method of Hemmerich.[40] Thiols were distilled under a N_2 stream before use.

Kinetic Measurements. The kinetic measurements for the oxidation of NADH model compounds by flavins were carried out aerobically under the recycle conditions by following the decrease in the absorption maximum of NADH model compounds: λ_{max} 357 nm for BNAH and 345 nm for BCQH. The decrease obeyed the first-order rate equation for up to 3 half-lives. The kinetic measurements for the oxidation of thiols and the adduct formation with SO_3^{2-} were carried out anaerobically by following the decrease in the absorption maximum of flavins: 502 nm for OHFl, 428 nm for CNFl, and 453 nm for MeLFl. The anaerobic reaction mixtures were prepared by using a Thunberg cuvette. The reactions also obeyed the first-order rate equation. All kinetic measurements were conducted at 30 °C.

Product Analysis. An attempt to obtain **2** on a preparative scale was the following: Na_2SO_3 (172.5 g, 1.30 mol) was dissolved in 1050 mL of deaerated water, and after a N_2 substitution OHFl (60.0 mg, 1.02 mmol) was added to the solution; the anaerobic reaction was continued at 30 °C for 30 h in the dark. The reaction mixture (red) turned immediately yellow and then faded slowly to a slightly yellow color. After 30 h we confirmed that the absorption spectrum of the reaction mixture resembles very closely spectrum 3 in Figure 1. In order to remove excess Na_2SO_3, concentrated HCl (650 mL) was added and N_2 was passed vigorously into the solution. By this means Na_2SO_3 was converted to SO_2 which was swept from the reaction mixture.[22,41] The completion of the SO_2 removal was confirmed with the wet pH-test paper. From this point on, no care was taken to exclude air from the system. The solution was concentrated in vacuo to about 50 mL and mixed with methanol (150

mL) to precipitate NaCl. The precipitated NaCl was filtered and washed with methanol. The combined solution was concentrated in vacuo to precipitate NaCl again. This operation was repeated three times. Finally, the filtrate was evaporated to dryness in vacuo: red crystals, yield 5.47 g. The product was purified by means of paper chromatography (PC) (developing solvent, ethanol:water = 1:1 v/v, R_f 0.87): yield 44.0 mg. Under the identical PC conditions OHFl gave R_f 0.73. ^{1}H NMR (Me_2SO-d_6) δ 4.16 (s, N-CH_3), 7.66 (s, 6'-H), 8.60 (s, 4'-H), 8.99 (s, 9-H). The ^{1}H NMR spectrum indicates that there are three aromatic protons and each proton gives a singlet peak. The titration after treatment with ion-exchange resin gave the reasonable neutralization value to assume disulfonated OHFl. These data support the final product isolated from the reaction mixture of OHFl and SO_3^{2-} to be **2**.

The OHFl solutions after the reactions with BNAH, 1,4-butanedithiol, and 2-mercaptoethanol were analyzed under aerobic conditions by using a high-speed TLC scanner (Shimadzu CS-920). The result indicated that OHFl is the sole colored material present in the product mixtures.

Miscellaneous. The polarographic half-wave potentials ($E_{1/2}$) were determined at 30 °C in a thermostated cell with Yanagimoto P8 polarographic equipment: [flavin] = (2–5) × 10^{-4} M, pH 6.90 with 0.010 M phosphate, μ = 0.10 with $NaNO_3$.

Registry No. 2, 98170-66-2; 1,5-H_2-**2**, 98193-88-5; OHFl, 91077-96-2; BNAH, 952-92-1; BCQH, 17260-79-6; CNFl, 51595-98-3; MeLFl, 18636-32-3; K_2SO_3, 10117-38-1; HS(CH_2)$_4$SH, 1191-08-8; HO(CH_2)$_2$SH, 60-24-2; Na_2SO_3, 7757-83-7; 3-methyltetra-O-acetylriboflavin, 21066-33-1; 10-phenylisoalloxazine, 6851-14-5.

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Synthesis, Structure, and Electronic Properties of (η-C5Me5)2V(μ-OC)V(CO)5. A Complex with a Linear V–O–C–V Bond

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Abstract: The reaction between V(CO)6 and (η-C5Me5)2V yields the μ-isocarbonyl complex, I (η-C5Me5)2V(μ-OC)V(CO)5. Crystals of I belong to the space group C2/c with Z = 4, a = 14.140 (5) Å, b = 14.303 (3) Å, c = 13.212 (3) Å, β = 94.72 (2)°, and V = 2663.0 Å^3. For the 1802 reflections that had F_o > 2.50F_o solution by direct methods led to a final R of 0.0461 and R_w of 0.0568. An important aspect of the structure is the linear V–O–C–V moiety with V–O = 2.075 (4) Å, C–O = 1.167 (6) Å, and V–C = 1.899 (5) Å. Complex I is paramagnetic, contains two unpaired electrons, and obeys the Curie law between 5 and 298 K. SCC-Xα-DV calculations of (η-C5H5)2V(μ-OC)V(CO)5 show that nearly degenerate frontier orbitals localized on the (η-C5Me5)2V$^+$ fragment lead to a high-spin $^3B_1$ ground state. The V–O bond arises mainly from an electrostatic interaction between (η-C5Me5)2V$^+$ and V(CO)6$^-$; however, a small covalent π back-donation from a d(t_{2g}) orbital on V(CO)6$^-$ into a partly occupied b_1 π orbital on the (η-C5H5)V$^+$ fragment is observed. Photolysis of I as well as its thermal reaction with carbon monoxide in solution yields [(η-C5Me5)2V(CO)2][V(CO)6].

Few compounds have been synthesized[2-8] for which carbon monoxide, bound at both carbon and oxygen, bridges two metal centers (hereafter denoted μ-isocarbonyl). Weakening of the carbon–oxygen bond and strengthening of the metal–carbon bond, as evidenced by IR stretching frequencies and bond lengths, raise the question of μ-isocarbonyl reactivity. In this context it is desirable to better understand the bridging bond.

Complexes that have been structurally characterized exhibit bending about the M–O–C bond, with the angle varying from 135.35 (46)° in Cp2Ti(THF)(μ-OC)MoCp(CO)2[3] to 167.7 (9)°

in (OC)5V(μ-CO)V(THF)4(μ-OC)V(CO)5.[7] While packing forces may account for the slight bending in the latter compound, the other known examples must bend either to relieve steric inter-

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actions or to allow binding between CO π^* and metal d orbitals in a σ sense.[6]

Over 20 years ago, Calderazzo and Bacciarelli reported[9] that the reaction between vanadocene and vanadium hexacarbonyl gave a mixture of products and that the same reaction in the presence of CO yielded the diamagnetic compound $[Cp_2V(CO)_2][V(CO)_6]$. Recent work in our laboratory[10] revealed that tendency of deca-methylvanadocene to act as a one-electron reductant; vanadium hexacarbonyl is known[11] to be a one-electron oxidant. Here we report that the reaction between decamethylvanadocene (Cp^*_2V) and vanadium hexacarbonyl yields a molecule that exhibits the first crystallographically linear μ-isocarbonyl bond. Molecular orbital calculations, the first for a μ-isocarbonyl complex, suggest that the bridge bond arises primarily from electrostatic attraction between the charged fragments; however, there is π donation from a $d(t_{2g})$ orbital of $V(CO)_6^-$ into a partly occupied π orbital on $Cp^*_2V^+$.

Experimental Section

Synthetic manipulations were carried out under an atmosphere of nitrogen by standard Schlenk techniques. Solids were transferred in a nitrogen-filled Vacuum Atmospheres glovebox equipped with a Dri-train. Glassware was dried in a 180 °C oven before use. Hydrocarbon and ether solvents were dried over sodium benzophenone ketyl and distilled under nitrogen. Methylene chloride was refluxed over CaH_2 for 24 h and distilled under nitrogen. Solvent transfers and filtrations used 18-gauge stainless steel cannulae.

Bulk magnetic susceptibilities were determined in CH_2Cl_2 solution by the Evans NMR method[12] on a Varian EM-390 spectrometer. Varia-ble-temperature magnetic data were obtained with a SHE SQUID magnetometer in the range 5–300 K. EPR spectra were obtained at 9.5 GHz with a Varian E-3 spectrometer, and IR spectra were obtained with a Perkin-Elmer 1320 spectrophotometer. Analyses were performed by Schwarzkopf Microanalytical Laboratories.

Vanadium hexacarbonyl,[13] 1,2,3,4,5-pentamethylcyclopentadiene,[14] and decamethylvanadocene[15] were prepared by literature methods. The solubility of freshly sublimed $V(CO)_6$ (used in all preparations) is sig-nificantly greater than that of aged samples. Sodium pentamethyl-cyclopentadienide was prepared by treating pentamethylcyclopentadiene with 1 equiv of sodium amide in dry THF. Following filtration, the THF was removed in vacuo and the resulting solid was washed with several portions of dry ether. Pale yellow crystals of the sodium salt were pro-duced in 75% yield.

Preparation of (μ-Carbonyl-O,C)bis(pentamethylcyclopentadienyl)-vanadium(III) Pentacarbonylvanadate(–I), $Cp^*_2V(\mu$-OC)V(CO)$_5$ (I). Freshly sublimed $V(CO)_6$ (0.25 g, 1.14 mmol) was dissolved in 15 mL of pentane. The light yellow solution was filtered via a cannula into a stirred red pentane solution of Cp^*_2V (0.35 g, 1.09 mmol). The solution immediately became opaque red and a solid precipitated. After the mixture was stirred at room temperature for 3 h, the dark green super-natant was removed by filtration to yield an air-sensitive, dark red solid (0.49 g, 0.91 mmol, 84%). Recrystallization from CH_2Cl_2 yielded deep red rectangular prisms: IR (THF) ν_{CO} 2032 (m), 1945 (m), 1890 (s), 1857 (s), 1708 (m br) cm^{-1}. Anal. Calcd for $C_{26}H_{30}V_2O_6$: C, 57.79; H, 5.60. Found: C, 58.20, H, 6.22.

Preparation of Dicarbonylbis(pentamethylcyclopentadienyl)vanadium-(III) Hexacarbonylvanadate(–I), $[Cp^*_2V(CO)_2]V(CO)_6]$ (II). Compound 1 (0.29 g, 0.54 mmol) was dissolved in 25 mL of dry toluene to give an intensely colored red-purple solution. Carbon monoxide was bubbled into the stirred solution for 5 min until the solution cleared and a light yellow compound precipitated. The supernatant was removed via filtration and the precipitate was washed with 10 mL of toluene and was dried in vacuo to yield 0.28 g (0.47 mmol, 87%) of II. This solid was recrystallized by

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Table I. Crystal, Data Collection, and Refinement Parameters of $[(CH_3)_5C_5V][(\mu$-OC)V(CO)$_5]$

formula	$C_{26}H_{30}O_6V_2$
crystal system	monoclinic
space group	$C2/c$
a, Å	14.140 (5)
b, Å	14.303 (3)
c, Å	13.212 (3)
β, deg	94.72 (2)
V, Å^3	2663.0 (13)
Z	4
μ, cm^{-1}	7.71 (Mo Kα, λ = 0.71073)
ρ (calcd), g cm^{-3}	1.35
diffractometer	Nicolet R3
temp, °C	22
data collected	2 octants, $\pm$ h,k,l
2θ scan limits, deg	4–50
scan speed, deg min^{-1}	var, 5–20
scan technique	Wyckoff
crystal size, color	0.29 × 0.29 × 0.38, red-black
unique data	2339 (2448 nonsystematically absent collected)
unique data ($2.5\sigma(F_o)$)	1802
$R(I)$	0.024
monitored rflns	3/97 (21% decay)
R_F, R_{wF}, GOF	0.0461, 0.0568, 1.010
mean shift, esd max (final cycle)	0.062
g^a	0.0015
highest peak, final diff map, e$^-$ Å^{-3}	0.29

$^a w^{-1} = \sigma^2(F) + g(F^2)$.

slow vapor diffusion of Et_2O into a CH_2Cl_2 solution of II: ^1H NMR (CH_2Cl_2) δ 1.81 (s); IR (CH_2Cl_2) ν_{CO} 2008 (m), 1954 (m), 1853 (s br) cm^{-1}. Anal. Calcd for $C_{28}H_{30}V_2O_8$: C, 56.39; H, 5.07. Found: C, 56.96; H, 5.16.

Theoretical Studies. Calculations of the electronic structure of $[Cp_2V(\mu$-OC)V(CO)$_5]$ employed the SCC–Xα–DV method.[16] The coordinates for the atoms were derived from the structure of 1 and idealized to C_{2v} symmetry with the z axis lying along the V–OC–V bond and the xz plane being the mirror plane between the Cp rings. Hydrogen atoms replaced the methyl groups (of 1) on the Cp rings, with the C–H bond length being 1.08 Å.

Numerical basis orbitals were generated via exact HFS calculations on the neutral atoms. Atomic orbitals through 4p, 2p, 2p, and 1s were used as bases for V, C, O, and H, respectively. The core 1s electrons on carbon and oxygen and the core orbitals through 2p on vanadium were frozen in the molecular calculation. The size of the calculation was reduced by assigning the carbon and hydrogen atoms of the cyclo-pentadienyl rings and the carbon and oxygen atoms of the terminal carbonyl groups each to a single potential type. Calculations with a DEC VAX 11/750 computer required ~7 min per iteration, and the calcu-lation converged after 15 iterations. A mixing factor of 5% was used to calculate the new potential for each iteration.

Crystallographic Structure Determination. A red black crystal of $[(Cp^*_2V)(\mu$-OC)V(CO)$_5]$, obtained by recrystallization from CH_2Cl_2, was affixed to a fine glass fiber with epoxy. Preliminary photographic characterization revealed $2/m$ Laue symmetry, and systematic absences in the reflection data require either of the centered monoclinic space groups $C2/c$ or Cc. Unit-cell dimensions were obtained from the angular settings of 25 reflections, 25° < 2θ < 30°, and are given in Table 1 along with other crystal, data collection, and refinement parameters. The data were corrected for a linear 21% decay in reflection intensity, Lp effects, and absorption (empirical Ψ-scan technique). All data reduction, structure solution, and refinement programs used are from the SHELXTL (4.1) system distributed by Nicolet Corp., Madison, WI.

Statistics based on E values, $\langle |E^2 - 1| \rangle = 0.97$, are consistent with the centrosymmetric space group $C2/c$; the initial assumption was affirmed by the chemically reasonable and well-behaved solution and refinement of the structure. The V(1),V(2) vector represents a crystallographically imposed twofold rotational axis in $C2/c$.

The structure was solved by direct methods (SOLV) that located the two metal atoms; subsequent difference Fourier syntheses located the remaining atoms. In the final cycles of blocked-cascade refinement, all

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Table II. Atom Coordinates ($\times 10^4$) and Temperature Factors
($\text{Å}^2 \times 10^3$)

atom	x	y	z	U^a
V(1)	5000	10872 (1)	2500	50 (1)
V(2)	5000	7278 (1)	2500	31 (1)
O(1)	5000	8729 (2)	2500	63 (2)
O(2)	5000	13036 (3)	2500	181 (5)
O(3)	3028 (3)	10781 (3)	1291 (3)	108 (2)
O(4)	5845 (3)	10888 (3)	410 (3)	94 (2)
C(1)	5000	9545 (4)	2500	45 (2)
C(2)	5000	12246 (4)	2500	96 (3)
C(3)	3743 (4)	10835 (4)	1765 (4)	70 (2)
C(4)	5546 (3)	10886 (3)	1189 (4)	62 (2)
C(11)	3626 (2)	6458 (3)	2113 (3)	46 (1)
C(12)	3384 (2)	7415 (2)	2236 (3)	46 (1)
C(13)	3625 (2)	7645 (2)	3259 (3)	43 (1)
C(14)	4037 (3)	6869 (3)	3758 (3)	48 (1)
C(15)	4031 (2)	6128 (2)	3066 (3)	46 (1)
C(16)	3366 (4)	5893 (5)	1167 (5)	80 (2)
C(17)	2884 (3)	8028 (4)	1439 (4)	75 (2)
C(18)	3402 (4)	8559 (3)	3754 (4)	75 (2)
C(19)	4328 (6)	6811 (6)	4883 (4)	87 (3)
C(20)	4184 (3)	5118 (3)	3348 (4)	78 (2)

^{a} Equivalent isotropic U defined as one third of the trace of the or-
thogonalized U_{ij} tensor.

Table III. Selected Bond Distances and Angles for
$\{(Cp^*_2V)(\mu\text{-}OC)V(CO)_5\}$

(a) Bond Distances, Å

V(1)–C(1)	1.899 (5)	C(1)–O(1)	1.167 (6)
V(1)–C(2)	1.965 (6)	C(2)–O(2)	1.130 (8)
V(1)–C(3)	1.955 (5)	C(3)–O(3)	1.147 (6)
V(1)–C(4)	1.954 (5)	C(4)–O(4)	1.143 (6)
		V(2)–O(1)	2.075 (4)
		V(2)–CNT^a	1.966 (5)

(b) Bond Angles, deg

C(1)–V(1)–C(3)	88.4 (1)	CNT–V(2)–CNT'	148.9 (2)
C(1)–V(1)–C(4)	90.6 (1)	CNT–C(11)–C(16)	173.6 (4)
C(2)–V(1)–C(3)	91.6 (1)	CNT–C(12)–C(17)	176.6 (4)
C(2)–V(1)–C(4)	89.4 (1)	CNT–C(13)–C(18)	175.4 (4)
C(3)–V(1)–C(4)	88.3 (1)	CNT–C(14)–C(19)	175.2 (4)
C(3)–V(1)–C(3')	176.8 (3)	CNT–C(15)–C(20)	168.0 (4)
C(4)–V(1)–C(4')	178.9 (2)		

^{a} CNT = centroid of Cp*.

non-hydrogen atoms were refined anisotropically and the hydrogen atoms
isotropically. The final data/parameter ratio was 7.8. Table II provides
the fractional atomic coordinates and Table III selected bond distances
and angles. Additional crystallographic data are available as supple-
mentary material.

Results and Discussion

Complex I was prepared by combining a solution of (η-
$C_5Me_5)_2V$ with a filtered solution of $V(CO)_6$ in pentane solvent.
The carbonyl stretches in the IR spectra of I closely resemble those
of the known complex $(OC)_5V(\mu\text{-}CO)V(THF)_4(\mu\text{-}OC)V(CO)_5$
(Table IV). These spectral data taken together with the one-
electron oxidizing ability of $V(CO)_6$ and the one-electron reducing
ability of (η-$C_5Me_5)_2V$ make the formulation of I as a μ-iso-
carbonyl complex seem reasonable. Andersen's group[5,8,17] has used
the one-electron reductant (η-$C_5Me_5)_2Yb(OEt_2)$ to prepare μ-
isocarbonyl derivatives by its reaction with $Mn_2(CO)_{10}$, $Co_2(CO)_8$,
and $Fe_3(CO)_{12}$. In these cases the formation of μ-isocarbonyl-
bridged species can be attributed to the exceptional oxophilicity
of the lanthanide metal. If one accepts the hypothesis that ox-
ophilic metals are necessary to prepare μ-isocarbonyl-bridged
compounds, then the stability of I raises two questions: (1) Why
does the $V(CO)_6^-$ group resist displacement by more basic "hard"
donors such as THF (e.g., IR spectra of I in THF and in the solid
state are similar)? (2) How covalent is the bond from vanadium
to the carbonyl oxygen?

X-ray Structure. The molecular structure I (Figure 1) is the
first example of a crystallographically linear M–O–C–M bond.
Previous examples of μ-isocarbonyl bridges[2-6,8,17] to a Cp_2M or
Cp^*_2M moiety all have a second ligand bound in the plane between
the C_5 rings. The M–O–C angle varies between about 135.35
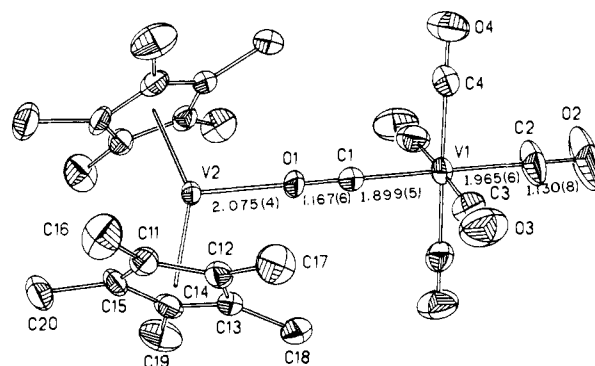
Figure 1. Molecular structure and labeling scheme for $(Cp^*_2V)(\mu\text{-}$
$OC)V(CO)_5$ (1). The atoms V(2), O(1), C(1), V(1), C(2) and O(2) lie
on a crystallographically imposed twofold rotational axis.

$(46)°$ in $Cp_2Ti(THF)(\mu\text{-}OC)MoCp(CO)_2$[3] and 163.0 (2)° in
$Cp^*_2Yb(THF)(\mu\text{-}OC)Co(CO)_3$;[5] the O–C–M angles remain
within a few degrees of linearity in every case. It has been sug-
gested[6] that bending about the M–O–C angle allows σ-type
bonding between the $1a_1$ orbital[18] on the Cp_2M fragment (bending
in an outward direction) or with the $2a_1$ orbital (bending inward).
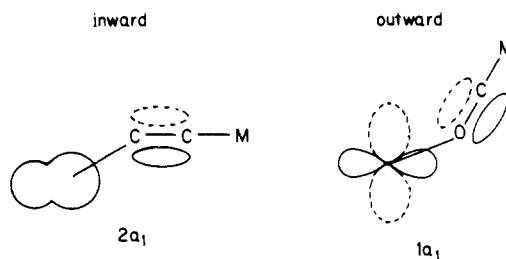
The equal distribution of known cases between inward[6] and
outward[2-5] bending reflects a balance between steric interactions
at the binding site and greater overlap between the CO π orbital
and the metal $2a_1$ orbital vs. the smaller $1a_1$ orbital. Linearity
of the bridging group in I resembles the linear binding[19] of CO
and CN^- to Cp^*_2V.

The equatorial carbonyls of I have V–C bond lengths of 1.954
(5) Å that are more similar to those in $V(CO)_6^-$ (1.931 (9) Å)[20]
than to those in $V(CO)_6$ (2.001 (2) Å).[21] Carbon–oxygen bond
lengths are also equal in the first two cases (1.145 (6) vs. 1.146
(11) Å) and are marginally longer than found in $V(CO)_6$ (1.128
(2) Å). These observations support the formulation of 1 as a
product of electron transfer from Cp^*_2V to $V(CO)_6$.

Bonds along the molecular C_2 axis of I exhibit some interesting
relationships. The V(2)–O(1) bond distance is the same as that
found in $(OC)_5V(\mu\text{-}CO)V(THF)_4(\mu\text{-}OC)V(CO)_5$[7] (2.075 (4) and
2.079 (5) Å, respectively); therefore, the primary interactions are
similar in both cases. In I the V(1)–C(1) bond is 0.05 Å shorter
than the corresponding bonds to the equatorial CO's and trans
axial CO. Although it borders on statistical significance, the
C(1)–O(1) bond length is 0.02–0.04 Å longer than terminal C–O
distances. Such variations in bond lengths are typical of other
μ-isocarbonyl complexes.[2-6,8]

The Cp^*–V(2)–Cp^* angle of 148.9 (2)° is similar to that found
in Cp^*_2VCO (153.6 (4)°)[19] and Cp^*_2VCN (151.5 (3)°);[19] cy-
clopentadienyl methyl groups are displaced from the plane by 0.03
Å. This deviation resembles that found in similar molecules and

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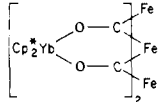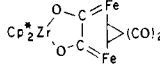Chem. Soc., Chem. Commun.* **1984**, 809–810.

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Table IV. CO Stretching Frequencies (cm⁻¹) for Compounds with Oxygen- and Carbon-Bound CO

compound	terminal CO stretches					μ-CO		ref
$Cp*_2V(\mu$-$OC)V(CO)_5$		2032	1945	1890	1857	1708[a]		this work
		2025	1918	1902	1870	1727[b]		this work
$V(CO)_6$		1970						25
$V(CO)_6^-$					1850			25
$(OC)_5V(\mu$-$CO)V(THF)_4(\mu$-$OC)V(CO)_5$		2039	1960	1889	1860	1684		25
$Cp_2Zr(Me)OCMo(CO)_2Cp$			1948		1863	1545		2
$[Cp(CO)_2Mo(\mu$-$CO)TiCp_2]_2$			1920		1750	1710		3b
$Cp_2*Yb(THF)(\mu$-$OC)Co(CO)_3$	2023	1973	1939	1917	1824	1796	1761	5
${Cp_2*Yb(\mu$-$OC)_2Mn(CO)_3}_2$	1965	1937	1928	1882	1840	1775		8
$Cp_2*Ti(Me(\mu$-$OC)MoCp*(CO)_2$		1927	1918	1849	1830	1623		6
$Cp_2Ti(THF)(\mu$-$OC)Mo(CO)_2Cp$		1920	1830			1650		3a
[structure: Cp_2^*Yb bridged via O—C to three Fe]						1667	1604	17b
${Cp_2*Yb}{Co_3(C_5H_4R)_2(\mu_3$-$CO)_4}^c$						1575		17d
[structure: Cp_2^*Zr O—C bridged to Fe, $(CO)_2$] [d]				1768	1709	1295	1282	17a
$Cp_2Ti(Cl)(\mu$-$OC)[Co_3(CO)_9]$		2088	2076	2018	1996	1980		17c

[a] Solution spectrum recorded in THF. [b] Solid-state spectrum recorded as a Nujol mull. [c] Structure is similar to preceding complex. [d] The binding to Zr is similar to an oxalate where the two carbonyl oxygens are replaced by iron atoms bridged by two CO's.

is constant among them.[19,22,23] Notice (Figure 1) that the Cp* rings adopt a staggered configuration. It is also noteworthy that the Cp*–V(2)–Cp* plane coincides with a dihedral plane through the $V(CO)_6$ center, bisecting the C(4)–V(1)–C(3)' angle.

Physical Properties. Compound I presents a carbonyl stretching pattern in the IR spectrum similar to that found for $(OC)_5V(\mu$-C-$O)V(Et_2O)_4(\mu$-O-$C)V(CO)_5$.[24] We assign the IR absorption of I at 1708 cm⁻¹ to the μ-isocarbonyl bridge. This frequency resembles that found in other μ-isocarbonyl species[24,25] (Table IV). Although exact assignments of the terminal carbonyl stretches are not possible, one absorption must be attributed to the axial carbonyl and the three remaining to equatorial CO's. If pseudofourfold symmetry was maintained for the equatorial CO's, then only two IR stretches (a_1 + e) are expected. The observation of three equatorial stretches suggests that the electronic symmetry has been significantly perturbed by interaction with the $Cp*_2V^+$ fragment. As seen below, there is a non fourfold π interaction.

Solution bulk magnetic susceptibility measurements by the Evans method[12] yield 2.68 μ_B for the moment of I that is consistent with the presence of two unpaired electrons. Since the reactant $Cp*_2V$ contains three unpaired electrons, d^3, and $V(CO)_6$ contains one unpaired electron, d^5, the product could represent one of two cases. In the first instance the paramagnetism arises from one unpaired electron on the $V(CO)_6$ center and the other on the $Cp*_2V$ center (i.e., no electron transfer). Splitting the metallocene e_{2g} and a_{1g} orbitals into one b_1 and two a_1 orbitals permits pairing of two of the electrons on $Cp*_2V$ and yields two centers with one unpaired electron each. One might expect to see an EPR signal from one or both of the metal centers. A methylene chloride solution EPR spectrum of I exhibits an octet with $g = 1.99$ and $a = 54.2 \times 10^{-4}$ cm⁻¹ and a multiplet centered at $g = \sim2.00$ with a small a value. The latter signal varies from sample to sample and is attributed to an impurity. The source of the first signal ($g = 1.99$) is unknown. The g and a values are consistent with those found for V(IV) systems[26] and are assigned to a trace impurity. As mentioned previously the metrical parameters of the $V(CO)_6$ fragment suggest it bears a −1 charge.

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Table V. Magnetic Susceptibility Data[a]

T, K	$1/\chi_M$	T, K	$1/\chi_M$
5.15	5.69	120.0	132.5
10.00	10.16	135.1	150.9
15.00	15.42	149.4	169.1
20.00	20.75	164.6	189.0
25.00	26.19	179.3	208.3
30.00	31.71	196.0	227.4
40.00	42.08	239.2	288.1
50.08	53.08	254.2	310.3
60.05	63.95	269.2	332.2
75.3	82.92	284.1	355.6
90.4	98.28	299.2	374.0
104.8	115.3		

[a] Crystals of 1 (0.0591 g, 0.1094 mmol) were wrapped in Parafilm wax (0.0798 g). This was suspended into the magnetometer with cotton thread. The observations were corrected for wax diamagnetism and the diamagnetic susceptibility of the complex using Pascal's constants (Figgis, B. N.; Lewis, J. *Techn. Inorg. Chem.* **1965**, *4*, 137–248).

The second possible bonding mode, that favored by the structural parameters, requires transfer of an electron from $Cp*_2V$ to $V(CO)_6$, giving a paramagnetic V(III), d^2, center and a diamagnetic V(−I), d^6, center. Vanadocene alkyls and halides, Cp_2VR, may also be considered as V(III), d^2, species and often exhibit two unpaired electrons.[19,26,27] In this second case the resonances seen for I in the EPR spectrum are attributed to impurities because it would be unusual for a triplet to exhibit room-temperature EPR spectra. Furthermore, there were no half-field absorptions in the EPR spectra to support a triplet assignment of these signals.

Magnetic susceptibility data (Table V) follow the Curie law between 5 K and room temperature. Using data of Table V between 0 and 50 K, we calculate $\mu_{eff} = 2.77$ (3) μ_B, to be compared with the spin-only value of 2.82 expected for two unpaired electrons. Were the two vanadium centers to have one unpaired electron each, then antiferromagnetic spin coupling would be expected. This is not observed; simple paramagnetism is maintained down to 5 K.

The presence of two unpaired electrons in complexes Cp_2VR requires an explanation. The highest symmetry that this type of molecule could possess is C_{2v}. As there are no degenerate orbitals in C_{2v}, the HOMO–LUMO separation for the hypothetical dia-

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Table VI. Atomic Orbital Populations

V$_1$	V$_2$	bridging		terminal		Cp	
		C	O	C	O	C	H
3p 5.988	3p 5.984	2s 1.364	2s 1.699	2s 1.382	2s 1.794	2s 1.168	1s 0.784
3d 3.934	3d 3.596	2p 2.746	2p 4.536	2p 2.668	2p 4.353	2p 3.126	
4s 0.009	4s 0.026						
4p 0.238	4p 0.124						
Q^a + 0.831	+1.275	−0.109	−0.235	−0.050	−0.146	−0.294	+0.216

^{a} Q denotes the atomic charge from a Mulliken population analysis.
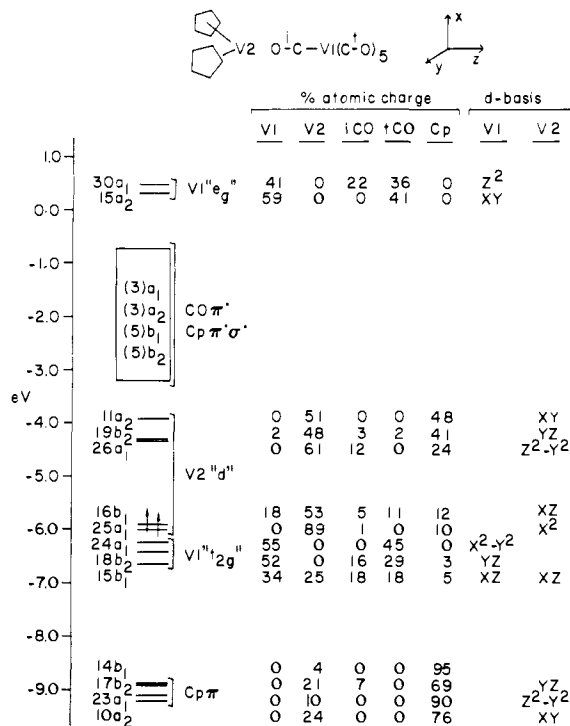
Figure 2. Summary of SCC–Xα–DV calculations for $(\eta$-C$_5$H$_5)_2$V(μ-O–C)V(CO)$_5$. Note the choice of coordinates with the xz plane bisecting the Cp–V–Cp angle.

magnetic case must be less than the electron pairing energy. We undertook the Xα calculation to gain insight into this matter.

Theoretical Studies. Results of spin-restricted SCC–Xα–DV[16] calculations also suggest that compound I consists of [Cp*$_2$V]$^+$ and [V(CO)$_6$]$^-$ fragments. The energy levels and charge distributions of the frontier molecular orbitals are shown in Figure 2, and the Mulliken atomic orbital population analysis is shown in Table VI. Charge distributions for low-lying carbonyl σ- and π-bonding orbitals, the cyclopentadienyl σ and π orbitals, and the empty CO and Cp π* orbitals lying between −3.5 and 0.0 eV that exhibit typical charge distributions are available as supplementary material. The orbitals of energy −8.78 through −9.11 eV are cyclopentadienyl π orbitals. These interact with metal orbitals of a$_2$ and b$_2$ symmetry (d$_{xy}$ and d$_{yz}$ − p$_y$, respectively) to form the principal bonding orbitals between the two Cp's and vanadium in the cation fragment. Metal d orbitals localized on the metallocene center are grouped between 16b$_1$ and 11a$_2$, inclusive. These include the HOMO (25a$_1$) and LUMO (16b$_1$) that are separated by a mere 0.05 eV in the spin-restricted calculations. This HOMO–LUMO gap is certainly small enough to warrant a high-spin ^{3}B$_1$ ground state, consistent with the magnetic data measured for complex I.

Orbitals of the [V(CO)$_6$]$^-$ fragment are those expected from a metal with near-octahedral symmetry. There is a set of three filled orbitals (Figure 2) of principal metal d character that correspond to octahedral t$_{2g}$ orbitals (d$_{xz}$, d$_{yz}$, and d$_{x^2-y^2}$ for the coordinate system used here). These are separated from the "e$_g$" orbitals by the metallocene-based d orbitals (mentioned above) and the CO π* and some Cp π* orbitals, the value of 10Dq being approximately 6.68 eV.

Calculations done by Lauher and Hoffmann[18] for the σ-bonded
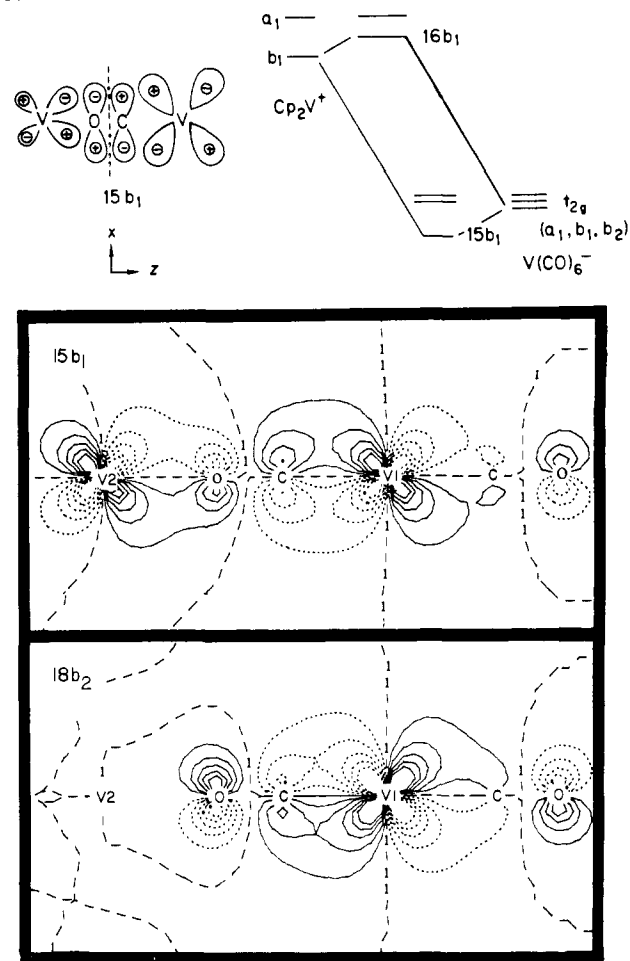
Scheme I

Figure 3. Plots of the t$_{2g}$ π orbitals (15b$_1$ and 18b$_2$) localized on the V(CO)$_6^-$ fragment in $(\eta$-C$_5$H$_5)_2$V(μ-O–C)V(CO)$_5$. The contour interval is 0.270 e/Å^3.

species of Cp$_2$MH show a bonding orbital of a$_1$ character resulting from the interaction of the a$_1$ σ orbital of the ligand and the 2a$_1$ orbital of the bent metallocene fragment. No such orbital is found for compound I (the deep-lying 10a$_1$ orbital contains only 1% V(2)d$_{z^2}$ and 75% μ-isocarbonyl oxygen) in further support of the assignment of the primary bonding interaction between V(CO)$_6^-$ and Cp$_2$V$^+$ as electrostatic. The electron distribution in the V(CO)$_6^-$ fragment polarizes to maximize the ionic interaction. A Mulliken analysis of the charge distribution of this fragment (Table VI) shows a −0.344 e charge for the μ-isocarbonyl group as compared with that of −0.196 e found for the terminal carbonyls. A recent X-ray diffraction study[28] of the weak ligand O$_3$SCF$_3^-$ also concluded that short metal–oxygen distances can result from primarily ionic interactions. In this context one can rationalize why most examples[2-8,17] of μ-isocarbonyls contain an anionic metal carbonyl fragment bound to a cationic metal acceptor fragment.

Although the bonding between the V(CO)$_6^-$ and Cp$_2$V$^+$ frag-

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Properties of $(\eta\text{-}C_5Me_5)_2V(\mu\text{-}OC)V(CO)_5$

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ments is primarily ionic, the availability of a π acceptor on the Cp_2V^+ fragment plays a role in the bonding and linearity of the V–O–C–V unit. On the basis of the analysis of Lauher and Hoffmann,[18] the $b_1 \pi$ (d_{xz}) orbital on the Cp_2V^+ fragment will be either empty or half-filled. The combination of this π-acceptor orbital with the $b_1 \pi$ orbital derived from the t_{2g} orbitals of V-$(CO)_6^-$ will result in a net π-bonding interaction as sketched in Scheme I. The b_1 orbitals described above are $15b_1$ and $16b_1$ in the Xα calculation. This interaction polarizes the t_{2g}-derived $(15b_1)$ orbital (Figure 3) so that the bridging CO π contribution (12% C and 8% O) is much greater than that of the terminal CO groups (8% C and 16% O or 2.6% C and 5.3% O per terminal carbonyl).

This argument is too simple. Inspection of Figure 2 reveals that the $18b_2$ orbital is stabilized nearly as much as $15b_1$ and contains an unusually high percentage of bridging CO π character (9% C and 9% O). This cannot be attributed to delocalization into the $Cp^*_2V^+$ fragment, which does not contribute to this orbital. An additional factor favoring occupation of μ-CO π^* orbitals in preference to the terminal CO groups is the electric field from the Cp_2V^+ fragment. We previously noted the polarization of the electron charge distribution in the $V(CO)_6^-$ fragment toward the μ-isocarbonyl group, and this is seen in the plot of the $18b_2$ orbital (Figure 3). The local electric field of the cation Cp_2V^+ stabilizes all the orbitals of the bridging μ-CO group and enhances its π-acceptor ability. This explanation is similar to that used by Darensbourg and co-workers[29] to explain low-frequency IR shifts of metal carbonylates that form contact ion pairs with alkali metal cations. The greater involvement of bridging CO π^* orbitals in μ-isocarbonyl complexes explains the linear geometry, increased C–O bond length, decreased M–C bond lengths, and the decreased IR stretching frequency observed for the μ-isocarbonyl group.

The reaction between $CoCp_2$ and $V(CO)_6$ has recently been reported[11] to yield $[Cp_2Co][V(CO)_6]$; however, IR and structural information was not given. Since the bis(cyclopentadienyl)cobalt cation does not have an available acceptor orbital, it may exist as a simple salt and not the molecular complex seen here for the decamethylvanadocene derivative.

It would seem that the accidental degeneracy of the $25a_1$ and $16b_1$ orbitals might be general for compounds Cp_2VX, where X is an anionic ligand. For the complexes where X is halide, H, or alkyl and aryl both Cp and Cp* derivatives[10,18,26,27] are paramagnetic and contain two unpaired electrons; however, the germyl and stannyl derivatives[30] are diamagnetic. In the latter instance we speculate that π-acceptor orbitals on the Sn and Ge ligands

of b_1 symmetry interact with the metal d_{xz} orbital. Lowering $b_1(d_{xz})$ relative to the $a_1(d_{x^2})$ orbital breaks the accidenal degeneracy and yields a diamagnetic complex (electrons paired in b_1). This "π back-bonding" should result in an increased bond order for the V–E bond (E = Ge or S) over a V–C bond. The stability of the V–Ge bond in comparison to the V–C bond toward cleavage by HCl[31] is chemical evidence that $d\pi$–Eπ interaction may be occurring. The diamagnetism of $[V(N(SiMe_3)_2)Cp_2]$[32] is explained similarly by Vd_{xz}–Np_x π bonding from N to V. Here, b_1 (d_{xz}) would be destabilized relative to $a_1(d_{x^2})$.

Lability of the $V(CO)_6^-$ Ligand. Infrared spectra of I show that the isocarbonyl bridge is not cleaved in solvents such as toluene, THF, or CH_2Cl_2. Nitrogen-donor ligands such as pyridine or CH_3CN immediately displace $V(CO)_6^-$ as seen in the IR spectra (free $V(CO)_6^-$ at 1850 cm^{-1}). Addition of CO to a dichloromethane solution of I yields $[Cp^*_2V(CO)_2][V(CO)_6]$ (II), which exhibits three peaks in the IR spectrum (2005, 1953, and 1853 cm^{-1}). The compound $[Cp^*_2V(CO)_2]PF_6$ is reported[15] to exhibit ν_{CO} at 1989 and 1954 cm^{-1}. Complex I is also photosensitive.

Exposure of a CH_2Cl_2 solution of I in an EPR tube to room light for 3 h resulted in a pale yellow solution having a simple eight-line EPR spectrum, $g = 1.990$, $a = 31.7 \times 10^{-4}$ cm^{-1}. The IR spectrum shows peaks at 2005, 1953 and 1853 cm^{-1} that correspond to those observed for II. The photochemical reaction probably involves loss of CO that then adds to the vanadocene center. Whether the complex first dissociates to form $Cp^*_2V^+$ and $V(CO)_6^-$ or whether the photolysis promotes transfer of CO within the molecule is uncertain. The vanadocene center is not reduced in either process. Were reduction to occur, one might expect to observe the known compound[19] Cp^*_2VCO in the reaction products, none of which was found. Thus complex I is a ready thermal and photochemical source of the $Cp^*_2V^+$ moiety, consistent with the ionic character of the $Cp^*_2V–V(CO)_6$ bond. We are examining the mechanistic chemistry of this intriguing molecule.

Supplementary Material Available: Tables of observed and calculated structure factors, bond distances and angles, anisotropic temperature factors, hydrogen atom coordinates and a charge analysis for all valence molecular orbitals of $(\eta\text{-}C_5H_5)V(\mu\text{-}OC)V(CO)_6$ (18 pages). Ordering information is given on any current masthead.

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