volved in ion-pair interactions in the low-temperature molten salts under consideration, the formation of Cl_3^- should be even easier.

The convective diffusion-controlled wave of chloride oxidation can be applied successfully to studies of stoichiometry of many complexation reactions occurring in these molten salts. This is of particular importance in the case of nonelectroactive chloride-containing complexes, such as the rare earths. Since the Cl^- oxidation current is proportional to RCl concentration over a wide range of concentrations—up to at least 0.1 mol dm^{-3}—the complexation reactions can be studied under conditions of a large excess of the ligand (Cl^-) over the metal ion. In addition, the ability to obtain a discrete reduction wave for the heptachlorodialuminate ion[14] suggests that the interaction of a metal ion with the $Al_2Cl_7^-$ ion may be studied in a similar manner. For instance, if a metal chloride, MCl_2, is dissolved in a "neutral" melt containing a small excess of $Al_2Cl_7^-$, the tendency of the metal ion to yield a chloride to the $Al_2Cl_7^-$ species will result in a decrease of the $Al_2Cl_7^-$ wave; if the metal chloride accepts a chloride from the "neutral" melt, the wave due to $Al_2Cl_7^-$ will increase. Preliminary experiments indicate that this approach is both feasible and useful.[38]

Acknowledgment. We thank Dr. Zenon Karpinski and Dr. Saeed Sahami for helpful discussions and assistance. This work was supported by the Air Force Office of Scientific Research.

Note Added in Proof. We have recently learned from Dr. John Wilkes, Frank J. Seiler Research Laboratory, United States Air Force Academy, Colorado Springs, CO, that he has observed, via NMR studies, a fairly slow reaction between chlorine and the 1-methyl-3-ethylimidazolium chloride melt to form 4,5-dichloro-1-methyl-3-ethylimidazolium chloride as a substitution product. This could explain the disappearance of chlorine referred to in this paper in the discussion under Coulometry and Spectroscopy.

Registry No. Cl^-, 16887-00-6; Cl_3^-, 18434-33-8; $AlCl_3$, 7446-70-0; BuPyCl, 1124-64-7; ImCl, 65039-09-0; carbon, 7440-44-0; tungsten, 7440-33-7; platinum, 7440-06-4.

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Decamethylvanadocene Chemistry: Synthesis, Structure, and Reactions of Vanadium(II) and Vanadium(III) Derivatives with Carbon Monoxide and Isocyanides

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Received June 2, 1983

The synthesis and structure of decamethylvanadocene $(cp^*)_2V$ ($cp^* = \eta^5\text{-}C_5Me_5$) are reported. Decamethylvanadocene contains planar C_5Me_5 rings [$cp^*\text{-}V_{av} = 1.91$ (5) Å] in a sandwich structure. The magnetic moment for $(cp^*)_2V$ is in agreement with the presence of three unpaired electrons (3.71 μ_B at 291.5 K). It reacts with carbon monoxide leading to a 17-electron monocarbonyl compound, $(cp^*)_2V(CO)$ (1.75 μ_B at 293 K), which has a very low C–O stretching frequency [ν(C–O)(Nujol) = 1845 cm^{-1}] and whose structure was determined by an X-ray analysis. A structural change from a sandwich to a bent arrangement occurs when carbon monoxide is bonded [V–C = 1.879 (8), C–O = 1.17 (1) Å]. Decamethylvanadocene reacts with isocyanides, RNC (R = C_6H_{11}, *t*-Bu), promoting the homolytic cleavage of the R–N bond to form $(cp^*)_2V(CN)(RNC)$ complexes [ν(C–N)(Nujol): R = C_6H_{11}, 2050 and 2070 cm^{-1}; R = *t*-Bu, 2020 and 2060 cm^{-1}]. The structure of $(cp^*)_2V(CN)(C_6H_{11}NC)$ shows a bent $(cp^*)_2V$ unit bonding in the equatorial plane of the CN^- and RNC ligands. The V–C and C–N bond distances are very close for both ligands [$V\text{-}C_{av} = 2.04$ (2), $C\text{-}N_{av} =$ 1.18 (2) Å]. Dealkylation of *t*-BuNC is promoted by $(cp^*)_2V(CO)$, which is a free-radical-like reagent. The reaction allowed the isolation of the two interrelated complexes $(cp^*)_2V(CO)(CN)$ [ν(C–O) = 1910, ν(C–N) = 2070 cm^{-1}] and $(cp^*)_2V(CN)$ [ν(C–N) = 2080 cm^{-1}], which is isostructural with $(cp^*)_2V(CO)$. One-electron oxidation of decamethylvanadocene with various reagents leads to the corresponding vanadium(III) complexes, $(cp^*)_2V(X)$ (X = Cl, I, SC_6H_4Me-*p*), which are paramagnetic *per* two electrons. They absorb carbon monoxide (X = I, SC_6H_4Me-*p*) in nonpolar solvent to form the corresponding diamagnetic monocarbonyl $(cp^*)_2V(X)(CO)$ [ν(C–O): X = I, 1890 cm^{-1}; X = SC_6H_4Me-*p*, 1890 cm^{-1}]. If the reaction is carried out in a polar solvent or in the presence of an ionizing agent, the formation of $[(cp^*)_2V(CO)_2]^+$ is observed. *tert*-Butyl isocyanide promotes the ionization of the V–X bond in $(cp^*)_2V(X)$ complexes, forming the corresponding diisocyanide compounds $[(cp^*)_2V(t\text{-}BuNC)_2]X$ (X = Cl, I, SC_6H_4Me-*p*). Crystallographic details for $(cp^*)_2V$: space group *Cmcm* (orthorhombic), *a* = 15.049 (6) Å, *b* = 8.660 (4) Å, *c* = 29.663 (10) Å, *Z* = 8. The final *R* factor is 0.12 for 464 observed reflections. Crystallographic details for $(cp^*)_2V(CO)$: space group $P2_1/n$ (monoclinic), *a* = 15.699 (7) Å, *b* = 13.353 (6) Å, *c* = 9.452 (5) Å, β = 99.26 (5)° for *Z* = 4. The final *R* value is 0.055 for 1563 observed reflections. Crystallographic details for $(cp^*)_2V(CN)(CNC_6H_{11})$: space group $P2_1/c$ (monoclinic), *a* = 10.342 (5) Å, *b* = 13.146 (7) Å, *c* = 18.956 (10) Å, β = 92.60 (6)° for *Z* = 4. The final *R* value is 0.067 for 1163 observed reflections. Crystallographic details for $(cp^*)_2V(CN)$: space group $P2_1/n$ (monoclinic), *a* = 15.895 (4) Å, *b* = 13.441 (3) Å, *c* = 9.209 (2) Å, β = 97.92 (2)° for *Z* = 4. The final *R* value is 0.051 for 1508 observed reflections.

Introduction

Bis(cyclopentadienyl)metal derivatives have been considered among the most promising model compounds for studying the activation of small molecules and organic functional groups, including some general aspects of a few classes of organometallic reactions.[1]

Such a utilization may be ascribed to some peculiarities of these complexes, namely (i) the $(cp)_2M$ unit has a limited number or orbitals available for the intraction with a molecule

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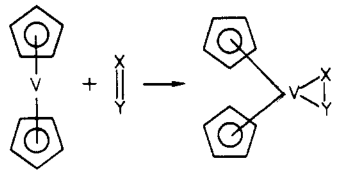
to be activated, (ii) electronically flexible ligands like cp rings are present on the metal, and (iii) the $(cp)_2M$ unit remains intact through several reactions. This last property is, however, strongly dependent on the nature of the metal and its electronic configuration.

Vanadocene, which is the unique, stable, and easily accessible metallocene of the early transition metals, is an electronically and coordinatively unsaturated molecule. It behaves as a carbene-like unit, adding to many organic functional groups (eq 1). Vanadocene and vanadocene-derived species, namely $(cp)_2V^+$ and $(cp)_2V(X)$[8] compounds containing vanadium(III), have been found to be among the most versatile metallic reagents in coordinative addition reactions, in which the $(cp)_2V$ unit and the cp ligand remain intact. A significant improvement in metallocene chemistry was achieved by the substitution of the $C_5H_5^-$ ring by the more "innocent" pentamethyl derivative $C_5Me_5^-$. The introduction into this chemistry of the $C_5Me_5^-$ ligand was due to King.[9a] The importance of such an introduction is emphasized by the work from Bercaw and his group,[9b] who were obliged to find an innocent cp-type ligand in titanocene and zirconocene chemistry, while other reasons have been lucidly emphasized by Maitlis.[9c] Some main effects resulting from the substitution of η^5-$C_5H_5^-$ by the η^5-$C_5Me_5^-$ ligand can be summarized as follows: (i) The electron-donating ability of $C_5Me_5^-$ is significantly higher than that of $C_5H_5^-$. Such a property may have a remarkable role in stabilizing a low oxidation state of the metal and in affecting the stability of the metal-to-ligand (L) bond in $(cp^*)_2ML_n$-type complexes;[10a] (ii) The $(\eta^5$-$C_5Me_5)_2M$ bent unit makes a cavity in the equatorial plane for binding one, two, or three more monodentate ligands. The size of such a cavity may have a significant influence, in case of a small ion like vanadium, in forcing the proximity between these groups, in imposing a special bonding mode of a ligand (L), or in affecting its reactivity. Electronic effects consistent with the substitution of a cp ligand by cp* in a wide series of metallocenes have been recently discussed.[10b]



(1)

$\overset{*}{X}=\overset{*}{Y} \equiv \overset{*}{C}=\overset{*}{C}$,[2] $-\overset{*}{C}\equiv\overset{*}{C}-$,[2] $=\overset{*}{C}=\overset{*}{O}$,[3] $=\overset{*}{C}=\overset{*}{S}$,[4] $=\overset{*}{C}=\overset{*}{N}R$,[5] $\overset{*}{C}H_2=\overset{*}{O}$,[6] $=\overset{*}{C}=\overset{*}{N}=N$[7]

The aim of the present report is to describe the structure of decamethylvanadocene, $(cp^*)_2V$, ($cp^* = \eta^5$-C_5Me_5) and its chemistry with carbon monoxide and isocyanide ligands. One-electron oxidation of decamethylvanadocene leads to various vanadium(III) complexes, $(cp^*)_2V(X)$ (X = Cl, I, CN, SR), whose structural properties[10c] and reactivity were explored toward carbon monoxide and isocyanides. The synthesis and electronic and magnetic properties of decamethylvanadocene have been recently reported.[10b]

Experimental Section

All the reactions described were carried out under an atmosphere of purified nitrogen. Solvents were purified by standard methods. Pentamethylcyclopentadiene was prepared as in the literature.[11] A conventional synthesis, similar to that reported[10b] when this work was in progress, was used for decamethylvanadocene. IR spectra were measured with a Perkin-Elmer 283 spectrophotometer. Magnetic susceptibilities were measured with a Faraday balance. ^1H NMR spectra were recorded on a EM-360 Varian spectrophotometer (60 MHz). Analytical data and selected IR bands have been reported in Table I.

Synthesis of Lithium Pentamethylcyclopentadienide. To a THF solution (50 mL) of pentamethylcyclopentadiene (30.0 g, 220.6 mmol) was added LiMe (240 mmol) dropwise, under vigorous stirring. A light yellow solid formed. At the end of the addition, the suspension was kept on stirring for 2 h. The solid, after being filtered and washed with Et_2O (200 mL), became white. It was dried in vacuo for 5 h (25.5 g).

Synthesis of Decamethylvanadocene (I). A suspension of VCl_3 (5.25 g, 33.36 mmol) and C_5Me_5Li (14.2 g, 100 mmol) in THF (500 mL) was refluxed for 48 h. The resulting mixture was filtered and the solution evaporated to dryness. The residue was sublimed at 170–190 °C to give $(cp^*)_2V$ (7.50 g, 70%). The red complex (I) can be recrystallized from *n*-hexane. The use of solid LiC_5Me_5 and the filtration of LiCl are essential operations in order to have high yields.

Reaction of Decamethylvanadocene with Carbon Monoxide: Synthesis of $(cp^*)_2V(CO)$ (II). An *n*-hexane (50 mL) solution of complex I (0.88 g, 2.74 mmol) was exposed to carbon monoxide for 2 h [ν(C–O) = 1850 cm^{-1}]. The color of the solution changed from red to maroon. When it was concentrated and cooled at −78 °C, the solution gave red-maroon crystals of $(cp^*)_2V(CO)$ (0.5 g, 52.2%).

Reaction of Complex I with Cyclohexyl Isocyanide. An *n*-hexane (50 mL) solution of I (0.422 g, 1.31 mmol) was reacted with neat distilled $C_6H_{11}NC$ (0.15 g, 1.37 mmol). The solution changed suddenly from red to yellow-maroon [ν(C–N) = 1770 cm^{-1}]. When the solution was cooled at −78 °C, yellow-brown crystalline solid, $(cp^*)_2V(C_6H_{11}NC)$, formed (0.22 g, 39%). The band at 1770 cm^{-1} disappeared, and a new sharp band at 2070 cm^{-1} appeared when the suspension was heated. The addition of a second mole of isocyanide generated again the band at 1770 cm^{-1} and that of the free isocyanide at 2120 cm^{-1}. Further heating caused the disappearance of both bands, while the intensity of the band at 2070 cm^{-1} increased. The solution filtered when hot and concentrated was allowed to stand. Black-maroon crystalline solid, $(cp^*)_2V(CN)(C_6H_{11}NC)$, whose preparation was carried out as reported below, was obtained.

Synthesis of $(cp^*)_2(CN)(C_6H_{11}NC)$ (R = C_6H_{11}) (V). An *n*-hexane (30 mL) solution of I (1.30 g, 4.05 mmol) was reacted with freshly distilled $C_6H_{11}NC$ (1.00 g, 9.17 mmol). The color of the solution changed from red to yellow-maroon, and a crystalline solid formed. It dissolved when the suspension was refluxed for 20 min. The solution gave, on standing, a maroon-black crystalline solid, $(cp^*)_2V(CN)(C_6H_{11}NC)$ (0.49 g, 26.5%). The filtered solution analyzed by GLC showed the presence of a significant amount of cyclohexane (ca. 3.5 mmol).

Reaction of Complex I with *t*-BuNC and Synthesis of $(cp^*)_2V(CN)(t$-BuNC) (R = *t*-Bu) (V). An *n*-hexane (50 mL) solution of I (1.035 g, 3.22 mmol) was reacted with neat *t*-BuNC (0.80 mL, 7.03 mmol). The reaction produced suddenly a crystalline solid [ν(C–

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Table I. Analytical, IR, and Magnetic Data

	anal.,[a] %					
compd	C	H	N	other elements	μ_{eff},[b] μ_B (T, K)	IR data, cm^{-1}
(cp*)$_2$V (I)	74.74 (74.76)	9.41 (9.35)			3.71 (291.5)	
(cp*)$_2$V(CO) (II)	71.94 (72.20)	8.81 (8.81)			1.71 (299)	ν(C–O)(Nujol) = 1845, ν(C–O)(hexane) = 1850
(cp*)$_2$V(C$_6$H$_{11}$NC) (III)	73.94 (75.34)	9.53 (9.34)	3.26 (3.26)		1.78 (299)	ν(C–N)(Nujol) = 1770
(cp*)$_2$V(C$_6$H$_{11}$NC)(CN) (V)	73.73 (73.68)	9.21 (8.99)	5.65 (6.14)		d[c]	ν(C–N)(Nujol) = 2050, 2070
(cp*)$_2$V(t-BuNC)(CN) (V)	72.23 (72.55)	9.16 (9.07)	5.75 (6.51)		d	ν(C–N)(Nujol) = 2020, 2060
(cp*)$_2$V(CO)(CN) (VII)	69.49 (70.40)	8.16 (8.00)	3.62 (3.73)		d	ν(C–O)(Nujol) = 1910, ν(C–N)(Nujol) = 2070, ν(C–O)(hexane) = 1910, ν(C–N)(hexane) = 2080
(cp*)$_2$V(CN) (VIII)	71.99 (72.62)	8.68 (8.64)	4.00 (4.03)		2.71 (299)	ν(C–N)(Nujol) = 2080, ν(C–N)(THF) = 2080
(cp*)$_2$V(Cl) (IX)	66.99 (67.32)	8.31 (8.42)		Cl 10.32 (9.96)	2.75 (299)	
(cp*)$_2$V(I) (X)	53.29 (53.37)	6.65 (6.70)		I 29.28 (28.35)	2.79 (299)	
(cp*)$_2$V(I)$_2$	41.88 (41.73)	5.22 (5.22)		I 44.82 (44.12)	1.85 (299)	
(cp*)$_2$V(SC$_6$H$_4$Me-p) (XI)	71.22 (72.97)	8.33 (8.33)		S 7.22 (7.21)	2.51 (299)	
(cp*)$_2$V(CO)(I) (XII)	52.43 (52.94)	6.22 (6.30)		I 27.71 (26.68)	d	ν(C–O)(Nujol) = 1890, ν(C–O)(THF) dec
(cp*)$_2$V(CO)(SC$_6$H$_4$Me-p) (XIII)	71.21 (71.18)	8.14 (7.83)		S 6.81 (6.78)	d	ν(C–O)(Nujol) = 1890, ν(C–O)(THF) = 1895
[(cp*)$_2$V(t-BuNC)$_2$]Cl (XIV)	68.79 (68.90)	9.24 (9.19)	5.37 (5.36)	Cl 7.48 (6.79)	d	ν(C–N)(Nujol) = 2030, 2070, 2100
[(cp*)$_2$V(t-BuNC)$_2$]I (XIV)	58.37 (58.43)	7.96 (7.95)	4.42 (4.56)	I 20.93 (20.68)	d	ν(C–N)(Nujol) = 2030, 2070, 2100
[(cp*)$_2$V(t-BuNC)$_2$](SC$_6$H$_4$Me-p) (XIV)	71.73 (72.54)	9.14 (9.02)	4.25 (4.59)	S 5.19 (5.25)	d	ν(C–N)(Nujol) = 2020, 2090
[(cp*)$_2$V(CO)$_2$](BPh$_4$) (XV)	79.71 (79.30)	7.28 (7.18)			d	ν(C–O)(CHCl$_3$) = 1955, 2000, ν(C–O)(Nujol) = 1952, 1995
[(cp*)$_2$V(CO)$_2$]I (XVI)	52.24 (52.38)	5.99 (5.95)		I 26.27 (25.20)	d	ν(C–O)(Nujol) = 1935, 1995, ν(C–O)(THF) = 1950, 2000

[a] Calculated values are given in parentheses. [b] Results expressed *per* metal atom. [c] d ≡ diamagnetic.

N)(hexane) = 2020, 2060 cm^{-1}]. The mixture heated up to the boiling point gave a solution that was filtered when hot. The solution gave, on standing, black crystals of (cp*)$_2$V(CN)(t-BuNC) (0.85 g, 61.4%). When a t-BuNC:I molar ratio higher than 2 was used, unreacted isocyanide was identified in solution.

Synthesis of (cp*)$_2$V(CN) (VIII). An n-hexane solution (40 mL) of complex I (0.729 g, 2.27 mmol) was exposed to a carbon monoxide atmosphere [ν(C–O) = 1850 cm^{-1}] and then reacted with t-BuNC (0.27 mL, 2.37 mmol). The color of the solution changed from red to yellow, and a light yellow solid separated. The IR spectrum of the solution showed four bands at 1850, 1910, 1950, and 2070 cm^{-1}. After the suspension was boiled, a green solution (three bands at 1850, 1910, and 2070 cm^{-1}) was obtained with a small amount of green crystalline solid, (cp*)$_2$V(CO)(CN) (VII), which was filtered out (0.10 g). ^{1}H NMR (CDCl$_3$): singlet at τ 8.22. The resulting solution [ν(C–N) = 2080 cm^{-1}] gave, on standing, crystals (0.35 g) of (cp*)$_2$V(CN).

Synthesis of (cp*)$_2$V(Cl) (IX). An n-hexane solution (100 mL) of I (6.93 g, 21.56 mmol) was refluxed with a large excess of PhCH$_2$Cl (3.5 mL) for 2 h. The final deep blue solution gave, on standing, deep blue crystals of (cp*)$_2$V(Cl) (4.90 g). The solid is very sensitive to air.

Synthesis of (cp*)$_2$V(I) (X) and (cp*)$_2$V(I)$_2$. An n-hexane solution (100 mL) of complex I (2.953 g, 9.20 mmol) was treated with I$_2$ (1.16 g, 4.57 mmol) and heated to the boiling point. The solution changed from red to deep green. The solution was filtered when hot and allowed to stand. Deep green crystals of (cp*)$_2$V(I) (2.50 g, 60.6%) were obtained. The solid is very sensitive to air. If the reaction is carried out with an I$_2$:complex I molar ratio of 1:1, a maroon-orange solid, (cp*)$_2$V(I)$_2$, formed in almost quantitative yield.

Synthesis of (cp*)$_2$V(SC$_6$H$_4$Me-p) (XI). An n-hexane (50 mL) solution of complex I (2.47 g, 7.69 mmol) was reacted at room temperature with p-tolyl disulfide (1.10 g, 4.47 mmol). The final deep yellow solution gave, on standing for 2 days, a deep yellow crystalline solid, (cp*)$_2$V(SC$_6$H$_4$Me-p) (2.36 g, 72.3%).

Reaction of (cp*)$_2$V(X) (X = Cl, I, CN, SC$_6$H$_4$Me-p) with Carbon Monoxide (Complexes VII, XII, and XIII). n-Hexane solutions of (cp*)$_2$V(X) were reacted with carbon monoxide at room temperature and atmospheric pressure. The chloride derivative did not absorb carbon monoxide, while solutions of (cp*)$_2$V(X) (X = I, CN, SC$_6$H$_4$Me-p) gave, on standing, crystals of the corresponding monocarbonyl (cp*)$_2$V(X)(CO) (X = CN, complex VII; X = I, complex XII; X = SC$_6$H$_4$Me-p, complex XIII). When a stirred suspension of XII was pumped in vacuo with gentle heating, the starting (cp*)$_2$V(I) was recovered in good yields. ^{1}H NMR (CDCl$_3$): for XII, singlet at τ 8.12; for XIII, three singlets at τ 8.35, 7.80, and 3.20.

Reaction of (cp*)$_2$V(X) (X = Cl, I, SC$_6$H$_4$Me-p) with t-BuNC (Complexes XIV). A THF solution of (cp*)$_2$V(X) reacted with t-BuNC in a 1:2 molar ratio, forming crystalline solids of [(cp*)$_2$V(t-BuNC)$_2$]X.

Synthesis of [(cp*)$_2$V(CO)$_2$]X (X = BPh$_4$, I) (Complexes XV and XVI). A THF (25 mL) solution of (cp*)$_2$V(Cl) (1.043 g, 2.93 mmol) containing NaBPh$_4$ (1.10 g, 3.21 mmol) was exposed to carbon monoxide for 12 h. An orange crystalline solid was formed along with a white powder (NaCl). NaCl was separated from the yellow crystals of [(cp*)$_2$V(CO)$_2$](BPh$_4$) (1.32 g). ^{1}H NMR (CDCl$_3$): τ 8.41 (30 H, s, cp*), 2.83 (20 H, m, Ph).

When THF solutions of (cp*)$_2$V(I) are exposed for 3 days to carbon monoxide, they form yellow needles of [(cp*)$_2$V(CO)$_2$]I. ^{1}H NMR (CDCl$_3$): τ 8.12 (s, cp*).

X-ray Crystallography. The crystals of complexes I, II, V, and VIII selected for X-ray analysis were sealed in glass capillaries under nitrogen and mounted in a random orientation on a Philips PW 1100 automated four-circle diffractometer. Details specific to the data collection and processing are reported in Table II. Data were collected at room temperature (22 °C) by using an equatorial diffraction

Table II. Summary of Crystal Data Collection

	complex I	complex II	complex V	complex VIII
diffractometer	Philips PW 1100			
radiation	graphite-monochromated Mo Kα (λ = 0.710 69 Å)			
cryst syst	orthorhombic	monoclinic	monoclinic	monoclinic
space group	*Cmcm* (D_{2h}^{17}, No. 63)	$P2_1/n$ (C_{2h}^5)[a]	$P2_1/c$ (C_{2h}^5, No. 14)	$P2_1/n$ (C_{2h}^5)[a]
a, Å	15.049 (6)	15.699 (7)	10.342 (5)	15.895 (4)
b, Å	8.660 (4)	13.353 (6)	13.146 (7)	13.441 (3)
c, Å	29.663 (10)	9.452 (5)	18.956 (10)	9.209 (2)
β, deg	90	99.26 (5)	92.60 (6)	97.92 (2)
V, Å^3	3866 (3)	1956 (2)	2574 (2)	1948.7 (8)
mol formula	$C_{20}H_{30}V$	$C_{21}H_{30}OV$	$C_{28}H_{41}N_2V$	$C_{21}H_{30}NV$
mol wt	321.4	349.4	456.6	347.4
Z	8	4	4	4
F(000)	1384	748	984	744
D_{calcd}, g/cm^3	1.10	1.19	1.18	1.18
reflcns measd	*hkl*	$-h_{max} < h < h_{max}$ with *k* and $l > 0$		
scan type	*ω*	*ω*/2*θ*	*ω*/2*θ*	*ω*
θ range, deg	3.0–25.0	2.5–26.0	2.5–25.0	2.5–26.5
scan speed, deg/s	0.075	0.075	0.075	0.075
scan width, deg	1.00	1.30	1.40	1.50
bkgd time	5 s at beginning and end of the scan			
stds	1 every 1 h (no significant changes)			
no. of unique total reflcns	1808	3842	4518	4047
no. of obsd reflcns [$I > 3\sigma(I)$]	464	1563	1163	1508
cryst size, mm	~0.48 × 0.26 × 0.76	~0.37 × 0.16 × 0.67	~0.57 × 0.10 × 0.57	~0.21 × 0.45 × 0.68
abs coeff, cm^{-1}	4.9	4.9	3.9	4.9
abs cor	not applied			
max-min transmissn factors	1.38–1.12	1.32–1.08	1.26–1.03	1.32–1.09

[a] Coordinates of equivalent positions for the nonstandard $P2_1/n$ setting: $x, y, z; \bar{x}, \bar{y}, \bar{z}; \frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z; \frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$.

Table III. Fractional Atomic Coordinates (×10^4) for Complex I

atom	*x*/*a*	*y*/*b*	*z*/*c*	atom	*x*/*a*	*y*/*b*	*z*/*c*
V1	0 (0)	6630 (11)	2500 (0)	C8A	510 (31)	−1769 (67)	506 (14)
V2	0 (0)	0 (0)	0 (0)	C16A	0 (0)	2309 (173)	931 (45)
C1	1268 (31)	5209 (67)	2500 (0)	C17A	1806 (30)	−471 (57)	651 (15)
C2	1270 (17)	6370 (33)	2129 (9)	C18A	959 (33)	−3349 (68)	379 (15)
C3	1215 (19)	7831 (36)	2267 (8)	C6B	0 (0)	−1826 (130)	479 (30)
C11	1299 (51)	3638 (98)	2500 (0)	C7B	894 (32)	−703 (64)	568 (15)
C12	1293 (25)	5924 (45)	1609 (12)	C8B	526 (50)	876 (87)	756 (22)
C13	1253 (27)	9309 (48)	1932 (14)	C16B	0 (0)	−3611 (235)	440 (57)
C6A[a]	0 (0)	455 (106)	729 (26)	C17B	1538 (75)	−2293 (141)	471 (33)
C7A	628 (40)	−286 (63)	685 (16)	C18B	1234 (43)	1746 (83)	821 (20)

[a] Site occupation factors for disordered carbons: 0.25 for C6A, C6B, C16A, and C16B (lying on the mirror plane); 0.50 for C7A, C7B, C8A, C8B, C17A, C17B, C18A, and C18B.

geometry. The reduced cells quoted were obtained by using TRACER[12] and the lattice constants by a least-squares refinement of 21 reflections having 2*θ* for all the complexes. All data were corrected for Lorentz and polarization effects but not for absorption in view of the small absorption coefficients and the irregular shapes of the samples. Only the observed reflections were used in the structure analyses.[13]

The structures were solved by the heavy-atom method (Patterson and Fourier) and refined by full-matrix least squares minimizing the function $\sum w|\Delta F|^2$. The reflections were weighted according to the scheme $w = k/[\sigma^2(F_o) + gF_o^2]$, where *k* is redetermined after each structure factor calculation and refined by fitting $(|F_o| - |F_c|)^2$ to $[\sigma^2(F_o) + |g|(F_o^2)]/k$. The value for *g* was that giving the smallest variation of the mean values of $w(|F_o| - |F_c|)^2$ as a function of the magnitude of F_o. Neutral-atom scattering factors for V,[14] O, N, C,[15] and H[16] were used and the real ($\Delta f'$) and imaginary ($\Delta f''$)[14] corrections for anomalous dispersion were included in all structure factor calculations. For each structure, refinement was continued until shifts in all parameters were less than 0.4 times the estimated standard deviation in the respective parameter. Further details of refinement of the individual structures are given below. No corrections for secondary extinction were deemed necessary.

Structure Solution and Refinement for Complex I. The systematic absences were consistent with the space groups $Cmc2_1$ (C_{2v}^{12}, No. 36) or *Cmcm* (D_{2h}^{17}, No. 63). *E* statistics calculated as a function of sin *θ* favor the centric case, $\langle|E^2 - 1|\rangle$ being equal to 0.90. The examination of the vector distribution of a Patterson map did not afford a distinction between the two possible space groups but gave clearly evidence for the existence of two independent vanadium atoms in the asymmetric unit. They were assumed to lie on the *yz* mirror plane of the noncentrosymmetric $Cmc2_1$ space group or in the special positions *m*/*m* (V1) and 2/*m* (V2) in the centrosymmetric one, *Cmcm*, according to the number of molecules per unit cell (*Z* = 8). The Fourier map, computed in the space group *Cmcm*, showed a disordered distribution of the cyclopentadienyl rings bonded to V2 around the *yz* mirror plane. Disorder was interpreted in terms of particle occupancy considering the six independent carbon atoms of the cp* ring (C6, C7, C8, C16, C17, C18) statistically distributed over two positions (A and B) having the same site occupancy factor. No disorder was shown by the rings bonded to V1. The disordered model was refined first isotropically down to *R* = 0.13 and then anisotropically only for V1 and V2 down to *R* = 0.12. Unit weights were used.

Disorder prevented obtainment of a better fit and accounts for the low accurancy of this analysis. As can be seen from Table IV, the

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(12) Lawton, S. L.; Jacobson, R. A. "TRACER, a cell Reduction Program"; Ames Laboratory, Iowa State University of Science and Technology: Ames, IA, 1965.

(13) Data reduction and structure solution and refinement were carried out on a Cyber 7600 computer of the Centro di Calcolo dell'Italia Nord-Orientale, using the SHELX-76 system of crystallographic computer programs: Sheldrick, G. M. "SHELX-76, Program, for Crystal Structure, Determination"; University of Cambridge: Cambridge, England, 1976. Calculations were performed with the financial support of the University of Parma.

(14) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, pp 99, 149.

(15) Cromer, D. T.; Mann, J. B. *Acta Crystallogr.* **1968**, *A24*, 321–4.

(16) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175–87.

Table IV. Anisotropic[a] and Isotropic Thermal Parameters (X10^4) for Complex I

atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
V1	450 (63)	524 (72)	590 (64)	0 (0)	0 (0)	0 (0)
V2	687 (70)	544 (68)	446 (56)	162 (62)	0 (0)	0 (0)

atom	U, Å^3	atom	U, Å^2	atom	U, Å^2	atom	U, Å^2
C1	1079 (164)	C13	1650 (164)	C17A	548 (149)	C8B	805 (206)
C2	696 (85)	C6A	475 (237)	C18A	595 (140)	C16B	2575 (746)
C3	932 (108)	C7A	279 (137)	C6B	718 (291)	C17B	2028 (135)
C11	2177 (321)	C8A	300 (103)	C7B	263 (146)	C18B	1053 (218)
C12	1349 (142)	C16A	1880 (584)				

[a] The anisotropic temperature factor is in the form $\exp[-2\pi^2 \Sigma_i \Sigma_j U_{ij} a^*_i a^*_j h_i h_j]$ where $i, j = 1-3$. a^*_i is the ith reciprocal cell dimension. The isotropic thermal parameter is defined as $\exp(-8\pi^2 (\sin^2 \theta)/\lambda^2)$.

Table V. Fractional Atomic Coordinates (X10^4) for Complex II

atom	x/a	y/b	z/c	atom	x/a	y/b	z/c
V	3944 (1)	2558 (1)	1334 (1)	H122	4215 (51)	5197 (65)	752 (89)
C21	5067 (5)	3081 (6)	1763 (10)	H123	4906 (54)	5101 (66)	2593 (86)
O	5763 (4)	3417 (5)	2067 (10)	H131	4122 (52)	3877 (66)	5577 (86)
C1	3074 (5)	3925 (6)	862 (8)	H132	4774 (53)	4218 (61)	4574 (89)
C2	3778 (5)	4189 (5)	1931 (9)	H133	4503 (52)	3076 (65)	5141 (87)
C3	3754 (5)	3568 (6)	3155 (7)	H141	2346 (48)	2662 (72)	4523 (83)
C4	3029 (5)	2951 (6)	2859 (8)	H142	3148 (55)	1907 (64)	4713 (92)
C5	2591 (5)	3172 (6)	1448 (8)	H143	2420 (55)	1810 (65)	3467 (92)
C6	3426 (7)	1043 (6)	514 (14)	H151	1239 (54)	3151 (66)	1072 (90)
C7	4136 (9)	871 (7)	1530 (11)	H152	1606 (47)	2593 (68)	−297 (81)
C8	4845 (6)	1273 (7)	1023 (12)	H153	1585 (53)	2272 (64)	1383 (89)
C9	4542 (6)	1732 (6)	−326 (10)	H161	2502 (53)	−35 (69)	191 (91)
C10	3658 (6)	1575 (6)	−612 (9)	H162	2316 (52)	486 (63)	1520 (92)
C11	2804 (6)	4428 (7)	−542 (10)	H163	2204 (52)	977 (66)	−95 (88)
C12	4348 (6)	5098 (6)	1844 (10)	H171	4423 (54)	−386 (65)	3038 (86)
C13	4340 (6)	3692 (7)	4600 (9)	H172	3598 (53)	199 (66)	2960 (82)
C14	2725 (6)	2255 (8)	3938 (10)	H173	4347 (54)	790 (63)	3727 (87)
C15	1717 (5)	2818 (7)	756 (10)	H181	6065 (52)	813 (62)	945 (88)
C16	2536 (8)	540 (9)	481 (20)	H182	6220 (52)	1688 (67)	2149 (87)
C17	4189 (14)	293 (10)	2933 (15)	H183	5732 (52)	540 (64)	2398 (87)
C18	5784 (8)	1103 (10)	1615 (17)	H191	5630 (46)	2596 (71)	−765 (79)
C19	5091 (8)	2171 (8)	−1364 (14)	H192	5508 (51)	1624 (65)	−1567 (88)
C20	3082 (8)	1833 (10)	−2038 (12)	H193	4475 (47)	2547 (71)	−2038 (79)
H111	3235 (56)	4563 (66)	−1020 (86)	H201	2948 (47)	2452 (73)	−2143 (79)
H112	2577 (54)	3947 (65)	−1322 (86)	H202	2586 (55)	1411 (64)	−2043 (89)
H113	2435 (56)	4999 (67)	−565 (88)	H203	3441 (52)	1652 (64)	−2860 (89)
H121	4095 (53)	5639 (64)	2234 (89)				

thermal parameters of the methyl carbon atoms reached values so high that the refinement of any anisotropic model did not converge. Attempts to refine the structure in the noncentrosymmetric space group $Cmc2_1$, where disordered is not however released, obviously were unsuccessful.

In the last difference map there were no peaks greater than 0.5 e Å^{-3} and no holes less than −0.6 e Å^{-3}. Final atomic and thermal parameters are listed in Tables III and IV, respectively.

Structure Refinement for Complex II. The refinement was carried out first isotropically down to $R = 0.11$ and then anisotropically for all non-hydrogen atoms to $R = 0.075$. All the hydrogen atoms were located in a ΔF map, and their inclusion in the last cycles of refinement with free isotropic thermal parameters lowered the R value to 0.055. Unit weights were used. The NO:NV overdetermination ratio was 1563:329 = 4.8 (NO is the number of observations; NV is the number of variables). The final difference map showed no unusual feature with no peak above the general background.

Final atomic coordinates are listed in Table V, and thermal parameters are given in Table SII.[17]

Structure Refinement for Complex V. The refinement of the positional and isotropic thermal parameters of the non-hydrogen atoms stopped at $R = 0.12$. The subsequent anisotropic refinement gave $R = 0.080$. At this stage, all the hydrogen atoms, but those associated to the cyclohexyl ring (which were put in idealized positions), were found in a difference map and introduced in calculations as fixed contributors ($B_{iso} = 9.5$ Å^2). No attempts were made to refine them owing to the low percentage of observed reflections. The refinement converged with $R = 0.067$, $R_w = 0.071$, and GOF = 1.6 (GOF means "goodness of fit"). The values of k and g were 1.3723 and 0.003, respectively. The NO:NV ratio was 1163:267 = 4.3. In the final difference map no peak was greater than 0.4 e Å^{-3}.

Final atomic coordinates for non-hydrogen atoms are quoted in Table VI. Hydrogen coordinates and thermal parameters are given in Tables SI and SIII, respectively.[17]

Structure Refinement for Complex VIII. The structure was refined first isotropically ($R = 0.11$) and then anisotropically ($R = 0.074$) for all the non-hydrogen atoms. At this point, a difference Fourier synthesis revealed the positions of all hydrogen atoms, which were subsequently introduced in the refinement with isotropic thermal parametrs. The final R and R_w values were 0.051 and 0.048, respectively, and GOF was 2.1 ($k = 1.2657$, $g = 0.000155$). The NO:NV ratio was 1508:329 = 4.6. In the final difference map there was no peak above the general background.

Final atomic coordinates are listed in Table VII, and thermal parameters are given in Table SIV.[17]

Results and Discussion

(a) Synthesis and Reactivity of Decamethylvanadocene. The synthesis of decamethylvanadocene was pursued by the conventional route employing VCl_3 and an excess of $LiMe_5C_5$ in refluxing THF (eq 2). The final suspension was filtered out, and the resulting solution evaporated to dryness left a residue, whose sublimation gave I as red crystals, which can be recrystallized by cooling an n-hexane solution. The magnetic moment of 3.71 μ_B at 291.5 K is that expected for three unpaired electrons.[10b] There is no reason, a priori, for a structure of I different from that of vanadocene, which is a ferrocene-like compound.[18a] The structure was determined by an X-ray

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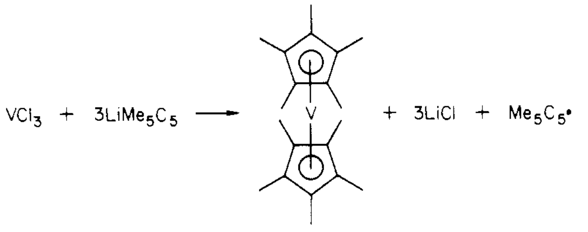
[17] See paragraph at end of paper regarding supplementary material.



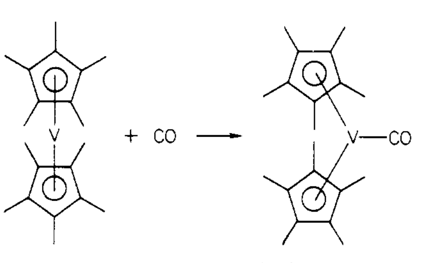
(2)

$(cp^*)_2V$ (I)

analysis. This confirmed the ferrocene-like and decamethylferrocene-like structure for complex I.[18b] In the asymmetric unit there are two crystallographically independent molecules. Although the low accuracy of the data, due to the presence of disorder, limits the use of the V–C and C–C bond lengths (Table SV[17]) as a guide to discussion, it does not preclude obtaining useful information on the conformations of the complex molecules. Molecule 1 (Figure 1) shows a crystallographic *Cmm* symmetry, so the conformation of the two cp rings is eclipsed for symmetry requirements, in contrast with that observed in vanadocene itself[18a] where the complex molecule has a crystallographically imposed symmetry center. The two rings are parallel, the dihedral angles they form being 177 (2)°. Molecule 2 (Figure 2) was found to be statistically disordered over two positions (A and B) not related by any symmetry operation. The set of atoms corresponding to this molecule is distributed in such a way that it can be described as two staggered molecules (A–V–A^i, B–V–B^i; $i = \bar{x}, \bar{y}, \bar{z}$) rotated with respect to each other by 36° or as two eclipsed molecules (A–V–B^i, B–V–A^i) rotated one with respect to the other by the same angle. The resulting situation justifies the crystallographic $2/m$ symmetry. In all cases the rings are parallel, the two disordered A and B rings being coplanar within experimental errors. No methyl group deviated significantly from the ring planes (Table SVII[17]). The V–cp bond lengths (V1–cp1 = 1.90 (3), V2–cp2A = 1.95 (4), V2–cp2B = 1.87 (6) Å) and all the other bond distances and angles appear normal within the estimated standard deviations (Table SV[17]).

Complex I, like vanadocene, is able to bind various ligands.[2–9] It reacts, however, with π acids, i.e. CO, or electron-acceptor organic functional groups, while it is completely unreactive with nucleophilic σ-donor ligands, in agreement with its basic character.

An *n*-hexane solution of I reacted with carbon monoxide significantly more slowly than vanadocene does (eq 3),[2a] giving



(3)

$(cp^*)_2V$ (I) $(cp^*)_2V(CO)$ (II)

a maroon solution [ν(C–O) = 1850 cm^{-1}] from which II can be isolated on cooling as maroon crystals [ν(C–O)(Nujol) = 1845 cm^{-1}]. Such a very low C–O stretching frequency for a terminal neutral metal carbonyl is diagnostic for a strong basic metal, and it must be compared with the frequency found for $(cp)_2V(CO)$ occurring at 1893 cm^{-1} (heptane solution).[2a]

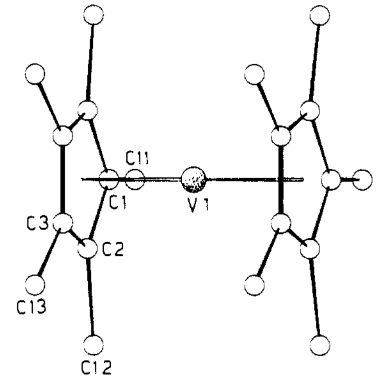


Figure 1. Projection of molecule 1 of complex I showing the crystallographic *mm* symmetry.

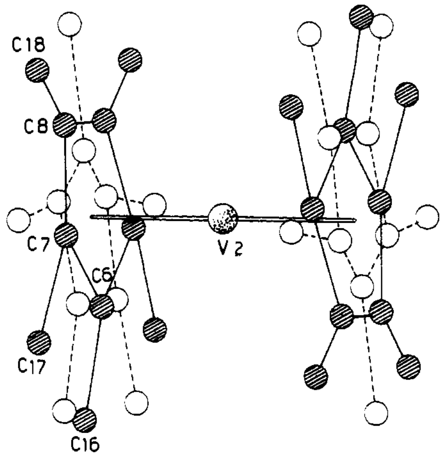


Figure 2. Projection of molecule 2 of complex I. The A and B disordered positions are represented by continuous and dashed lines, respectively. The V–cp bond has been drawn between the vanadium atom and the averaged coordinates of the cpA and cpB centroids.

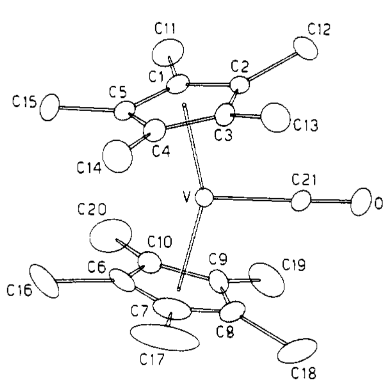


Figure 3. ORTEP diagram of complex II (20% probability ellipsoids).

The presence of methyl groups on the cp ring increases considerably the basicity of the metal. Vanadium has, in complex II, a 17-electron configuration (μ_{eff} = 1.71 μ_B at 299 K). A structural change from a sandwich to a bent arrangement of the cp* rings occurs when complex I adds a ligand. Figure 3 shows an ORTEP view of the molecular structure of complex II, whose main bond distances and angles are reported in Table VIII. The two cp* rings are coordinated in a conventional η^5 mode [cp1–V = 1.923 (8), cp2–V = 1.933 (9) Å].[10] Their mutual orientation is eclipsed. The cp–V distances are essentially unaffected by the presence of methyl groups on the ligand.[2–6] The two cp* rings are bent away to make room in the equatorial plane for the CO ligand. The cp1–V–cp2 angle [153.6 (4)°] is significantly larger than the corresponding one found for any cp_2V derivative, independently of the oxidation state of the metal.[2–6] This depends on the methyl groups

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(18) (a) Antipin, M. Yu.; Lobkovskii, E. B.; Semenenko, K. N.; Soloveichik, G. L.; Struchkov, Yu. T. *Zh. Strukt. Khim.* **1979**, *20*, 942–6. Almenningen, A.; Haaland, A.; Samdal, S. *J. Organomet. Chem.* **1978**, *149*, 219–29. (b) Freyberg, D. P.; Robbins, J. L.; Raymond, K. N.; Smart, J. C. *J. Am. Chem. Soc.* **1979**, *101*, 892–7.

Table VI. Fractional Atomic Coordinates ($\times 10^4$) for Complex V

atom	*x/a*	*y/b*	*z/c*	atom	*x/a*	*y/b*	*z/c*
V	3170 (2)	3427 (2)	6621 (1)	C14	4160 (25)	2072 (17)	5125 (11)
N2	2762 (14)	1039 (13)	6389 (8)	C15	2273 (18)	3850 (21)	4879 (10)
N1	5257 (12)	2722 (11)	7849 (7)	C16	287 (14)	4788 (13)	6132 (9)
C1	3757 (20)	4658 (14)	5829 (10)	C17	69 (14)	2500 (13)	6492 (10)
C2	4839 (17)	4349 (16)	6217 (9)	C18	1811 (16)	2108 (14)	7942 (9)
C3	5085 (15)	3350 (18)	6041 (10)	C19	3061 (17)	4256 (14)	8371 (9)
C4	4146 (19)	3026 (13)	5569 (9)	C20	2203 (17)	5859 (14)	7245 (10)
C5	3332 (14)	3839 (16)	5426 (8)	C31	2920 (14)	1930 (13)	6472 (8)
C6	1183 (13)	4268 (11)	6677 (8)	C22	2673 (18)	−24 (14)	6339 (11)
C7	1030 (12)	3221 (11)	6852 (8)	C23	1581 (22)	−418 (13)	6736 (11)
C8	1766 (14)	3070 (11)	7470 (9)	C24	1197 (26)	−1408 (21)	6577 (18)
C9	2347 (14)	4013 (16)	7676 (9)	C25	932 (24)	−1581 (24)	5780 (19)
C10	2008 (15)	4750 (14)	7186 (10)	C26	1997 (34)	−1192 (24)	5420 (14)
C11	3360 (24)	5735 (19)	5663 (14)	C27	2457 (40)	−292 (20)	5557 (20)
C12	5770 (22)	4991 (18)	6665 (11)	C21	4533 (14)	2987 (11)	7392 (8)
C13	6304 (19)	2720 (20)	6252 (12)				

Table VII. Fractional Atomic Coordinates ($\times 10^4$) for Complex VIII

atom	*x/a*	*y/b*	*z/c*	atom	*x/a*	*y/b*	*z/c*
V	1000 (1)	2582 (1)	8610 (1)	H122	3395 (26)	2286 (31)	8638 (47)
N	−875 (3)	3493 (4)	7782 (8)	H123	3616 (31)	3293 (40)	9405 (59)
C21	−222 (4)	3164 (5)	8081 (8)	H131	2680 (49)	1803 (57)	6403 (87)
C1	1891 (4)	3932 (4)	9184 (7)	H132	2500 (45)	2595 (54)	5410 (79)
C2	2362 (4)	3170 (5)	8593 (7)	H133	1890 (48)	1913 (54)	5576 (80)
C3	1993 (4)	2982 (5)	7123 (7)	H141	590 (36)	3138 (51)	4890 (65)
C4	1293 (4)	3637 (5)	6801 (7)	H142	312 (43)	4219 (53)	5371 (76)
C5	1245 (4)	1234 (4)	8057 (7)	H143	1055 (46)	4139 (59)	4623 (85)
C6	130 (4)	1249 (5)	8952 (9)	H151	896 (33)	5646 (41)	7912 (62)
C7	807 (5)	887 (5)	8327 (8)	H152	648 (42)	5271 (47)	9165 (78)
C8	1529 (4)	1049 (5)	9355 (9)	H153	170 (38)	5066 (48)	7462 (65)
C9	1291 (4)	1545 (4)	10585 (7)	H161	−795 (39)	1037 (51)	7205 (73)
C10	410 (4)	1676 (5)	10313 (8)	H162	−1043 (32)	1696 (42)	8860 (61)
C11	2120 (4)	1410 (5)	10657 (8)	H163	−919 (40)	381 (55)	8492 (78)
C12	3215 (4)	2787 (5)	9326 (7)	H171	935 (49)	670 (63)	6095 (88)
C13	2333 (4)	2315 (5)	6050 (8)	H172	161 (52)	441 (59)	6548 (85)
C14	754 (4)	3750 (6)	5325 (8)	H173	714 (50)	−216 (63)	7047 (85)
C15	679 (4)	5124 (5)	8137 (8)	H181	2292 (41)	−57 (53)	9639 (74)
C16	−812 (5)	1086 (6)	8339 (11)	H182	2559 (47)	591 (58)	8333 (92)
C17	822 (8)	330 (7)	6900 (10)	H183	2837 (50)	825 (65)	9941 (98)
C18	2394 (5)	554 (5)	9302 (11)	H191	1774 (42)	1348 (57)	12804 (81)
C19	1832 (4)	1786 (6)	12018 (8)	H192	2414 (46)	1559 (55)	11816 (83)
C20	−129 (5)	2104 (7)	11376 (9)	H193	1744 (48)	2452 (64)	12457 (87)
H111	1627 (33)	1568 (41)	11007 (57)	H201	6 (14)	1757 (65)	12201 (89)
H122	2209 (44)	3862 (53)	11524 (77)	H202	−606 (46)	2441 (52)	10738 (80)
H113	2478 (46)	4954 (56)	10651 (76)	H203	50 (50)	2582 (64)	11959 (91)
H121	3200 (25)	2592 (32)	10406 (44)				

Table VIII. Selected Bond Distances (Å) and Angles (deg) for Complex II (X = O), for Complex V (X = N1), and for Complex VIII (X = N)[a]

	complex II	complex V	complex VIII	complex V	
V-cp1	1.923 (8)	2.00 (2)	1.964 (7)	V-C31	2.00 (2)
V-cp2	1.933 (9)	2.00 (2)	1.977 (7)	C31-N2	1.19 (2)
V-C21	1.879 (8)	2.07 (2)	2.088 (7)	N2-C22	1.40 (2)
C21-X	1.17 (1)	1.17 (2)	1.127 (8)		
cp1-V-cp2	153.6 (4)	142.1 (7)	151.5 (3)	C31-V-cp2	105.0 (6)
C21-V-cp2	102.9 (4)	103.5 (6)	103.5 (3)	C31-V-cp1	103.5 (7)
C21-V-cp1	103.5 (4)	103.7 (7)	105.0 (3)	C21-V-C31	84.5 (6)
V-C21-X	178.1 (8)	177 (1)	178.7 (6)	V-C31-N2	179 (1)
				C31-N2-C22	175 (2)

[a] cp1 and cp2 refer to the centroids of the rings C1⋯C5 and C6⋯C10, respectively.

residing on the cp rings. This stereochemical feature along with the improved metal basicity will play the major role in distinguishing the chemistry of $(cp^*)_2V$ from that of vanadocene. Bond distances concerning the V–C–O unit [V–C21 = 1.879 (8), C21–O = 1.17 (1) Å] are shorter and longer, respectively, than those found in $[(cp)_2V(CO)_2]^+(BPh_4)^-$, where the metal is an oxidation state of +3.[19] The attention is drawn on structure II, which is rather unique in metallocene chemistry. Two characteristics of complex II have to be considered, the electronic configuration of a free-radical-like complex (vide infra) and the presence on the metal of a very nucleophilic carbon monoxide.

Reaction of I with isocyanides led to results different from that expected for a simple coordination of the isocyanide group. Hexane solutions of I react with alkyl isocyanides, RNC [R = *t*-Bu, C_6H_{11}]; the results are only partially dependent on the nature of the alkyl group, as illustrated by eq 4. Reaction 4, when carried out with cyclohexyl isocyanide, allowed the isolation of complex III as a crystalline solid [ν(C–N)(Nujol)

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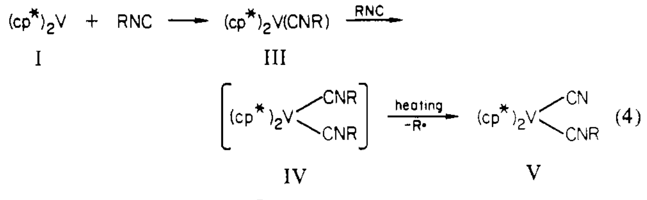
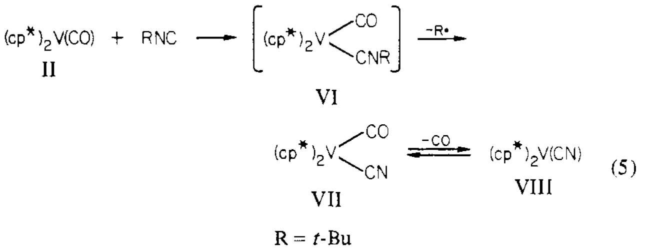
(19) Atwood, J. L.; Rogers, R. D.; Hunter, W. E.; Floriani, C.; Fachinetti, G.; Chiesi-Villa, A. *Inorg. Chem.* **1980**, *19*, 3812–7.



= 1770 cm^{-1}; 1.78 μ_B at 299 K]. On heating, complex III was transformed to complex V [ν(C–N)(Nujol) = 2050, 2070 cm^{-1}]. During the transformation of III into V the IR spectrum of the solution showed the appearance of a broad band centered around 1930 cm^{-1}. This may be due to the plausible intermediate diisocyanide complex IV. The interaction of *t*-BuNC with I followed the same pathway, except for the fact that the isolation of III was unsuccessful, while the intermediate complex IV could be the species having the broad band centered at 1950 cm^{-1}. The complete transformation of I requires two molecules of RNC *per* metal atom. The surprisingly low frequency of the CN group in complex III can be due either to the high basicity of the metal or to a side-on bonding mode of the isocyanide group.[20] Precedence for reaction 4 exists in the literature,[21] even though only cationic complexes are involved. The dealkylation reaction was mainly due to the electrophilic properties of the metal and to the presence of an alkyl substituent leaving the complex as a stable carbonium ion. Dealkylation of coordinated *tert*-butyl isocyanide was recently reported to occur in seven-coordinate molybdenum(II) complexes.[21] The identification of the organic part formed from R was neglected in spite of the fact that it can give some information on the nature of the leaving group. Unlike the reported dealkylations, reaction 4 occurs *via* one-electron transfer from the metal to the isocyanide ligand to form the free radical R•. A free-radical-like reactivity can be expected from complexes having a 17-electron configuration. Therefore, we can admit that the first molecule of isocyanide generates III (17 electron), which is able to promote a free-radical activation of the second molecule of isocyanide causing the homolytic cleavage of the N–R bond. The significant amount of cyclohexane identified in the solution from which V (R = C_6H_{11}) was isolated supports the proposed pathway.



In agreement with the proposed hypothesis, complex II was found able to induce the same kind of free-radical activation on *tert*-butyl isocyanide, as summarized in reaction 5. Isocyanide did not displace carbon monoxide from complex II, rather it generated a 19-electron species (VI) undergoing the N–R bond breaking of the isocyanide as proposed to occur in complex IV. Under the reaction conditions, VII partially lost CO to form VIII. Both complexes have been isolated as crystalline solids and fully characterized (see Experimental Section and Table I). Although complexes V are diamagnetic in the solid state, they show some paramagnetism in solution (^{1}H NMR spectrum) that can be due to the lability of the isocyanide ligand. This is supported by the simultaneous isolation of VII and VIII in reaction 5, due to the major lability of CO.

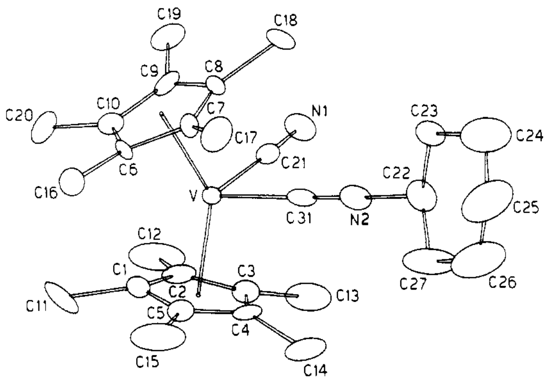


Figure 4. ORTEP diagram of complex V (20% probability ellipsoids).

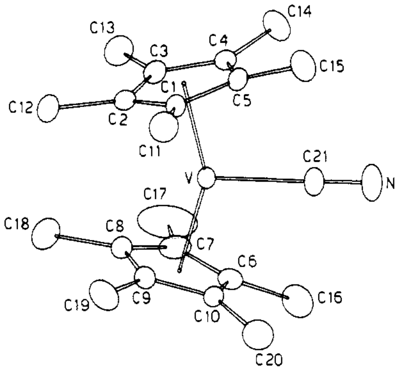


Figure 5. ORTEP diagram of complex VIII (20% probability ellipsoids).

Figures 4 and 5 show ORTEP views of the molecular structure of complexes V and VIII, respectively. The structural parameters concerning the (cp*)$_2$V unit are very close in both complexes (Table VIII), except for the mutual orientation of the two cp* rings, which are eclipsed in VIII and staggered in V, and for the cp1–V–cp2 angle, which increases from 142.1 (7°) (complex V) to 151.5 (3)° (complex VIII). Regardless of the chemical differences, the parameters concerning the three V–C–N units in both complexes are very close. Vanadium–carbon bond distances are V–C21 = 2.088 (7) Å in complex VIII and V–C21 = 2.07 (2) Å and V–C31 = 2.00 (2) Å in complex V. Such values are in agreement with a metal–carbon σ bond having a weak double-bond character.[2b,3–6] They are significantly longer than the V–CO bond distance found in complex II [1.879 (8) Å], in which the back-donation to CO increases the V–C double-bond character. C–N bond distances are very close to the expected values for a triple bond [C21–N = 1.127 (8) Å in complex VIII and C21–N1 = 1.17 (2) Å and C31–N2 = 1.19 (2) Å in complex V]. The longer distances found in complex V are the consequence of the symbiotic effect of the two ligands, CN$^-$ and RNC, bonded to vanadium. Complexes II and VIII are isostructural. Nevertheless, in addition to the difference observed for the V–CO and V–CN distances, there is a significant lengthening of the V–cp bond length and a significant narrowing of the cp1–V–cp2 angle in VIII with respect to II (Table VIII).

The structural analyses of the four complexes indicate a high conformational flexibility of the cp*$_2$V unit, which can assume staggered or eclipsed conformations mainly depending on the nature of the other ligands and on the packing of the molecules. The flexibility finds its explanation in the possibility of methyl group displacement from the plane of the ring atoms[22] (Table

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[20] No isocyanide ligand displaying a side-on bonding mode has been indentified so far: Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 4th ed.; Wiley: New York, 1980; p 1060–1.

[21] References to dealkylation of isocyanide ligands are listed in: Giandomenico, C. M.; Hanau, L. H.; Lippard, S. J. *Organometallics* **1982**, *1*, 142–8. Dewan, J. C.; Giandomenico, C. M.; Lippard, S. J. *Inorg. Chem.* **1981**, *20*, 4069–74.

SVII), releasing in this way the nonbonded methyl–methyl repulsion. The greatest displacements from planarity are observed for the methyl groups that are involved in the shortest intramolecular contacts. Complex II: 0.230 (9) Å for C15, 0.288 (14) Å for C16 [C15···C16 = 3.33 (2) Å], 0.263 (9) Å for C12 and C18 [C12···O = 3.14 (1), C18···O = 3.12 (1) Å] complex V: 0.414 (26) Å for C11, 0.226 (18) Å for C20 [C11···C20 = 3.28 (3) Å]. Complex VIII: 0.274 (7) Å for C12, 0.320 (8) Å for C18 [C12···C18 = 3.27 (1) Å], 0.204 (7) Å for C15, 0.231 (9) Å for C16 [C15···N = 3.28 (1), C16···N = 3.27 (1) Å]. It is worth noticing that the value of 3.27 (1) Å corresponds to the shortest intramolecular contact observed between methyl groups of two cp* rings.

(b) Bis(pentamethylcyclopentadienyl)vanadium(III) Derivatives. The synthesis of bis(pentamethylcyclopentadienyl)vanadium(III) derivatives can be performed by a mild oxidation with various reagents, as reported in reactions 6–8. All

$$(cp^*)_2V + ClCH_2Ph \rightarrow \underset{IX}{(cp^*)_2V(Cl)} + {}^1/_2(PhCH_2)_2 \qquad (6)$$

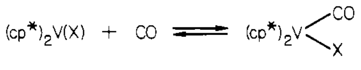
$$(cp^*)_2V + {}^1/_2I_2 \rightarrow \underset{X}{(cp^*)_2V(I)} \qquad (7)$$

$$(cp^*)_2V + {}^1/_2RSSR \rightarrow \underset{XI}{(cp^*)_2V(SR)} \qquad (8)$$

$$R = C_6H_4Me\text{-}p$$

the reactions have been carried out in hexane solution, and complexes IX–XI have been obtained as crystalline solids, whose characterizations are reported in Table I and in the Experimental Section. They are monomeric and paramagnetic, having two unpaired electrons (Table I). Decamethylvanadocene like vanadocene undergoes usually one-electron oxidations[9,23] (reactions 5–7). A preliminary account on these reactions in which the ferrocenium ion was used as an oxidizing agent for decamethylvanadocene to produce $[(cp^*)_2V(CH_3CN)]^+$ was reported.[10b] The presence of electron-releasing groups on the cp rings, however, seems to affect the redox potential of the metal since the reaction with an excess of iodine gave $(cp^*)_2VI_2$, while the corresponding $(cp)_2VI_2$ does not form from vanadocene even with a large excess of iodine.[3,5] Complexes IX–XI are the starting materials for the syntheses of organometallic derivatives of vanadium(III).

The nature of the ligand X in complexes VIII–XI, $(cp^*)_2V(X)$ (X = CN, Cl, I, SR), has a determining influence in the reaction with carbon monoxide. Complexes VIII and X absorb reversibly carbon monoxide, while when the ligand X is chlorine (complex IX), no absorption can be detected at room temperature. Only irreversible absorption was observed when X is $SC_6H_4Me\text{-}p$ (complex XI), to form complex XIII.



$$(cp^*)_2V(X) + CO \rightleftharpoons (cp^*)_2V(CO)(X) \qquad (9)$$

VII, X = CN
XII, X = I
XIII, X = $SC_6H_4Me\text{-}p$

Complexes VIII, X, and XI formed VII, XII, and XIII, respectively, which have been isolated as crystalline solids. They display higher stability than the corresponding vanadocene derivatives. This parallels the increased basicity of vanadium in $(cp^*)_2V(X)$ complexes vs. $(cp)_2V(X)$, as proven by the C–O stretching frequency [$(cp^*)_2V(I)(CO)$, 1890 cm^{-1}; $(cp)_2V(I)(CO)$,[9] 1953 cm^{-1}; $(cp^*)_2V(CO)(SC_6H_4Me\text{-}p)$, 1890 cm^{-1}; $(cp)_2V(CO)(SPh)$,[23] 1943 cm^{-1}]. Complexes IX and XI are the source, via the ionization of the V–X bond, of the decamethyltitanocene-like unit $[(cp^*)_2V]^+$, which can be stabilized either by π-acidic or σ-basic ligands.[2a]

Reaction of complexes IX–XI with *t*-BuNC led to the cationic species $[(cp^*)_2V]^+$, which coordinates two molecules of isocyanide (eq 10). Complexes XIV are diamagnetic, and they have C–N stretching frequencies that are significantly lower than in the corresponding vanadocene derivatives.[2a]

$$\underset{IX-XI}{(cp^*)_2V(X)} + 2t\text{-BuNC} \rightarrow \underset{XIV;\ X\,=\,Cl,\ I,\ SR}{[(cp^*)_2V(t\text{-BuNC})_2]X} \qquad (10)$$

Stabilization of the $[(cp)_2V]^+$ moiety can be achieved by using carbon monoxide as ligand. We found that if the carbonylation of $(cp^*)_2V(Cl)$, which does not absorb CO, is carried out in the presence of $NaBPh_4$

$$\underset{IX}{(cp^*)_2V(Cl)} + 2CO \xrightarrow[NaBPh_4]{-NaCl} \underset{XV}{[(cp^*)_2V(CO)_2]BPh_4} \qquad (11)$$

the dicarbonyl XV is formed from THF as deep orange crystals [ν(C–O)(CHCl$_3$) = 1955 and 2000 cm^{-1} vs. 2010 and 2050 cm^{-1} for $[(cp)_2V(CO)_2][BPh_4]$.[2a,24] The analogous carbonyl complex $[(cp^*)_2V(CO)_2]I$ (XVI) was obtained when the carbonylation of X was carried out in THF rather than in *n*-hexane. The carbonylation of the solvated cation $[(cp^*)_2V(CH_3CN)]^+$ led to the same results.[10b]

C–O stretching frequencies in complexes XV and XVI lower than those observed in unsubstituted vanadocenes parallel the increased basicity of the metal. Their slight difference is due to the presence of a different counteranion (Table I).

Conclusions. This article establishes the fundamental synthetic and structural chemistry of decamethylvanadocene and of the related vanadium(III) derivatives. Their reactivity with carbon monoxide and isocyanides provides novel and significant examples in metallocene chemistry.

Registry No. I, 74507-60-1; II, 83260-22-4; III, 89710-22-5; V (R = C_6H_{11}), 89710-23-6; V (R = *t*-Bu), 89710-24-7; VII, 89710-25-8; VIII, 89710-26-9; IX, 89710-27-0; X, 89710-28-1; XI, 89710-30-5; XII, 89710-31-6; XIII, 89710-32-7; XIV (X = Cl), 89710-33-8; XIV (X = I), 89710-34-9; XIV (X = $SC_6H_4Me\text{-}p$), 89710-36-1; XV, 89710-37-2; XVI, 89710-38-3; $(Cp^*)_2V(I)_2$, 89710-29-2; Cp*H, 41539-64-4; Cp*Li, 51905-34-1; VCl_3, 7718-98-1; $PhCH_2Cl$, 100-44-7; *p*-tolyl disulfide, 103-19-5.

Supplementary Material Available: Listings of atomic coordinates for V (Table SI), thermal parameters for II (Table SII), V (Table SIII), and VIII (Table SIV), bond distances and angles for I (Table SV) and II, V, and VIII (Table SVI), equations of least-squares planes (Table SVII), and observed and calculated structure factors (64 pages). Ordering information is given on any current masthead page.

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[22] This effect is normally observed in decamethylmetallocene at various degrees; see: Sikora, D. J.; Rausch, M. D.; Rogers, R. D.; Atwood, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 1265–7. Sanner, R. D.; Manriquez, J. M.; Marsch, R. E.; Bercaw, J. E. *Ibid.* **1976**, *98*, 8351–7.

[23] Fachinetti, G.; Floriani, C. *J. Chem. Soc., Dalton Trans.* **1974**, 2433–6.

[24] Calderazzo, F.; Bacciarelli, S. *Inorg. Chem.* **1963**, *2*, 721–3.