cp)₂I] (0.48 g, 1.56 mmol) was added pure C₆H₁₁NC (0.42 cm³, 3.43 mmol). The solution was decolourised rapidly, giving a maroon crystalline solid. This was collected and washed well with toluene (ca. 59%). The complex is insoluble in hydrocarbons, but is soluble in acetone.

We thank S.N.A.M. Progetti (Milan) and C.N.R. (Rome) for support, and Dr. G. Dell'Amico for some magnetic-susceptibility measurements.

[5/1428 Received, 21st July, 1975]

²² E. O. Fischer and S. Vigoureux, *Chem. Ber.*, 1958, **91**, 2205.

²³ H. J. De Liefde Meier, M. J. Janssen, and G. H. J. Van Der Kerk, *Rec. Trav. chim.*, 1961, **80**, 831.