constant. No ^{195}Pt–acetylenic proton coupling is observed for **12**. This would imply that no triple-bond coordination to the metal takes place (structure IIIb of Scheme II), unless there is rapid interconversion on the NMR time scale between the coordinated (III′b) and uncoordinated (IIIb) triple-bond forms (Scheme II). Also, there is no evidence for acetylene displacement of the phosphine from the ^{31}P NMR spectrum, which shows a sharp singlet flanked by ^{195}Pt satellites for the two trans phosphines. Thus, there is no unequivocal evidence for allyl or propargyl group coordination to the Pt(II), but it also cannot be ruled out.

Acknowledgment. R.J.A. and R.A.M. thank the National Science Foundation and CNR (Rome) for a grant from the U.S.-Italy Cooperative Science Program.

Registry No. **1**, 111139-87-8; **2**, 111159-37-6; **3**, 111139-89-0; **4**, 111139-91-4; **5**, 111139-93-6; **6**, 111139-95-8; **7**, 111139-97-0; **8**, 111139-99-2; **9**, 111159-38-7; **10**, 111159-40-1; **11**, 111140-01-3; **12**, 111140-03-5; *trans*-[(PPh$_3$)$_2$Pt(CNC$_6$H$_4$-*p*-OMe)Cl]BF$_4$, 110313-73-0; *trans*-[(PMePh$_2$)$_2$Pt(CNC$_6$H$_4$-*p*-OMe)Me]BF$_4$, 110330-07-9; *trans*-[(PPh$_3$)$_2$Pd(CN-*p*-C$_6$H$_4$OMe)Cl]BF$_4$, 110313-86-5; *trans*-[(PPh$_3$)$_2$Pd(CN-*p*-C$_6$H$_4$Me)Cl]BF$_4$, 110313-88-7; *trans*-[(PPh$_3$)$_2$Pd(CNMe)Cl]BF$_4$, 110313-90-1; *cis*-Cl$_2$Pt(CNC$_6$H$_4$-*p*-Me)(PPh$_3$), 111140-04-6; *cis*-Cl$_2$Pd(CNC$_6$H$_4$-*p*-Me)$_2$, 40927-16-0; Br[NH$_3$CH$_2$CH$_2$Br], 2576-47-8; allyl bromide, 106-95-6; propargyl bromide, 106-96-7.

Supplementary Material Available: Hydrogen atom coordinates (Table S-I), anisotropic thermal parameters (Table S-II), and bond distances and angles (Table S-IV) (13 pages); observed and calculated structural factors (Table S-III) (17 pages). Ordering information is given on any current masthead page.

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Synthesis, Reactivity, and Crystal Structure of CpV(CO)$_3$tht (tht = Tetrahydrothiophene). A Mild-Condition Synthetic Pathway to Substitution Derivatives of CpV(CO)$_4$ and Preparation and X-ray Characterization of *cis*-CpV(CO)$_2$bpy (bpy = 2,2′-Bipyridine)

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Received July 27, 1987

Irradiation of CpV(CO)$_4$ in the presence of tht (tht = tetrahydrothiophene) affords the complex CpV(CO)$_3$tht (**1**), in which one carbonyl group has been replaced by the thioether ligand. **1** reacts readily with several ligands including 2,2′-bipyridine (bpy) and pyrrolidine (pyrr), providing a mild-condition pathway to the new derivatives *cis*-CpV(CO)$_2$bpy (**2**) and CpV(CO)$_3$pyrr (**3**). The structures of **1** and **2** have been determined by X-ray analysis. Both complexes are orthorhombic: **1** has a *Pbca* space group with $a = 14.171$ (4) Å, $b = 14.184$ (5) Å, $c = 13.035$ (4) Å, $V = 2620$ (1) Å^3, $Z = 8$, and $D_{\mathrm{calcd}} = 1.461$ g cm^{-3}, and the final *R* factor for 1937 reflections was 0.054; **2** has a *Pnma* space group with $a = 7.687$ (4) Å, $b = 15.073$ (6) Å, $c = 12.593$ (5) Å, $V = 1459$ (1) Å^3, $Z = 4$, and $D_{\mathrm{calcd}} = 1.494$ g cm^{-3}, and the final *R* value for 1423 reflections was 0.035. The structure of **3** has been assigned on the basis of its ^{13}C and ^{1}H NMR, IR, and analytical data.

Introduction

The monocyclopentadienyl carbonyl complexes of transition metals have received much attention as versatile compounds in coordination chemistry, oxidative-addition reactions, and metal-promoted organic synthesis.[1] Attractive results have been obtained also in the field of dinitrogen fixation by using the manganese derivative CpMn(CO)$_3$.[2]

The chemistry of the vanadium analogue, CpV(CO)$_4$, is currently limited to the photosubstitution of one or two carbonyls by ligands such as phosphines, arsines, stibines, bismuthines,[3] aromatic alkynes,[4] and nitric oxide,[5] which are able to resist the harsh photochemical conditions.

The elusive CpV(CO)$_3$thf (thf = tetrahydrofuran), analogous to the well-known CpMn(CO)$_2$thf, has been recently obtained by low-temperature irradiation of dilute solutions of CpV(CO)$_4$, any attempt to isolate this species affording Cp$_2$V$_2$(CO)$_5$ in quite low yield.[6] The acetonitrile derivative, CpV(CO)$_3$CH$_3$CN, has been detected in solution as a complex too reactive to be isolated.[7] The utilization of tetrahydrothiophene (tht) instead of the isostructural tetrahydrofuran allowed the preparation of crystalline CpMn(CO)$_2$tht, in which the labile thioether ligand permits easy manipulation of the complex, while keeping intact the reactivity of the CpMn(CO)$_2$ moiety.[8]

We wish to report here the large-scale preparation of CpV(CO)$_3$tht (**1**) together with a brief investigation of its utilization for the synthesis of new CpV(CO)$_n$L derivatives.

Experimental Section

All operations were performed under dry nitrogen with use of standard Schlenk techniques or in a nitrogen-filled drybox (Braun MB 200). CpV(CO)$_4$ was prepared according to published procedures.[9] Solvents were dried and distilled by following standard procedures. Cyclohexyl isocyanide (Aldrich) was distilled before use, pyrrolidine (Aldrich) was dried over potassium pyrrolidide and distilled with the use of 15-in. Vigreux column, tetrahydrothiophene (Aldrich) was dried over potassium and distilled twice with the use of a 15-in. Vigreux column, and 2,2′-bipyridine (Pro Labo) was used without further purification. NMR solvents (benzene-d_6, thf-d_8) were vacuum-transferred from Na-K alloy. ^{1}H and ^{13}C NMR spectra were recorded on a Varian VXR 300 spectrometer. Chemical shifts are reported in units of δ, referenced to tet-

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Table I. Experimental Data for X-ray Diffraction Studies on Complexes **1** and **2**

	complex **1**	complex **2**
formula	$C_{12}H_{13}O_3SV$	$C_{17}H_{13}N_2O_2V$
M_f	288.2	328.2
cryst syst	orthorhombic	orthorhombic
reflcn conditions	$0kl$, $k = 2n$; $h0$, $l = 2n$; $hk0$, $h = 2n$	$0kl$, $k + l = 2n$; $hk0$, $h = 2n$
space group	*Pbca*	*Pnma*
t, °C	22	22
a, Å[a]	14.171 (4)	7.687 (4)
b, Å	14.184 (5)	15.073 (6)
c, Å	13.035 (4)	12.593 (5)
V, $Å^3$	2620 (1)	1459 (1)
Z	8	4
D_c g cm^{-3}	1.461	1.494
cryst size, mm	0.25 × 0.32 × 0.50	0.24 × 0.29 × 0.40
μ, cm^{-1}	8.78	6.64
diffractometer	Philips PW 1100	
radiation	graphite-monochromatized Mo Kα (λ = 0.7107 Å)	
2θ range, deg	5–47	6–50
no. of reflcns measd	*hkl*	*hkl*
no. of unique reflcns	1937	1423
criterion for obsn	$I > 3\sigma(I)$	$I\ \sigma\ 3\sigma(I)$
no. of unique obsd data	794	816
no. of variables	154	130
overdetermination ratio	5.2	6.3
max shift/error on last cycle	0.01	0.3
$R = \sum\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert/\sum\lvert F_o\rvert$	0.054	0.035

[a] Unit cell parameters were obtained by least-squares analysis of the setting angles of 2θ carefully centered reflections chosen from diverse regions of reciprocal space.

ramethylsilane, and calculated from the position of the solvent absorption. Infrared (IR) spectra were obtained on a Perkin-Elmer PE 283 instrument: Nujol mulls were prepared in the drybox with dried Nujol oil. Elemental analyses were performed at the Chemistry Department of the University of Groningen. Irradiation of $CpV(CO)_4$ was conveniently performed in a standard glass flask by using a 125-W medium-pressure Hg lamp. No significant yield improvement (apart from an increase in the reaction rate) was observed with the utilization of a Pyrex toroidal reactor with a quartz cold finger and a slow stream of nitrogen passed through the reaction mixture.

Preparation of $CpV(CO)_3$tht (1). A magnetically stirred solution of $CpV(CO)_4$ (11.5 g, 50.4 mmol) in 200 mL of toluene was irradiated in a water cooling bath in the presence of a 10-fold excess of tht. The irradiation was continued until the $CpV(CO)_4$ bands had disappeared from the IR spectrum of the reaction mixture. The reaction vessel was kept under reduced pressure, and occasionally the CO evolved from the reaction vessel was pumped out. The resulting cherry red solution was concentrated to a very small volume (10 mL). By addition of 200 mL of hexane, deep red crystals of **1** separated from the solution (9.6 g, 33.3 mmol; 66.6%). The crystalline product is indefinitely stable at room temperature. Anal. Calcd (found) for $C_{12}H_{13}O_3SV$: C, 50.00 (50.25); H, 4.51 (4.69); S, 11.11 (11.09); V, 17.71 (17.80). IR (KBr, Nujol mull), cm^{-1}: ν(CO) 1953, 1855, 1820. ^1H NMR (300 MHz, benzene-d_6): δ 4.62 (s, 5 H, Cp); δ 2.15, 1.21 (multiplets, 4 H, tht). $^{13}C\{^1H\}$ NMR (75.4 MHz, benzene-d_6): δ 92.17 (Cp); δ 41.73, 30.31 (tht).

Preparation of *cis*-$CpV(CO)_2$bpy (2). A 1.0-g portion of bpy (6.4 mmol) was added to a toluene solution (50 mL) of **1** (1.54 g, 5.3 mmol). On standing at room temperature overnight, the resulting deep purple solution formed deep blue crystals of **2** (0.85 g, 2.59 mmol; 48.9%). Anal. Calcd (found) for $C_{17}H_{13}N_2O_2V$: C, 62.20 (63.04); H, 3.96 (4.17); N, 8.53 (8.62); V, 15.54 (15.47). IR (KBr, Nujol mull), cm^{-1}: ν(CO) 1843, 1780. ^1H NMR (300 MHz, thf-d_8): δ 9.22 (pseudodoublet, 2 H), 8.25 (pseudodoublet, 2 H), 7.44 (pseudotriplet, 2 H), 6.81 (pseudotriplet, 2H) (bpy); δ 4.80 (s, 5 H, Cp). $^{13}C\{^1H\}$ NMR (75.431 MHz, thf-d_8): δ 167.91, 155.61, 131.03, 123.16, 117.33 (bpy); δ 96.55 (Cp).

Preparation of $CpV(CO)_3$pyrr (3). A 3-mL portion of neat pyrr (42.2 mmol) was added to a toluene solution (25 mL) of **1** (1.30 g, 4.5 mmol). No significant color change was observed except for a slight darkening of the solution. The solution was concentrated to a small volume (15 mL), and after 50 mL of *n*-hexane was added and the mixture was allowed to stand overnight at −30 °C, deep red crystals separated from the solution (0.70 g, 2.6 mmol; 57.8%). The complex is thermally unstable, and the crystalline solid cannot be stored at room temperature for more than 1 d. Anal. Calcd (found) for $C_{12}H_{14}O_3NV$: C, 53.14 (53.01); H, 5.17 (5.14); N, 5.16 (5.17); V 18.82 (18.79). IR (KBr, Nujol mull), cm^{-1}: ν(CO) 1950, 1850, 1825; ν(N-H) 3279. ^1H NMR (300 MHz, benzene-d_6): δ 4.63 (s, 5 H, Cp); δ 2.12 (multiplet, 2 H, CH_2), 1.58 (multiplet, 2 H, CH_2), 1.12 (quintuplet, 1 H, NH), 0.94 (multiplet, 2 H, CH_2), 0.64 (multiplet 2H,CH_2) (pyrr). $^{13}C\{^1H\}$ NMR (75.43 MHz, benzene-d_6): δ 251.16 (1 C, CO), 222.89 (2 C, CO), 92.04 (5 C, Cp); δ 56.77 (2 C), 25.70 (2 C) (pyrr).

Table II. Fractional Atomic Coordinates (×10^4) for Complex **1**

atom	x/a	y/b	z/c
V	56 (1)	2259 (1)	1027 (2)
S	851 (2)	737 (2)	673 (3)
C1A	−599 (8)	1892 (9)	−249 (11)
O1A	−995 (6)	1729 (7)	−984 (8)
C1B	−1266 (8)	2391 (10)	1311 (10)
O1B	−2064 (5)	2449 (8)	1487 (8)
C1C	−203 (8)	1526 (9)	2248 (11)
O1C	−364 (8)	1108 (7)	2980 (8)
C1	181 (8)	3792 (10)	672 (14)
C2	906 (11)	3342 (11)	124 (11)
C3	1508 (9)	2977 (9)	873 (14)
C4	1155 (11)	3159 (10)	1865 (12)
C5	321 (11)	3676 (10)	1719 (12)
C6	1474 (8)	717 (10)	−567 (10)
C7	2397 (10)	191 (12)	−366 (12)
C8	2751 (9)	545 (11)	645 (13)
C9	1937 (9)	529 (9)	1432 (11)

Table III. Fractional Atomic Coordinates (×10^4) for Complex **2**

atom	x/a	y/b	z/c
V	2509 (1)	2500 (0)	215 (1)
C1	3347 (10)	2500 (0)	1915 (5)
C2	4088 (7)	1745 (4)	1433 (4)
C3	5285 (6)	2031 (4)	667 (4)
C4	608 (6)	1727 (3)	501 (3)
O(1)	−578 (4)	1266 (2	696 (3)
N11	2813 (4)	1650 (2)	−1131 (3)
C12	2824 (6)	748 (3)	−1075 (4)
C13	3133 (7)	214 (3)	−1929 (5)
C14	3419 (7)	589 (3)	−2921 (4)
C15	3401 (7)	1497 (4)	−2994 (4)
C16	3095 (5)	2019 (3)	−2101 (3)
H1	2542 (92)	2500 (0)	2437 (57)
H2	3896 (71)	1162 (38)	1634 (44)
H3	5943 (58)	1688 (32)	172 (36)
H12	2661 (64)	465 (29)	−362 (36)
H13	3078 (70)	−380 (36)	−1846 (42)
H14	3668 (52)	237 (29)	−3507 (34)
H15	3526 (55)	1738 (29)	−3621 (35)

Preparation of $CpV(CO)_3L$ (L = PPh_3, dppe, dppm, Cyclohexyl Isocyanide). The syntheses of all these derivatives, using photochemical or thermal reaction conditions, have been previously reported in the literature.[3,10] The reactions with complex **1** were carried out in toluene at room temperature. After suitable workup and isolation of all the products in crystalline form, analytical and spectroscopic data in accordance with the literature were obtained.[3,10]

Results and Discussion

The room-temperature photoreaction of $CpV(CO)_4$ in a Pyrex glass apparatus, in the presence of a large excess of tht, led to the formation of crystalline **1** in good yield. The reaction mixture was maintained at room temperature and the reaction progress monitored by IR spectroscopy to avoid the unnecessary irradiation and heating responsible for fast decomposition reactions.

The structure, solved by a single-crystal X-ray diffraction analysis, consists of discrete η^5-$C_5H_5V(CO)_3(SC_4H_8)$ molecules. The coordination geometry is similar to that found in other derivatives of $CpV(CO)_4$[3] and can be described as a square pyramid. The molecular structure and numbering scheme are presented in Figure 1; bond distances and angles for complex **1** appear in Table IV. The basal plane is defined by the carbon atoms from the three carbonyls (C1A, C1B, C1C) and the sulfur atom of the tht. The vanadium atom lies 1.001 (1) Å above this plane. The $V–C_{CO}$ distances [mean value 1.95 (1) Å] and the angles subtended at

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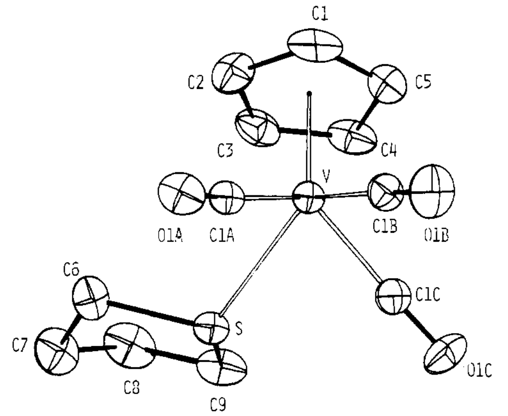


Figure 1. ORTEP drawing of complex **1** (50% probability ellipsoids).

Table IV. Selected Bond Distances: (Å) and Angles (deg) for Complex **2**

V–S	2.478 (3)	O1A–C1A	1.13 (2)
V–C1A	1.97 (1)	O1B–C1B	1.16 (1)
V–C1B	1.92 (1)	O1C–C1C	1.15 (2)
V–C1C	1.94 (1)	S–C6	1.84 (1)
V–Cp	1.93 (1)	S–C9	1.85 (1)
S–V–C1A	80.0 (4)	S–V–C1B	124.4 (4)
S–V–C1C	76.8 (4)	C1A–V–C1C	117.5 (5)
C1A–V–C1B	74.3 (5)	V–C1A–O1A	176 (1)
C1B–V–C1C	73.1 (5)	V–C1B–O1B	178 (1)
Cp–V–S	118.3 (4)	V–C1C–O1C	179 (1)
Cp–V–C1A	119.6 (6)	V–S–C6	113.2 (4)
Cp–V–C1B	117.3 (6)	V–S–C9	114.6 (4)
Cp–V–C1C	122.6 (6)	C6–S–C9	93.9 (6)

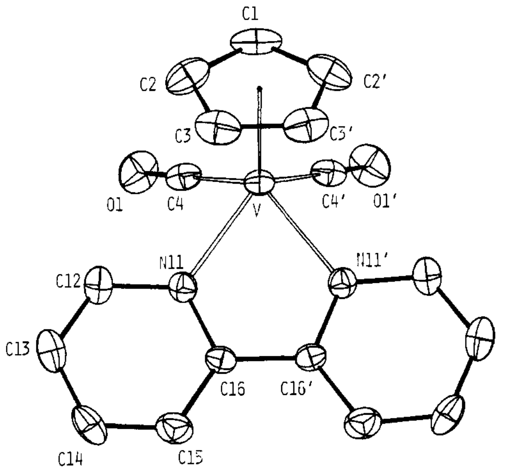


Figure 2. ORTEP drawing of complex **2** (50% probability ellipsoids). Prime indicates a transformation of x, $^1/_2 - y$, z.

Table V. Selected Bond Distances (Å) and Angles (deg) for Complex **1**[a]

V–N11	2.138 (4)	C4–O1	1.172 (5)
V–C4	1.903 (5)	N11–C12	1.361 (5)
V–Cp	1.941 (5)	N11–C1	1.360 (5)
C16–C16′	1.450 (6)		
C4–V–C4′	75.5 (2)	C4–V–N11′	126.9 (2)
N11–V–N11′	73.6 (1)	V–N11–C12	123.9 (3)
C4–V–N11	82.4 (1)	V–N11–C16	119.0 (3)
C4–V–Cp	117.2 (2)	C16–N11–C12	117.0 (4)
N11–V–Cp	115.8 (2)	V–C4–O1	178.3 (4)

[a] Prime indicates a transformation of x, $^1/_2 - y$, z.

the vanadium [mean value 76.1 (4)°] compare well with those found in related complexes.[3] Carbonyls are bonded linearly to vanadium, the V–C–O angles falling in the range 176 (1)–179 (1)°. The V–S distance [2.479 (3) Å] is in the range of values typically observed for transition-metal–sulfur bonds.[11] The cyclopentadienyl ring is η^5-bonded to the metal, and the direction of the V–Ct line (ct = centroid of the ring) is nearly perpendicular to the basal plane, with the dihedral angle between them equal to 83.5 (5)°. All other bond distances and angles are as expected.

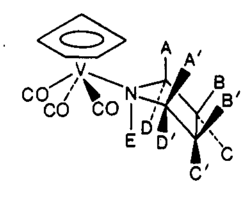
The spectroscopic data are consistent with the structure as demonstrated by the structural analysis. Three intense absorptions are present in the IR spectrum, attributable to the CO stretchings (ν_{sym} 1953 cm^{-1}; ν_{asym} 1855, 1820 cm^{-1}). The Cp ring resonances can be observed in both the ^{1}H and ^{13}C NMR spectra at 4.62 and 92.17 ppm, respectively. The coordinated tht shows two multiplets at 2.15 and 1.21 ppm in the ^{1}H spectrum (consistent with an AA′BB′ splitting pattern) and two resonances at 41.74 and 30.31 ppm in the ^{13}C NMR spectrum. No CO resonances can be observed in the 100–300 ppm range of the ^{13}C NMR spectrum, a common feature of $CpV(CO)_4$ derivatives.[12]

We can consider complex **1** as a source of the coordinatively unsaturated 16-electron species "$CpV(CO)_3$", permitting easy ligand-substitution reactions with several ligands:

$$CpV(CO)_3tht + L \xrightarrow{\text{toluene}} CpV(CO)_3L + tht \qquad (1)$$

(L = PPh_3, dppe, dppm, cyclohexyl isocyanide, pyrr). The complex $CpV(CO)_3pyrr$ (**3**), which can be isolated as air-sensitive crystals, is to our knowledge the first derivative of $CpV(CO)_4$ with an amine substituent. Surprisingly the utilization of several other nitrogen-containing ligands, such as Et_3N, CH_3CN, PhCN, pyridine, tmeda, or ammonia, catalyzes the thermal decomposition of **1** to $CpV(CO)_4$. The well-known $Cp_2V_2(CO)_5$ has never been observed, not even in traces, during all the reactions.

The structure of **3** has been assigned on the basis of its analytical and spectroscopic data. Three intense absorptions can be observed



in the IR spectrum (1950, 1850, 1825 cm^{-1}), attributable to three terminally bonded CO molecules. The coordinated pyrr is responsible for a narrow absorption in the IR spectrum at 3279 cm^{-1} due to the N–H stretching. The η^5-Cp ring shows a resonance in both the ^{1}H and ^{13}C NMR spectra at 4.63 and 92.04 ppm, respectively. The σ-bonded pyrr is responsible for five resonances observed in the ^{1}H NMR spectrum as finely structured multiplets [2.12, 1.58, 0.94, 0.64 ppm (ring); 1.12 ppm (N–H)]. As a result of the quaternization of the nitrogen atom, the AA′BB′C splitting pattern of the free pyrr [two multiplets (2.68–1.43 ppm), one singlet (1.11 ppm)] becomes AA′BB′CC′DD′E with five chemically and nine magnetically nonequivalent hydrogen atoms. Such nonequivalence does not affect the carbon atoms, which are present in the ^{13}C NMR spectrum with two signals at 56.77 and 25.70 ppm. The carbonyl resonances can be observed in the ^{13}C NMR spectrum at 251.16 and 222.89 ppm.

Reaction of complex **1** with bpy occurs even at 0 °C but can be more conveniently carried out at room temperature according to eq 2. Highly air-sensitive deep blue crystals, whose analytical

$$2CpV(CO)_3tht + bpy \xrightarrow{\text{toluene}} cis\text{-}CpV(CO)_2bpy + CpV(CO)_4 + tht \qquad (2)$$

and spectroscopic data are consistent with a *cis*-$CpV(CO)_2bpy$ structure, have been obtained in good yield. Reaction (2) is more noteworthy when remembering that bpy has been reported to react with $CpV(CO)_4$ in refluxing xylene to form $(bpy)_3V$ in very low yield (eq 3)[13] and that the direct irradiation of $CpV(CO)_4$ in the

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$$\mathrm{CpV(CO)_4 + bpy \xrightarrow{xylene} V(bpy)_3 + unidentified\ products} \qquad (3)$$

presence of bpy leads to the formation of unidentifiable products.

The structure of **2** consists of discrete *cis*-(η^5-C_5H_5)V(CO)$_2$·bpy molecules possessing an imposed crystallographic *Cm* symmetry (Figure 2). The vanadium lies on the mirror plane bisecting the C3–C3′ and C16–C16′ bonds. The coordination geometry around the metal center is square pyramidal with the two nitrogen atoms from bpy and two carbon atoms from the carbonyls on the basal plane and the centroid of η^5-bonded Cp ring on the apex. The vanadium lies at 0.898 (1) Å from the basal plane, which is perfectly planar for symmetry requirements. Bond distances and angles in the vanadium coordination sphere are in agreement with the corresponding ones observed in complex **1**, the V–N distance being 2.138 (4) Å. All bond distances and angles within the Cp ring and bpy are as expected.

Complex **2** does not display any special spectroscopic features. Two intense absorptions are present in the IR spectrum ($\nu(CO)_{sym}$ 1843 cm^{-1}; $\nu(CO)_{asym}$ 1780 cm^{-1}), as expected for a *cis*-dicarbonyl transition-metal derivative. The Cp resonances are present as singlets in the ^{1}H NMR (4.80 ppm) and ^{13}C NMR (96.55 ppm) spectra, and the resonances of the coordinated bpy are as expected for an ABCD spin system. No resonances attributable to carbonyl groups have been observed in the ^{13}C NMR spectrum.

Attempts to utilize **1** for oxidative-addition reactions with a diverse range of substrates such as CO_2, CO_2-like molecules, azobenzene, diazoalkanes, and organic azides have led to the formation of CpV(CO)$_4$ as the main product. We believe that the low affinity for CO of the mono(cyclopentadienylvanadium(III)) derivatives formed during the oxidative-addition reactions is responsible for such a failure. In other words, for each molecule of 1 that undergoes oxidative addition, three molecules of CO are released. Fast reaction of **1** with CO leads to the unreactive CpV(CO)$_4$ in 75% yield. Efforts to isolate other species from the reaction mixtures have been unsuccessful so far.

Acknowledgment. This work has been supported by the University of Groningen and the University of Parma. We are indebted to Bart Hessen for recording and discussing the NMR spectra.

Registry No. **1**, 111635-23-5; **2**, 99620-52-7; **3**, 111635-24-6; CpV(CO)$_4$, 12108-04-2; CpV(CO)$_3$PPh$_3$, 12213-09-1; CpV(CO)$_3$dppe, 73557-87-6; CpV(CO)$_3$dppm, 73574-37-5; CpV(CO)$_3$L (L = cyclohexyl isocyanide), 103903-19-1.

Supplementary Material Available: Details of the structure solutions and refinements with references and listings of coordinates for hydrogen atoms (Table SI) and thermal parameters (Table SII) for **1**, thermal parameters for **2** (Table SIII), and nonessential bond lengths and angles for both **1** and **2** (Tables SIV and SV) (6 pages); tables of calculated and observed structure factors for both structure determinations (8 pages). Ordering information is given on any current masthead page.

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Infrared Characterization of Group VI (6^1) Metal Carbonyls Adsorbed onto γ-Alumina

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Received March 27, 1987

The interactions of Cr(CO)$_6$, Mo(CO)$_6$, and W(CO)$_6$ with highly dehydroxylated γ-Al_2O_3 have been studied by the use of IR spectra, which show both a reversible adsorption and progressive room-temperature loss of CO. Adsorption of the three metal hexacarbonyls occurs via O-bonding between a CO ligand and different Lewis acid sites present at the γ-Al_2O_3 surface. These sites are as follows (in order of decreasing Lewis acid strength): (i) defective sites representing less than 1% of the surface cations; (ii) bulk tetrahedral Al^{3+} ions emerging on the surface; (iii) bulk octahedral Al^{3+} ions emerging on the surface. The sum of the last two types corresponds roughly to the total number of surface cations. Comparison of the IR spectra of the adsorbed metal carbonyls with the spectra of the homogeneous analogues formed by interaction in solution with Lewis acceptors of similar strength allowed full assignment of the IR spectra of adsorbed species and showed the close similarity between heterogeneous and homogeneous O-bonded carbonyl adducts. The major fraction of adsorbed hexacarbonyls is removed by pumping at room temperature. However, a small fraction (in the order Mo(CO)$_6$ > Cr(CO)$_6$ > W(CO)$_6$) undergoes reversible decarbonylation, giving a subcarbonyl species still O-bonded to the Lewis acid centers of the metal oxide support.

Introduction

Deposition of metal carbonyls on high surface area metal oxides can provide a convenient means to investigate ligand substitution reactions[2] and catalytic behavior.[3] Reactions catalyzed by supported group VI metal carbonyls, such as olefin metathesis and hydrogenation and Fischer–Tropsch synthesis, have recently been investigated.[4-8] A related approach is to use the immobilized carbonyls as precursor materials for the preparation of highly dispersed transition metals and to use metallic clusters for heterogeneous catalysis.[9-15] In all of these contexts, characterization of the supported metal carbonyl is a prime requirement to understand the subsequent chemical processes.

Transition aluminas[16] are among the most extensively used catalyst supports. γ-Alumina, which belongs to this group, shows a spinel-type lattice where Al^{3+} ions occupy tetrahedral and octahedral interstices in a cubic close-packed array of oxide ions. The structure of the oxide surface is not entirely clear,[17-19] particularly because relaxation of the underlying oxide structure gives

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(1) The periodic group notion in parentheses is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

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