Oxidation Products of Vanadocene and of Its Permethylated Analogue, Including the Isolation and the Reactivity of the Unsolvated [VCp$_2$]$^+$ Cation

Fausto Calderazzo, Isabella Ferri,[†] and Guido Pampaloni*

*Dipartimento di Chimica e Chimica Industriale, Università di Pisa, Via Risorgimento 35,
I-56126 Pisa, Italy*

Ulli Englert

*Institut für Anorganische Chemie der Rheinisch-Westfälischen Technischen Hochschule,
Professor Pirlet-Strasse 1, D-52074 Aachen, Germany*

The one-electron oxidation of vanadocene, VCp$_2$, by [FeCp$_2$]$^+$ in toluene affords the 14-electron [VCp$_2$]$^+$ cation, which has been isolated as an unsolvated species for the first time. Vanadium hexacarbonyl reacts with VCp$_2$ to give the μ-isocarbonyl derivative Cp$_2$V(μ-OC)V-(CO)$_5$ as a transient species, which has been characterized in solution by IR analysis. By reaction of VCp$_2$ with V(^{13}CO)$_6$ followed by treatment with ^{12}CO, the ionic dicarbonyl derivative [VCp$_2$(^{12}CO)$_2$][V(^{13}CO)$_6$] is formed, thus showing that during the formation of the ionic compound no redistribution of the carbonyl ligands between the two metal centers occurs. Bis(cyclopentadienyl)vanadium(II) and Co$_2$(CO)$_8$ give Cp$_2$VCo(CO)$_4$, which slowly decomposes in solution even at low temperature to give [VCp$_2$(CO)$_2$][Co(CO)$_4$], which was identified by conventional methods, including single-crystal X-ray diffraction. The reactivity of the unsolvated [VCp$_2$]$^+$ cation as well as that of the heterobimetallic compound containing vanadium and cobalt with several Lewis bases is reported.

Introduction

In contrast to the well-developed chemistry of cationic bis(cyclopentadienyl) derivatives of group 4 elements, bis(cyclopentadienyl) complexes of vanadium have attracted much less attention, despite their potential applications in many fields such as bioinorganic chemistry,[1] Ziegler−Natta catalysis,[2] and material chemistry.[3] As a matter of fact, although the aqueous solutions of the [VCp$_2$]$^+$ cation were obtained by Wilkinson and Birmingham more than 40 years ago by reduction of bis-(cyclopentadienyl)vanadium(IV) perchlorate with the Jones reagent in acidic aqueous solution,[4] a rather limited number of paper have appeared on the subject.[5]

Due to the electron count of 14, the [VCp$_2$]$^+$ cation gives adducts of general formula [VCp$_2$L$_n$]$^+$ by reaction with Lewis bases L. For example, adducts with CO,[6] isocyanides,[6a,b] tertiary phosphines,[6g7] nitriles,[8] THF,[7] and acetone[6g,9] have been obtained from bis(cyclopentadienyl)vanadium(III) halides or by direct oxidation of vanadocenes in the presence of the appropriate ligand. Moreover, some authors have reported the reaction of VCp$_2$ or substituted congeners with metal carbonyls,[6f,10–12] showing that, in some cases, heterobimetallic compounds can be obtained. In the case of

* To whom correspondence should be addressed.
‡ Present address: CRYOVAC SpA, Via Trento 7, I-20017 Passirana di Rho, Milano, Italy.
(1) Köpf-Maier, P.; Köpf, H. *Chem. Rev.* **1987**, *87*, 1137 and references therein.
(2) Spitz, R.; Pasquet, V.; Patin, M.; Guyot, A. The Activation of Supported Vanadium Catalysts in Ethylene Polymerization. In *Ziegler Catalysts*; Fink, G., Mühlhaupt, R., Brintzinger, H. H., Eds.; Springer-Verlag: Berlin, 1995; p 401. Doi, Y.; Tokuhiro, N.; Nunomura, M.; Miyake, H.; Suzuki, S.; Soga, K. Living Polymerization of Olefins with Highly Active Vanadium Catalysts. In *Transition Metals and Organometallics as Catalysts for Olefin Polymerization*; Kaminsky, W., Sinn, H., Eds.; Springer-Verlag: Berlin-Heidelberg, 1988; p 379. Evens, G. G.; Pijpers, E. M. J.; Seevens, R. H. M. Enhancement of the Activity of a Vanadium Catalyst for Ethylene Propylene Copolymerization. In *Transition Metal Catalyzed Polymerizations*; Quirk, R. P., Ed.; Cambridge University Press: Cambridge, U.K., 1988; p 782.
(3) Miller, J. S.; Epstein, A. J.; Reiff, W. A. *Chem. Rev.* **1988**, *88*, 201 and references therein.

(4) Wilkinson, G.; Birmingham, J. M. *J. Am. Chem. Soc.* **1954**, *76*, 4281.
(5) Connelly, N. G. Vanadium. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Abel, E. W., Stone, F. G. A., Eds.; Pergamon Press: Oxford, U.K., 1982; Vol. 4, p 647. Berno, P.; Gambarotta, S.; Richeson, D. Vanadium. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Abel, E. W., Stone, F. G. A., Eds.; Pergamon Press: Oxford, U.K., 1995; Vol. 4, p 1.
(6) (a) Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.* **1984**, *23*, 1739. (b) Fachinetti, G.; Del Nero, S.; Floriani, C. *J. Chem. Soc., Dalton Trans.* **1976**, 203. (c) Connelly, N. G.; Davies, J. D. *J. Organomet. Chem.* **1972**, *38*, 385. (d) Bocarsly, J. R.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.* **1987**, *26*, 1871. (e) Miller, G. A.; Therein, M. J.; Trogler, W. C. *J. Organomet. Chem.* **1990**, *383*, 271. (f) Calderazzo, F.; Bacciarelli, S. *Inorg. Chem.* **1963**, *2*, 721. (g) Fachinetti, G.; Del Nero, S.; Floriani, C. *J. Chem. Soc., Dalton Trans.* **1976**, 1046. (h) Atwood, J. L.; Rogers, R. D.; Hunter, W. E.; Floriani, C.; Fachinetti, G.; Chiesi-Villa, A. *Inorg. Chem.* **1980**, *19*, 3812.
(7) Choukroun, R.; Douziech, B.; Pan, C.; Dahan, F.; Cassoux, P. *Organometallics* **1995**, *14*, 4471.
(8) Robbins, J. L.; Edelstein, N.; Spencer, B.; Smart, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 1882.
(9) Gambarotta, S.; Pasquali, M.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.* **1981**, *20*, 1173.
(10) Martin, J.; Moïse, C. *J. Organomet. Chem.* **1982**, *232*, C55.
(11) Martin, J.; Fauconet, M.; Moïse, C. *J. Organomet. Chem.* **1989**, *371*, 87.
(12) Osborne, J. H.; Rheingold, A. L.; Trogler, W. C. *J. Am. Chem. Soc.* **1985**, *107*, 6292.

the reaction of VCp_2 with $V(CO)_6$ under a *nitrogen* atmosphere "a mixture of at least two different compounds was formed", but the individual components could not be resolved.[6f]

It was therefore of interest to examine in some detail the possibility of isolating and characterizing the still elusive, unsolvated, ligand-free $[VCp_2]^+$ cation. This paper shows that this cation can be isolated as the tetraphenylborate derivative. Attempts to isolate it in combination with carbonylate anions failed, due to the easy transformation of the unsolvated cation into the dicarbonyl compound $[VCp_2(CO)_2]^+$ by partial decomposition of the carbonylmetalate anion.

Experimental Section

All operations were carried out using standard Schlenk-tube techniques, under an atmosphere of prepurified argon. The reaction vessels were oven-dried prior to use. Solvents were dried by conventional methods.

Elemental analyses were performed with a Carlo Erba Model 1106 elemental analyzer at the Istituto di Chimica Farmaceutica of the Facoltà di Farmacia or at the Dipartimento di Chimica e Chimica Industriale of the Università di Pisa. Infrared spectra were recorded with a Perkin-Elmer Model FT 1725X instrument on solutions or Nujol and poly-(chlorotrifluoroethylene) mulls of the compounds prepared under rigorous exclusion of moisture and oxygen.

Ph_3SnCl (Fluka) and $Co_2(CO)_8$ (Fluka) were commercially available and were used without further purification. The compounds but-2-yne (Aldrich) and hexafluorobut-2-yne (Aldrich) were degassed and stored at low temperature under argon. CF_3COOH (Aldrich) was stored in the presence of 15% (v/v) $(CF_3CO)_2O$.

The following reagents were prepared according to the literature: [PPN]Cl (PPN = bis(triphenylphosphine)nitrogen-(1+) cation),[13] $[FeCp_2]BR_4$ (R = Ph, 4-C_6H_4F, 3,5-$C_6H_3(CF_3)_2$)[14] VCp_2,[15] $VCp*_2$,[6a] VCp_2Cl,[16] $CoCp_2$,[15] $Na[Co(CO)_4]$,[17] $Cp_2VCo-(CO)_4$,[10] $V(CO)_6$,[18] $nBu_4N[V(CO)_6]$,[19] $Mn_2(CO)_{10}$,[20] and $Na[Mn(CO)_5]$.[21]

Reaction of VCp_2 with $V(CO)_6$. VCp_2 (0.08 g, 0.44 mmol) was added to a solution of $V(CO)_6$ (0.08 g, 0.36 mmol) in toluene (10 mL). The IR spectrum of the solution recorded immediately after the reagents were mixed showed absorptions at 2040 m, 1970 w−m, 1896 vs, 1864 s, 1849 s, and 1652 m-s cm^{-1}. After 24 h the spectrum showed the absorption at 1850 s cm^{-1} to be the strongest one in the carbonyl stretching region. Two weak additional bands were observed at 2051 and 2013 cm^{-1}, and a solid was present within the reaction mixture. The suspension was then filtered, and the dark brown solid thus obtained was dried in vacuo (0.08 g). The solid had absorptions (Nujol mull) at 2051 m, 2010 m, and 1840 vs cm^{-1} typical of $[VCp_2(CO)_2][V(CO)_6]$.[6f]

(13) Ruff, J. K.; Schlientz, W. J. *Inorg. Synth.* **1974**, *15*, 84.

(14) Calderazzo, F.; Pampaloni, G.; Rocchi, L.; Englert, U. *Organometallics* **1994**, *13*, 2592.

(15) Zybill, C. E. Complexes with Cyclic Ligands C_nH_n. In *Synthetic Methods of Organometallic and Inorganic Chemistry (Herrmann/Brauer);* Herrmann, W. A., Ed.; Georg Thieme Verlag: Stuttgart, Germany, 1997; Vol. 8, p 5.

(16) Manzer, L. E. *Inorg. Synth.* **1982**, *21*, 135.

(17) Wender, I.; Sternberg, H. W.; Orchin, M. *J. Am. Chem. Soc.* **1952**, *74*, 1216.

(18) Calderazzo, F.; Pampaloni, G. *Organomet. Synth.* **1988**, *4*, 49.

(19) Calderazzo, F.; Pampaloni, G.; Zanazzi, P. F. *Chem. Ber.* **1986**, *119*, 2796.

(20) Herrmann, W. A.; Öfele, K.; Zybill, C. E. Introduction, Working Techniques, Metal Carbonyls and Other Complexes. In *Synthetic Methods of Organometallic and Inorganic Chemistry (Herrmann/Brauer);* Herrmann, W. A., Ed.; Georg Thieme Verlag: Stuttgart, Germany, 1997; Vol. 7, p 16.

(21) Hieber, W.; Schuster, L. *Z. Naturforsch.* **1957**, *12B*, 478; **1958**, *13B*, 339.

Reaction of VCp_2 with $V(^{13}CO)_6$ and Treatment of the Product with CO. Vanadocene, VCp_2 (0.05 g, 0.28 mmol), was added to a solution of $V(^{13}CO)_6$[19] (0.06 g, 0.27 mmol) in toluene (5 mL). The IR spectrum of the solution recorded immediately after the reagents were mixed showed absorptions at 1995 m, 1924 w-m, 1855 vs, 1818 m-w, 1811 s, and 1613 m cm^{-1}. Treatment of the solution with CO at atmospheric pressure caused the formation of an orange solid and decoloration. The solvent was removed via cannula, and the solid was dried in vacuo and identified as $[VCp_2(CO)_2][V(^{13}CO)_6]$ from its IR spectrum in THF solution (2046 m, 1999 m, 1818 vs cm^{-1}).

Reaction of VCp_2Cl with $Na[V(CO)_6]$. The hexacarbonylvanadate(−I) compound $Na[V(CO)_6]$ (0.30 g, 1.24 mmol) was added to a solution of VCp_2Cl (0.27 g, 1.25 mmol) in toluene (25 mL). The color of the solution changed rapidly from blue to dark red, and NaCl precipitated. The IR spectrum of the solution showed absorptions at 2042 m, 1969 w-m, 1897 vs, 1865 s, 1849 m-s, and 1652 m-s cm^{-1}. After 17 h the intensities of the absorptions at 2042 m, 1969 w-m, 1897 vs, 1865 s, and 1652 m-s cm^{-1} were reduced with respect to the band at 1849 cm^{-1}. A brown solid with absorptions at 2047 m, 1997 m, and 1851vs cm^{-1} (THF) was present.

Synthesis of $[VCp_2]BR_4$ (R = Ph, 4-C_6H_4F). Only the synthesis of $[VCp_2]BPh_4$ is described in detail. VCp_2 (0.31 g, 1.71 mmol) was added to a suspension of $[FeCp_2]BPh_4$ (0.76 g, 1.50 mmol) in toluene (20 mL). An immediate reaction took place with formation of a green-gray solid in a red-orange solution. The solid was recovered by filtration, washed with toluene (2 × 5 mL) and heptane (2 × 5 mL), and dried in vacuo (0.57 g, 76% yield). IR (Nujol mull): 3087 vw, 3055 m, 1612 vw, 1581 w, 1562 vw, 1427 m, 1266 w-m, 1022 m, 825 s, 737 vs, 612 m-s cm^{-1}. The solid was found to absorb CO in toluene at 20 °C up to a CO/V molar ratio of 2.0 to give $[VCp_2(CO)_2]BPh_4$, characterized by its IR spectrum in THF solution (IR (THF): 2047 s, 1999 s cm^{-1}).[6f]

Data for $[VCp_2][B(4-C_6H_4F)_4]$ are as follows. Yield: 72%. IR (Nujol mull): 1580 m-s, 1488 s, 1257 w, 1209 s, 1157 s, 1015 m, 814 vs, 732 m, 553 s cm^{-1}. The solid was found to absorb CO in toluene at 20 °C up to a CO/V molar ratio of 1.9 to give $[VCp_2(CO)_2][B(4-C_6H_4F)_4]$, characterized by its IR spectrum in THF solution (IR (THF): 2047 s, 2000 s cm^{-1}).

Reactions of $[VCp_2]BPh_4$. (a) [PPN]Cl. A suspension of $[VCp_2]BPh_4$ (0.25 g, 0.5 mmol) in toluene (25 mL) was treated with [PPN]Cl (0.29 g; 0.5 mmol). Immediate reaction with formation of a green-brown suspension was observed. The suspension was filtered, and the solid (0.39 g, 91% yield) was identified as $[PPN]BPh_4$ (IR spectrum in Nujol). The volume of the solution was reduced to 10 mL, and heptane (20 mL) was added, which caused the separation of VCp_2Cl[16] (0.09 g, 83% yield), identified by IR and analytical techniques.

(b) $CoCp_2$. A solution of $CoCp_2$ (0.305 g, 1.6 mmol) in toluene (25 mL) was treated with solid $[VCp_2]BPh_4$ (0.81 g, 1.62 mmol). Formation of a deep yellow solid was observed upon mixing the reagents. The solid was filtered and identified as $[CoCp_2]BPh_4$ (IR). The solution was dried in vacuo, and the residue was sublimed at ca. 80 °C/10^{-2} mmHg, affording 0.10 g (91% yield) of VCp_2.

(c) $^nBu_4N[V(CO)_6]$. A yellow solution of $^nBu_4N[V(CO)_6]$ (0.202 g, 0.44 mmol) in toluene (30 mL) was treated with solid $[VCp_2]BPh_4$ (0.217 g, 0.43 mmol). An infrared spectrum of the solution, recorded 10 min after the reagents were mixed, showed absorptions at 2043 m, 1969 w- m, 1896 vs, 1865 s, 1851 s, and 1653 m-s cm^{-1}. After 24 h of stirring at room temperature, the solution showed the absorption at 1851 cm^{-1} to be the most intense in the carbonyl stretching region. Two weak absorptions were observed at 2052 and 2008 cm^{-1}.

$[VCp_2(CO)_2][Co(CO)_4]$: Crystal Structure Solution and Refinement. Yellow transparent plates were obtained from

Table 1. Lattice Constants and Parameters of the Structure Determination of [VCp₂(CO)₂][Co(CO)₄]

compd	[VCp₂(CO)₂]Co(CO)₄
formula	C₁₆H₁₀CoO₆V
mol wt	408.13
cryst dimens (mm)	0.50 × 0.50 × 0.08
temp (K)	203
space group	P1̄ (No. 2)
cell constants	
a (Å)	13.81(1)
b (Å)	14.065(3)
c (Å)	9.238(9)
α (deg)	93.63(4)
β (deg)	94.63(8)
γ (deg)	66.36(4)
volume (Å³)	1637(2)
Z	4
D_{calcd} (g cm⁻³)	1.655
μ (cm⁻¹)	15.90
F(000)	816.0
data collecn range (θ, deg)	3−25
scan type	ω
no. of measd rflns	6922
abs cor	numerical
no. of indep rflns in refinement	3976 (with positive intensity)
no. of refined params	433
R^a	0.072
$R_w{}^b$	0.057
GOF	1.045

^{a} $R = \sum|\Delta F|/\sum|F_o|$, for reflections with $I > 1.0\sigma(I)$. ^{b} $R_w = [\sum w(\Delta F)_2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2|F_o|$.

a toluene solution of Cp₂VCo(CO)₄[10,11] after standing at ca. 0 °C for a few days. The structure was determined at −20 °C by using an ENRAF-Nonius CAD4 diffractometer with Mo Kα radiation ($\lambda = 0.71073$ Å, graphite monochromator). Crystal data, data collection parameters, and convergence results are compiled in Table 1. The structure was solved using direct methods(SHELXS-93[22])

Reactivity of VCp₂Co(CO)₄. (a) H₂O. A solution of VCp₂-Co(CO)₄ (0.12 g, 0.34 mmol) in toluene (10 mL) was treated with H₂O (13 μL, 0.7 mmol) at 0 °C. The addition caused the rapid formation of a green solid (0.09 g, 71% yield), which was analytically and spectroscopically identified as [VCp₂(OH₂)]-[Co(CO)₄]. Anal. Found (calcd) for C₁₄H₁₂CoO₅V: C, 45.2 (45.4); H, 3.1 (3.2). IR (Nujol mull): *3595* w, 3108 vw, 3022 w-m, 1854 vs, 999 w, 808 s, 555 vs, 411 m cm⁻¹. When the reaction was performed with D₂O, the IR spectrum showed the expected shift of the water frequencies (IR (Nujol mull): 3109 w, 3022 w-m, *2654* m-w, 1855 vs, 1008 m, 809 s, 555 vs, 410 m cm⁻¹. Wavenumbers in italics refer to the absorptions which shift on H/D substitution.

(b) CF₃COOH. CF₃COOH (0.2 mL, 2.3 mmol) was added to a solution of VCp₂Co(CO)₄ (0.80 g, 2.27 mmol) in heptane (50 mL). Immediately a violet solid precipitated out. The solid was decanted from the solution, washed with heptane (3 × 5 mL), and dried in vacuo (0.52 g, 78% yield). It was analytically and spectroscopically identified as VCp₂(OOCCF₃). Anal. Found (calcd) for C₁₂H₁₀F₃O₂V: C, 48.9 (49.0); H, 3.4 (3.4). IR (Nujol/PCTFE mull): 3091 w, 2957 w, 2930 w, 2857 vw, 2047 m, 1995 m, 1879 w-m, 1715 m-s, 1687 vs, 1417 s, 1207 vs, 1158 vs, 967 m-s, 805 s, 720 m, 549 vs, 409 m cm⁻¹. The IR spectrum of the solution showed strong absorptions at 2052 and 2030 vs cm⁻¹ typical of HCo(CO)₄.[23] Some Co₂(CO)₈[24] was also present, as evidenced by the 2070 m-s, 2043 s, and 1857 m absorptions.

(c) Ph₃SnCl. Ph₃SnCl (0.07 g, 0.17 mmol) was added to a solution of VCp₂Co(CO)₄ (0.06 g, 0.17 mmol) in toluene (5 mL). The blue solution that was obtained was evaporated to dryness, and heptane (10 mL) was added. The solution thus formed contained Ph₃SnCo(CO)₄ (IR (heptane): 2087 s, 2027 s, 1999 vs cm⁻¹) only.[25] The solid was analytically identified as VCp₂Cl[16] (IR spectrum and Cl analysis).

(d) Alkynes. A solution of VCp₂Co(CO)₄ (0.38 g, 1.08 mmol) in toluene (25 mL) was treated with an excess of the alkyne (but-2-yne or hexafluorobut-2-yne). A rapid reaction took place with formation of Co₂(CO)₆(alkyne), which was identified spectroscopically (IR (toluene) for but-2-yne[26] 2070 m, 2046 s, 2022 s cm⁻¹; IR (toluene) for hexafluorobut-2-yne[27] 2122 w, 2089 s, 2063 vs cm⁻¹). All attempts to identify the vanadium species failed.

(e) CO. A solution of VCp₂Co(CO)₄ (0.04 g, 0.11 mmol) in THF (5 mL) was treated with CO at atmospheric pressure: the IR spectrum in THF solution showed absorptions at 2047 s, 1998 s, and 1887 vs cm⁻¹, typical of [VCp₂(CO)₂][Co(CO)₄].

Reaction of VCp*₂ with Co₂(CO)₈; Synthesis of Cp*₂V-(μ-CO)Co(CO)₃ (8). VCp*₂ (0.37 g, 1.15 mmol) was added to a solution of Co₂(CO)₈ (0.20 g, 0.58 mmol) in toluene (25 mL). A fast reaction took place, affording a dark red solution. After treatment with heptane (25 mL) black crystals were obtained, which were isolated by filtration and dried in vacuo (0.12 g, 21% yield). The compound was analytically and spectroscopically identified as Cp*₂V(μ-CO)Co(CO)₃. Anal. Found (calcd) for C₂₄H₃₀CoO₄V: C, 57.3 (58.5); H, 5.9 (6.1). IR (toluene): 2000 s, 1934 vs, 1757 m-s cm⁻¹. IR (THF): 2000 s, 1930 vs, 1887 m-s, 1766 m-s cm⁻¹. IR (PCTFE mull): 2961 w, 2920 m, 2855 w, 1998 s, 1978 m-s, 1952 s, 1932 s, 1899 vs, 1880 vs, 1778 s, 1385 m-s cm⁻¹.

Reactivity of Cp*₂V(μ-CO)Co(CO)₃. (a) THF. Cp*₂V(μ-CO)Co(CO)₃ (0.05 g, 0.10 mmol) was dissolved in THF (5 mL). The IR spectrum of the solution recorded immediately after the addition of the solvent showed absorptions at 2000 s, 1930 s, 1887 vs, and 1776 m-s cm⁻¹. The spectrum recorded 30 min later showed only one main absorption at 1886 cm⁻¹ due to the [Co(CO)₄]⁻ anion.[28]

(b) CO. A freshly prepared solution of Cp*₂V(μ-CO)Co(CO)₃ (0.05 g, 0.10 mmol) in THF (5 mL) was treated with CO at atmospheric pressure with fast formation of [VCp*₂(CO)₂][Co-(CO)₄], spectroscopically identified in solution (IR (THF): 2001 s, 1946 s, 1886 vs cm⁻¹).

Attempted Reaction of VCp₂ with Mn₂(CO)₁₀. VCp₂ (0.15 g, 0.83 mmol) was added to a solution of Mn₂(CO)₁₀ (0.15 g, 0.38 mmol) in toluene (25 mL). Even after 1 h of heating at 60 °C, no reaction took place, as confirmed by the persistence of the bands due to the carbonyl stretching vibrations of Mn₂-(CO)₁₀ (IR (toluene): 2046 s, 2011 vs, 1981 m cm⁻¹).[20]

Reaction of VCp₂Cl with Na[Mn(CO)₅]. Na[Mn(CO)₅] (0.11 g, 0.50 mmol) was added to a suspension of VCp₂Cl (0.12 g, 0.55 mmol) in toluene (25 mL). A rapid reaction was observed with formation of Mn₂(CO)₁₀, which was spectroscopically identified in solution (IR (toluene): 2046 s, 2010 vs, 1981 m cm⁻¹).[20]

Results and Discussion

The VCp₂/V(CO)₆ System. Some years ago Calderazzo and Bacciarelli reported[6f] that the reaction of VCp₂ with V(CO)₆ in the presence of CO affords the ionic [VCp₂(CO)₂][V(CO)₆] (eq 1); when the same reaction was carried out under nitrogen, only a mixture of products

(22) Sheldrick, G. M. SHELXL-93, A Program for the Solution of Crystal Structures; University of Göttingen, Göttingen, Germany, 1993.

(23) Moore, E. J.; Sullivan, J. M.; Norton, J. R. *J. Am. Chem. Soc.* **1986**, *108*, 2257.

(24) Hileman, J. C. Metal Carbonyls. In *Preparative Inorganic Reactions*; Jolly, W. L., Ed.; Wiley: New York, 1964; Vol. 1, p 77.

(25) Patmore, D. J.; Graham, W. A. G. *Inorg. Chem.* **1967**, *6*, 981.

(26) Sternberg, H. W.; Greenfield, H.; Friedel, R. A.; Wotiz, J.; Markby, R.; Wender, I. *J. Am. Chem. Soc.* **1954**, *76*, 1457.

(27) Boston, J. L.; Sharp, D. W. A.; Wilkinson, G. *J. Chem. Soc.* **1962**, 3488.

(28) Edgell, W. F.; Lyford, J., IV; Barbetta, A.; Jose, C. I. *J. Am. Chem. Soc.* **1971**, *93*, 6403.

Table 2. CO Stretching Frequencies (cm^{-1}) of Compounds Containing Isocarbonyl Groups

compd	terminal CO	bridging CO	ref
$Cp_2V(\mu\text{-}OC)V(CO)_5$	2042, 1969, 1897, 1865	1652	this work
$Cp^*_2V(\mu\text{-}OC)Co(CO)_3$	2000, 1934, 1887	1757	this work
$Cp^*_2V(\mu\text{-}OC)V(CO)_5$	2032, 1945, 1890, 1857	1708	12
$(OC)_5V(\mu\text{-}CO)V(THF)_4(\mu\text{-}OC)V(CO)_5$	2039, 1960, 1889, 1860	1684	29
$Cp_2ZrMe(\mu\text{-}OC)Mo(CO)_2Cp$	1948, 1863	1545	30
$Cp^*_2Yb(THF)(\mu\text{-}OC)Co(CO)_3$	2023, 1973, 1939, 1917, 1824	1798, 1761	31
$[Cp^*_2Yb(\mu\text{-}OC)_2Mn(CO)_3]_2$	2030, 2010, 1934, 1903	1770	32
$Cp'_2TiMe(\mu\text{-}OC)Mo(CO)_2Cp^a$	1927, 1918, 1849, 1830	1623	33
$Cp_2Ti(THF)(\mu\text{-}OC)Mo(CO)_2Cp$	1920, 1830	1650	34
$Cp_2TiCl(\mu\text{-}OC)[Co_3(CO)_9]$	2088, 2076, 2018, 1996	1980	35

^{a} $Cp' = C_5(CH_3)_4{=}CH_2$.

was obtained. More recently, Trogler et al. reported that,

$$VCp_2 + V(CO)_6 + 2CO \rightarrow [VCp_2(CO)_2][V(CO)_6] \quad (1)$$
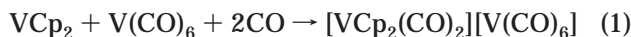
in the absence of CO, decamethylvanadocene reacts with $V(CO)_6$ to give the crystallographically established μ-isocarbonyl complex $Cp^*_2V(\mu\text{-}OC)V(CO)_5$ (eq 2).[12]

$$VCp^*_2 + V(CO)_6 \rightarrow Cp^*_2V(\mu\text{-}OC)V(CO)_5 \quad (2)$$

We have found that mixing VCp_2 and $V(CO)_6$ in toluene, under an argon atmosphere, gives a dark brown solution, whose IR spectrum in the carbonyl stretching region, recorded immediately after mixing the reagents, shows six absorptions at 2040 m, 1970 w-m, 1896 vs, 1864 s, 1849 s, and 1652 m-s cm^{-1}. Slowly, a dark brown solid forms, the IR spectrum of the solution showing a progressive decrease in the intensity of the bands with respect to the absorption at 1849 cm^{-1}. After 24 h, the spectrum showed several weak bands in the positions cited above. The solid isolated had an IR spectrum in agreement with that of $[VCp_2(CO)_2][V(CO)_6]$ (2051 m, 2010 m, and 1840 vs cm^{-1} (Nujol)), but the color of the solid (dark brown; $[VCp_2(CO)_2][V(CO)_6]$ is orange) and the C, H, N, and CO analysis clearly indicated that a mixture of compounds was formed.

The initial IR spectrum of the solution in the carbonyl stretching region (2042 m, 1969 m, 1897v s, 1865 s, and 1652 m-s cm^{-1}) is comparable to that of $Cp^*_2V(\mu\text{-}OC)V(CO)_5$ (2032, 1945, 1890, 1857, 1708 cm^{-1}).[12] In particular, the absorption at 1652 cm^{-1} is well in the range of the CO stretching frequencies generally observed for isocarbonyl groups (Table 2). Addition of Lewis bases, such as pyridine, DME, and CO, to the $VCp_2/V(CO)_6$ system directly after the mixing of the reagents causes the immediate cleavage of the isocarbonyl bridge without evolution of gas and probable formation of the ionic derivatives $[VCp_2L_n][V(CO)_6]$, as evidenced by the presence of a strong IR absorption at ca. 1850 cm^{-1}.

Due to the fact that pure $[VCp_2(CO)_2][V(CO)_6]$ is obtained under a CO atmosphere[6f] and that the treatment of the toluene solution of the intermediate species with CO produces pure $[VCp_2(CO)_2][V(CO)_6]$ (vide infra), it is believed that a partial electron transfer from V(0) to V(II) occurs within the thermally unstable intermediate. However, the covalent intermediate is not able to evolve to the ionic product, unless some ligands are present to complete the coordination of the $[VCp_2]^+$ cation. The counteranion $[V(CO)_6]^-$ can partially decompose and provide the required carbonyl groups. The overall reaction can be summarized as reported in Scheme 1.
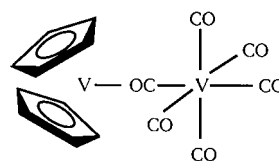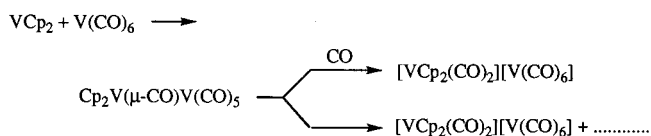

Figure 1. Proposed structure for $Cp_2V(\mu\text{-}OC)V(CO)_5$, containing a μ-isocarbonyl bridge.

Scheme 1

When a solution of VCp_2 in toluene was treated with $V(^{13}CO)_6$, the IR spectrum of the intermediate product showed the expected shift to lower wavenumbers of the CO stretching frequencies (1995 m, 1924 m, 1855 vs, 1818 m-w, 1811 s, 1613 m-s cm^{-1}, to be compared with 2042 m, 1969 m, 1897 vs, 1865 s, 1849 m-s, 1652 m-s cm^{-1} observed for the unlabeled compound). Further treatment with ^{12}CO afforded $[VCp_2(^{12}CO)_2][V(^{13}CO)_6]$ as the only product, as suggested by the IR spectrum of a solution in THF of the isolated orange solid, which shows absorptions at 2046 m, 1999 m, and 1818 vs cm^{-1}. The unlabeled compound, $[VCp_2(CO)_2][V(CO)_6]$, shows absorptions at 2050, 2001, and 1860 cm^{-1}, the last one belonging to the $[V(CO)_6]^-$ anion.[6f] This observation indicates that during the formation of the cationic $[VCp_2(CO)_2]^+$ moiety no redistribution of the carbonyl ligands between the two metal centers occurs. Thus, cleavage of the V–O isocarbonyl linkage must precede charge separation and CO addition to the cation thus formed.

The intermediate isocarbonyl product can also be obtained by treating a toluene suspension of $Na[V(CO)_6]$ with VCp_2Cl (eq 3). The reaction is fast, and the initially brown solution shows the typical IR absorptions at 2042 m, 1969 w-m, 1897 vs, 1865 s, 1849 m-s, and 1652 m-s cm^{-1}.

$$VCp_2Cl + Na[V(CO)_6] \rightarrow Cp_2V(\mu\text{-}OC)V(CO)_5 + NaCl \quad (3)$$
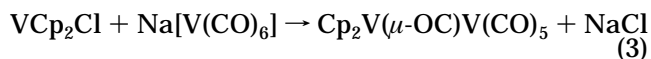
In conclusion, we can state that the primary product of these reactions is a μ-isocarbonyl complex like the one reported in Figure 1, i.e., with a structure similar to $Cp^*_2V(\mu\text{-}OC)V(CO)_5$.[12]

The VCp$_2$/[FeCp$_2$]$^+$ System. The chemistry of the previous section has clearly shown the impossibility of isolating the unsolvated $[VCp_2]^+$ cation through oxidation of VCp_2 by $V(CO)_6$.
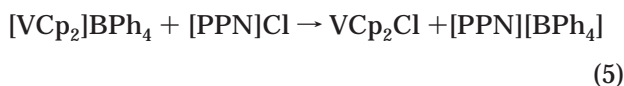
Ferrocenium salts have been largely used in these laboratories as one-electron oxidizing agents in toluene medium.[14,36] We therefore decided to study the VCp$_2$/[FeCp$_2$]$^+$ system.

By reaction of VCp$_2$ with the corresponding ferrocenium derivative in toluene the [VCp$_2$]BR$_4$ compounds containing the 14-electron [VCp$_2$]$^+$ cation have been obtained in high yields (eq 4). The compounds are gray-

$$VCp_2 + [FeCp_2]BR_4 \rightarrow [VCp_2]BR_4 + FeCp_2 \quad (4)$$

$$R = Ph, 4\text{-}C_6H_4F$$
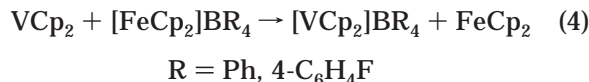
green solids extremely sensitive to air. No satisfactory elemental analyses could be obtained for these compounds, but it was possible to characterize them analytically by measuring the amount of CO absorbed in toluene during their conversion to the dicarbonyl complexes [VCp$_2$(CO)$_2$]BR$_4$. Absorption of CO up to a CO/V molar ratio of ca. 2 was observed, and the resulting products were identified from the IR spectrum in the solid state (Nujol mull) or in THF solution.[6f] The [B(3,5-C$_6$H$_3$(CF$_3$)$_2$)$_4$]$^-$ derivative separated out as an intractable oil, which however reacted with CO to give the expected dicarbonyl derivative.

The formulation of the compounds isolated according to eq 4 has been confirmed by some reactions performed on [VCp$_2$]BPh$_4$. As a matter of fact, [VCp$_2$]BPh$_4$ promptly reacts with [PPN]Cl or ^{n}Bu$_4$N[V(CO)$_6$], giving VCp$_2$Cl or Cp$_2$V(μ-OC)V(CO)$_5$ (eqs 5 and 6); it is also reduced by 1 equiv of CoCp$_2$ in toluene to vanadocene (eq 7).

$$[VCp_2]BPh_4 + [PPN]Cl \rightarrow VCp_2Cl + [PPN][BPh_4]$$

$$(5)$$

$$[VCp_2]BPh_4 + [^nBu_4N][V(CO)_6] \rightarrow$$
$$Cp_2V(\mu\text{-}OC)V(CO)_5 + [^nBu_4N][BPh_4] \quad (6)$$

$$[VCp_2]BPh_4 + CoCp_2 \rightarrow VCp_2 + [CoCp_2]BPh_4 \quad (7)$$

The VCp$_2$/Co$_2$(CO)$_8$ System. An earlier study of the vanadocene/Co$_2$(CO)$_8$ system showed that the treatment of a VCp$'_2$ solution (Cp$'$ = C$_5$H$_5$, C$_5$H$_4$CMe$_3$, C$_5$H$_4$Co$_2$-Me, C$_5$Me$_5$, C$_5$Me$_4$Et) with Co$_2$(CO)$_8$ affords heterobimetallic compounds whose composition depends on the substituents on the vanadocenes.[10,11]

In the framework of the present study, we have reexamined the VCp$_2$/Co$_2$(CO)$_8$ reaction, confirming the results of Moïse and co-workers[10,11] As a matter of fact, the reaction between VCp$_2$ and Co$_2$(CO)$_8$ at low temperature is fast and affords high yields of spectroscopi-
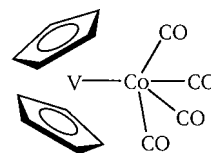

Figure 2. Proposed structure for VCp$_2$Co(CO)$_4$.

Table 3. Selected Bond Distances (Å) and Angles (deg) in [VCp$_2$(CO)$_2$][Co(CO)$_4$]

V(2)−centroid(1)	1.927	V(2)−centroid(2)	1.920
V(2)−C(2a)	1.950(9)	O(2a)−C(2a)	1.146(8)
V(2)−C(2b)	1.947(9)	O(2b)−C(2b)	1.130(9)
V(2)−C (av)	2.26	C(4)−O(4) (av)	1.16
Co(4)−C(4) (av)	1.76		
C(2a)−V(2)−C(2b)	87.8(4)	C(4)−Co(4)−C(4) (av)	109.3
V(2)−C(2a)−O(2a)	176.3(9)	Co(4)−C(4)−O(4) (av)	177.8
V(2)−C(2b)-O(2b)	177.9(7)		
centroid(1)−V(2)−centroid(2)	138.4		

cally pure Cp$_2$VCo(CO)$_4$, which can be isolated and safely handled in the solid state only at low temperature (ca. 0 °C). The absence of absorptions due to bridging carbonyls in the IR spectrum of Cp$_2$VCo(CO)$_4$ suggests[10,11] that Cp$_2$VCo(CO)$_4$ contains terminal carbonyl groups only and a V−Co bond[37] (see Figure 2). During our attempts to crystallize this material from toluene−heptane at −20 °C, orange crystals were isolated, which were shown by IR spectroscopy and X-ray diffractometry (vide infra) to be [VCp$_2$(CO)$_2$][Co(CO)$_4$], clearly resulting from partial decomposition of the anion.

Due to the fact that a previous report on the solid-state structure of the [VCp$_2$(CO)$_2$]$^+$ cation (as a BPh$_4^-$ salt) was characterized by severe disorder,[6h] we decided to study [VCp$_2$(CO)$_2$][Co(CO)$_4$] by X-ray crystallography.

The structure of [VCp$_2$(CO)$_2$][Co(CO)$_4$] consists of [VCp$_2$(CO)$_2$]$^+$ cations and [Co(CO)$_4$]$^-$ anions with two independent units in the unit cell. Due to the similarity of the two independent units, reference will be made to one of them only. The cobalt atom in the [Co(CO)$_4$]$^-$ anion has the expected tetrahedral coordination, with very few deviations from the ideal geometry, the average C−Co−C angle being 109.3° (Table 3); the average Co−C and C−O bond distances are in the range of those previously reported for the same anion.[38] A view of the [VCp$_2$(CO)$_2$]$^+$ cation is shown in Figure 3. The V−C−O angles in [VCp$_2$(CO)$_2$][Co(CO)$_4$] are 176.3(9) and 177.9-(7)° (161(5)° and 174(3)° in the [B(C$_6$H$_5$)$_4$]$^-$ derivative[6h]). The V−C$_{CO}$ bond lengths in [VCp$_2$(CO)$_2$][Co(CO)$_4$] (1.949-(9) Å, mean value) are in the range observed in terminal carbonyls, such as [PPN][V(CO)$_6$] (1.931(9) Å),[39] VCp-(CO)$_4$ (1.91(3) Å),[40] or [V(η^5-indenyl)$_2$(CO)$_2$]BPh$_4$ (1.975-(10) Å).[6d] The centroid(1)−V−centroid(2) angle (138.4°) is comparable to that in [V(η^5-indenyl)$_2$(CO)$_2$]BPh$_4$ (138.5(4)°)[6d] and is in the range 138−140°, which is usually observed for VCp$_2$ derivatives.[9]

(29) Schneider, M.; Weiss, E. *J. Organomet. Chem.* **1976**, *121*, 365.

(30) Marsella, J. A.; Huffmann, J. C.; Caulton, K. G.; Longato, B.; Norton, J. R. *J. Am. Chem. Soc.* **1982**, *104*, 6360.

(31) Tilley, T. D.; Andersen, R. A. *J. Chem. Soc., Chem. Commun.* **1981**, 985.

(32) Boncella, J. M.; Andersen, R. A. *Inorg. Chem.* **1984**, *23*, 432.

(33) Hamilton, D. M.; Willis, W. S.; Stucky, G. D. *J. Am. Chem. Soc.* **1981**, *103*, 4255.

(34) Merola, J. S.; Gentile, R. A.; Ansell, G. B.; Modrick, M. A.; Zentz, S. *Organometallics* **1982**, *1*, 1731.

(35) Schmidt, G.; Bätzel, V.; Stutte, B. *J. Organomet. Chem.* **1976**, *113*, 67.

(36) (a) Calderazzo, F.; Ferri, I.; Pampaloni, G.; Englert, U. *Organometallics* **1998**, *16*, 3100. (b) Calderazzo, F.; Pampaloni, G.; Tripepi, G. *Organometallics* **1998**, *16*, 4943.

(37) Calderazzo, F.; Fachinetti, G.; Marchetti, F.; Zanazzi, P. F. *J. Chem. Soc., Chem. Commun.* **1981**, 181. Fachinetti, G.; Fochi, G.; Funaioli, T.; Zanazzi, P. F. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 680. Selent, D.; Beckhaus, R.; Bartik, T. *J. Organomet. Chem.* **1991**, *405*, C15. Brammer, L.; McCann, M. C.; Bullock, R. M.; McMullan, R. K.; Sherwood, P. *Organometallics* **1992**, *11*, 2339.

(38) Bockman, T. M.; Kochi, J. K. *J. Am. Chem. Soc.* **1989**, *111*, 4669.

(39) Wilson, R. D.; Bau, R. *J. Am. Chem. Soc.* **1976**, *96*, 7601.

(40) Wilford, J. B.; Whitla, A.; Powell, H. M. *J. Organomet. Chem.* **1967**, *8*, 495.
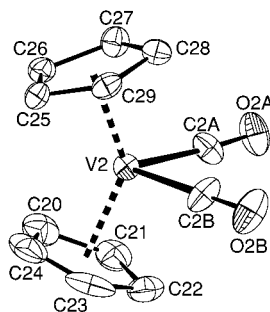
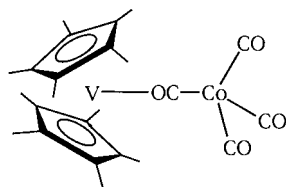**Figure 3.** Molecular structure of the $[VCp_2(CO)_2]^+$ cation in $[VCp_2(CO)_2][Co(CO)_4]$.

Figure 4. Proposed structure for $Cp^*_2V(\mu\text{-}OC)Co(CO)_3$ containing a μ-isocarbonyl bridge.

It is interesting to compare the structure of the $[VCp_2(CO)_2]^+$ cation with the isoelectronic neutral derivatives of group 4 metals, $MCp_2(CO)_2$ (M = Ti, Zr, Hf). For the titanium and vanadium derivatives, the C_{CO}–M–C_{CO} and the centroid–M–centroid angles are almost the same (M = Ti, 87.9(6) and 138.6°;[41] M = V, 87.8(4) and 138.4°, respectively). In the recently reported $[TiCp_2(CO)_2]^{2+}$ dication, the OC–Ti–CO angle is 86.8°, as calculated on the basis of the IR spectra.[36b] The M–C_{CO} and M–centroid average bond distances are longer in the titanium derivative (2.030(11) and 2.025 Å[41]) than in the vanadium analogue (1.949(9) and 1.924 Å), due to the smaller ionic radius of vanadium(III) with respect to titanium(II). When comparing the zirconium and hafnium $MCp_2(CO)_2$ complexes with $[VCp_2(CO)_2]^+$, it is possible to anticipate longer bond distances (M–C_{CO}: M = Zr, 2.187(4) Å;[6h] M = Hf, 2.16(2) Å[42]) and larger angles (C_{CO}–M–C_{CO}: M = Zr, 89.2(2)°; M = Hf, 89.3-(9)° [42]), as expected on the basis of the greater ionic radii of the 4d and 5d metals.

The reaction between VCp^*_2 and $Co_2(CO)_8$ affords a black solid of composition $VCp^*_2Co(CO)_4$ (eq 8) whose IR spectrum in solution shows absorptions at 2000 s, 1930 vs, and 1766 s cm^{-1}; the low-wavenumber absorp-

$$VCp^*_2 + Co_2(CO)_8 \rightarrow Cp^*_2V(\mu\text{-}OC)Co(CO)_3 \quad (8)$$

tion suggests the presence of a bridging carbonyl, as already observed in $Cp^*_2V(\mu\text{-}OC)V(CO)_5$ (1708 cm^{-1}), and therefore a similar structure can be envisaged for the cobalt–vanadium compound (Figure 4). The methyl-substituted derivative $Cp^*_2V(\mu\text{-}OC)Co(CO)_3$ is more robust in solution than the nonmethylated analogue; nevertheless, it slowly decomposes, as evidenced by the formation of a solid together with the appearance in solution of the absorptions typical of $Co_4(CO)_{12}$.[10,11]

The treatment of a freshly prepared toluene solution of $Cp^*_2V(\mu\text{-}OC)Co(CO)_3$ with THF gives a solution whose

Scheme 2
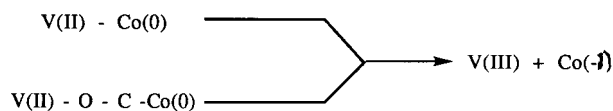
IR spectrum shows absorptions typical of the isocarbonyl derivative, and only after 30 min can a main band at 1886 cm^{-1} be observed, indicative of the presence of the $[Co(CO)_4]^-$ anion.[28,43]

The reaction of either $Cp_2VCo(CO)_4$ or $Cp^*_2V(\mu\text{-}OC)Co(CO)_3$ with THF proceeds without evolution of gas (as evidenced by gas volumetric measurements), therefore ruling out any $Co(0) \rightarrow Co(-I)/Co(II)$ disproportionation reaction after the formation of a neutral carbonyl derivative; it can be concluded that THF promotes the charge separation between the two organometallic fragments of the V–Co heterobimetallic derivatives (Scheme 2), with probable formation of the THF-solvated cations $[VCp_2(THF)_2]^+$ and $[VCp^*_2(THF)_2]^+$, respectively.

Reactivity of the Vanadium/Cobalt Systems. If $Cp_2VCo(CO)_4$ contains a vanadium–cobalt bond, it should be highly reactive and undergo easy cleavage of the metal–metal bond. This bond can be anticipated to be weak, due to the observation that $V(CO)_6$ is mononuclear and that the cobalt–cobalt bond in $Co_2(CO)_8$ has been estimated to be 87.8 kJ/mol.[44] Moreover, the formation of $[VCp_2(CO)_2][Co(CO)_4]$ from $VCp_2Co(CO)_4$ indicates that the vanadium–cobalt bond in the latter complex is cleaved by treatment with Lewis bases.

Previous studies[6g] suggested that in aqueous solution the $[VCp_2]^+$ cation is present as the monoaquo complex $[VCp_2(OH_2)]^+$, even though no direct observation of this species was made. For instance, the reaction of VCp_2Cl_2 with $AgClO_4$ in water gives AgCl and a pale green solution thought to contain $[VCp_2(H_2O)_n](ClO_4)_2$;[4] the latter, after reduction, afforded a purple solution containing a species with two unpaired electrons. Moreover, the $[VCp_2(OH_2)_2]^{2+}$ cation, prepared by reaction of VCp_2Cl_2 with $HPO_2(OC_6H_5)_2$ in water, has been structurally characterized.[45]

Addition of water to a cold solution of $VCp_2Co(CO)_4$ in toluene caused the immediate formation of a green solid in a colorless solution. The solid was analytically identified as the monoaquo adduct $[VCp_2(OH_2)][Co(CO)_4]$ (eq 9). The IR spectrum in the solid state shows

$$VCp_2Co(CO)_4 + H_2O \rightarrow [VCp_2(OH_2)][Co(CO)_4] \quad (9)$$

an absorption at 3595 cm^{-1} assigned to the O–H stretching vibration of the coordinated water. By using D_2O, the band shifts to 2654 cm^{-1} as a consequence of the isotopic substitution ($\tilde{\nu}_{OH}/\tilde{\nu}_{OD} = 1.35$; the theoretical value is 1.41).

The treatment of a solution of $VCp_2Co(CO)_4$ with CF_3COOH afforded a violet compound, sparingly soluble in toluene, which was identified as $VCp_2(O_2CCF_3)$. The IR spectrum of the solution revealed the presence of $HCo(CO)_4$. The reaction can, therefore, be described as in

(41) Atwood, J. L.; Stone, K. E.; Alt, H. G.; Hrncir, D. C.; Rausch, M. D. *J. Organomet. Chem.* **1977**, *132*, 367.

(42) Sikora, D. J.; Rausch, M. D.; Rogers, R. D.; Atwood, J. L. *J. Am. Chem. Soc.* **1979**, *101*, 5079.

(43) Edgell, W. F.; Yang, M. T.; Koizumi, N. *J. Am. Chem. Soc.* **1965**, *87*, 2563.

(44) Pilcher, G.; Skinner, H. A. Thermochemistry of Organometallic Compounds. In *The Chemistry of Metal–Carbon Bond*; Harley, F. R., Patai, S., Eds.; Wiley: Chichester, U.K., 1982; Vol. 2, p 43.

(45) Toney, J. H.; Brock, C. P.; Marks, T. J. *J. Am. Chem. Soc.* **1986**, *108*, 7263.
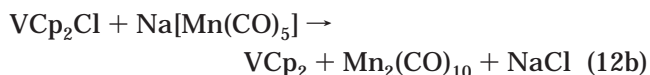
eq 10. The IR spectrum in the solid state of the violet

$$VCp_2Co(CO)_4 + CF_3COOH \rightarrow$$
$$VCp_2(O_2CCF_3) + HCo(CO)_4 \quad (10)$$
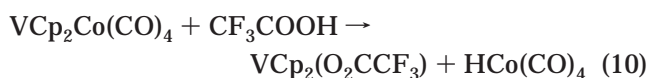
solid shows absorptions at 1687s and 1417m cm^{-1}, respectively, due to the asymmetric and symmetric C−O stretching vibrations of the trifluoroacetato group. Additional bands at 1207 and 1158 cm^{-1} denote the presence of CF$_3$ groups. As far as the coordination mode of the trifluoroacetato group is concerned, the separation between the asymmetric and the symmetric C−O stretching frequencies (Δ) is consistent with unidentate coordination,[46] which is in agreement with the marked tendency of the 14-electron [VCp$_2$]$^+$ species to attain at least the 16-electron configuration, as shown by the reactions with water (vide supra), acetone,[9] or pyridine.[6g]

By reaction with Ph$_3$SnCl the vanadium−cobalt bond in VCp$_2$Co(CO)$_4$ was replaced by a tin−cobalt bond together with formation of VCp$_2$Cl (eq 11). Similar

$$Ph_3SnCl + VCp_2Co(CO)_4 \rightarrow$$
$$VCp_2Cl + Ph_3SnCo(CO)_4 \quad (11)$$
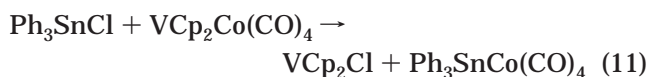
compounds, containing main-group-metal−cobalt bonds, of the type R$_3$MCo(CO)$_4$, were obtained from the reaction of Co$_2$(CO)$_8$ in methanol with R$_3$MCl (R = Me, Ph; M = Ge, Sn, Pb) systems.[25]

The VCp$_2$/Mn$_2$(CO)$_{10}$ System. When a solution of VCp$_2$ was placed in contact with Mn$_2$(CO)$_{10}$, no reaction took place, even after heating at ca. 60 °C (eq 12a). On

$$VCp_2 + {}^1\!/_2Mn_2(CO)_{10} \nrightarrow [VCp_2][Mn(CO)_5] \quad (12a)$$

$$VCp_2Cl + Na[Mn(CO)_5] \rightarrow$$
$$VCp_2 + Mn_2(CO)_{10} + NaCl \quad (12b)$$

the other hand, when solid Na[Mn(CO)$_5$] was added to a solution of VCp$_2$Cl in toluene, a rapid reaction was observed and the IR spectrum of the solution showed the presence of Mn$_2$(CO)$_{10}$ (eq 12b). It seems therefore that VCp$_2$, which smoothly reduces both V(CO)$_6$ and Co$_2$(CO)$_8$, is not a strong enough reducing agent for Mn$_2$-(CO)$_{10}$. This finding is in agreement with the values of the reduction potentials recently obtained in an electrochemical study on CoCp$_2$/metal carbonyl systems (Table 4).[47] In fact, the reduction potential of the

Table 4. Redox Potentials for V(CO)$_6$, Mn$_2$(CO)$_{10}$, Co$_2$(CO)$_8$, and [VCp$_2$]$^+$

compd	$E_{Ox/Red}{}^a$	ref	compd	$E_{Ox/Red}{}^a$	ref
Mn$_2$(CO)$_{10}$	−1.52	47	Co$_2$(CO)$_8$	−0.63	47
[VCp$_2$]$^+$	−1.10	48	V(CO)$_6$	−0.14^b	47

^{a} All potentials are referred to the potential of a ferrocene/ferrocenium couple at 0.400 V vs SCE. ^{b} E(V(CO)$_6$/[V(CO)$_6$]$^-$).

[VCp$_2$]$^+$/VCp$_2$ couple is more positive than that of the Mn$_2$(CO)$_{10}$/[Mn(CO)$_5$]$^-$ couple and is observed at potentials more negative than those of the Co$_2$(CO)$_8$/[Co-(CO)$_4$]$^-$ and V(CO)$_6$/[V(CO)$_6$]$^-$ couples. A determining factor in the failure to observe reaction 12a is connected with the presence of a manganese−manganese bond (BDE = 158 kJ/mol[49]) which is considerably stronger than that of Co$_2$(CO)$_8$ (BDE = 87.8 kJ/mol[44]).

Conclusions

The reaction of vanadocene with [FeCp$_2$]$^+$ in toluene gives the unsolvated [VCp$_2$]$^+$ cation, which has been isolated and characterized for the first time both by analysis and by studying its reactivity toward Lewis bases such as chloride ions or reducing agents such as cobaltocene. Moreover, this study has shown that the oxidation of VCp$_2$ by V(CO)$_6$ occurs *under argon* via the intermediate formation of an unstable isocarbonyl derivative, which has been identified in solution by IR spectroscopy as Cp$_2$V(μ-OC)V(CO)$_5$.

A detailed study of the reactivity of VCp$_2$Co(CO)$_4$ has shown that this compound undergoes charge separation on addition of Lewis bases such as CO, THF, py, H$_2$O, and CF$_3$COOH, affording either ionic or neutral derivatives of general formula [VCp$_2$L$_n$]$^{0/+}$.

Supporting Information Available: Tables of structural data for [VCp$_2$(CO)$_2$][Co(CO)$_4$], including positional parameters of non-hydrogen atoms, positional parameters of hydrogen atoms, all bond distances and angles, and displacement parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

(46) Deacon, G. B.; Phillips, R. J. *Coord. Chem. Rev.* **1980**, *33*, 227.
(47) Pampaloni, G.; Kölle, U. *J. Organomet. Chem.* **1994**, *481*, 1.
(48) Holloway, J. D. L.; Bowden, W. L.; Geiger, W. E., Jr. *J. Am. Chem. Soc.* **1977**, *99*, 7089.
(49) Pugh, J. R.; Meyer, T. J. *J. Am. Chem. Soc.* **1992**, *114*, 3784.