Inorg. Chem. **1991**, *30*, 775-778 **775**

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Studies on Organometallic Oxidants: Structure, Redox Properties, and Magnetism of $(C_5H_5)VBr_3$ and $(C_5H_5)VI_3$

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Received May 22, 1990

The preparation and properties of $CpVBr_3$ and $CpVI_3$ ($Cp = \eta^5\text{-}C_5H_5$) are described. The compound $CpVBr_3$ exhibits an $E_{1/2}$ of 510 mV (vs Ag/AgCl) and is able to oxidize ferrocene. The salt $[Cp_2Fe][CpVBr_3]$ was characterized by infrared spectroscopy ($\nu_{CH}(Cp_2Fe) = 857\ cm^{-1}$), ^{57}Fe Mössbauer spectroscopy at 295 K ($\delta_1 = 0.35$, $\delta_2 = 0.421$ mm/s) and 150 K, variable-temperature magnetic susceptibility ($\mu_{eff}(300\ K) = 3.75\ \mu_B$), and ^1H NMR spectroscopy. While $CpVBr_3$ is more oxidizing than $CpVCl_3$, we find that $CpVI_3$ is less oxidizing ($E_{1/2} = 425$ mV). In solution $CpVI_3$ exists as two distinct species as shown by ^1H NMR spectroscopy. The structure of $CpVI_3$ was solved in the orthorhombic space group $Pn2_1a$ (no. 33, alternate setting) with the lattice constants $a = 11.847$ (4) Å, $b = 11.304$ (3) Å, $c = 7.532$ (1) Å, and $Z = 4$.

Introduction

There is currently considerable interest in organometallic compounds containing metals in high formal oxidation states. Many of these complexes feature cyclopentadienyl ligands and maintain their high oxidation states by virtue of electronegative, π-donor ligands such as F^-, Cl^-, O^{2-}, N^{3-}, and S^{2-}.[1] These compounds represent soluble and synthetically tractable analogues of traditional binary and ternary metal halides, oxides, and oxyhalides. In fact, the existence of a stable oxyhalide MO_nX_m often portends the stability of an analogous cyclopentadienyl compound, $(C_5R_5)MO_{n-1}X_m$. Despite their high oxidation state, few examples of these organometallic compounds are particularly good oxidants for either atom transfer[2] or electron abstraction. One reason for this situation may be that most studies have focused on the easily ionized second- and third-row metals.

We have recently described a series of cyclopentadienyl compounds that are good oxidants in terms of either their electrochemistry or their O-atom transfer ability. Thus $CpVCl_3$, which was first prepared by Fischer in 1960,[3] has an $E_{1/2}$ of 655 mV versus the standard hydrogen electrode (SHE).[4] The oxide $CpVOCl_2$ while *more highly oxidized* is ca. 100 mV *less oxidizing*, illustrating the stabilizing effect of the oxo ligand. Similarly, while Cp^*CrBr_3 ($Cp^* = \eta^5\text{-}C_5Me_5$) is a polyhalogen complex, not a Cr(IV) complex, the compound $Cp^*Cr^VOBr_2$ is an isolable intermediate in the O_2 oxidation of phosphines and sulfides.[5]

The compound $CpVCl_3$ is *oxidizing* for two reasons. First, it features a first-row transition metal in a high oxidation state. Second, its coordination environment consists of nonoxidizable (versus the metal d levels) ligands, which provide weak π stabilization. This report deals with the situation where the halide to vanadium π stabilization is further weakened. We already know that in the extreme case the halide is lost as halogen, e.g., $Cp^*CrBr_3 \rightarrow [Cp^*CrBr_2]_2 + Br_2$. Having previously investigated the properties of $CpVCl_3$, we describe in this paper the properties of $CpVBr_3$, probably the strongest known (neutral) organometallic oxidant. We then move one step further to reduce π donation from the halide to the vanadium in the form of the unusual species $CpVI_3$.

Results

Preparation and Properties of $CpVBr_3$. In 1960, Fisher, Vigoureux, and Kuzel described the reaction of $CpV(CO)_4$ and Br_2 which produced $CpVBr_3$ in high yield and purity.[3] Since that time, no reports of this compound have appeared. Indeed, the only bromide analogue of the general class of $CpVX_3$ that has been reported is Cp^*VBr_3,[6] but it is well-known that permethylation of the Cp ring lowers the redox potential by ca. 250 mV. The reduction potential of $CpVBr_3$ is quite oxidizing at 510 mV (vs Ag/AgCl, or 730 mV vs SHE). Under precisely the same experimental conditions, we find that ferrocene is oxidized at 500 mV.

Solid and Solution Characterization of $[Cp_2Fe][CpVBr_3]$. The ability of the $CpVBr_3$ to oxidize ferrocene was demonstrated by chemical synthesis. Microcrystalline samples of $[Cp_2Fe][CpVBr_3]$ are thermally sensitive; at room temperature in vacuo we observed the loss of about 5% of the ferrocene by sublimation. The IR spectrum of solid $[Cp_2Fe][CpVBr_3]$ shows a ν_{C-H} band at 857 cm^{-1} in the infrared spectrum, typical of other $[Cp_2Fe]^+$ salts. The ^{57}Fe Mössbauer spectrum of the salt at 295 and 150 K displays a distorted quadrupole doublet characterized by parameters $\delta_1 = 0.35$ (fwhh = 1.72) and $\delta_2 = 0.421$ (0.676) mm/s (at 295 K). Again, these data are typical for ferrocenium salts.[7] The magnetic susceptibility of the salt at 300 K gives an effective magnetic moment of 3.75 μ_B, whereas the spin-only value for $S = 1$ (V) and $S = {}^1/_2$ (Fe) is 3.32 μ_B. These data indicate slight ferromagnetic coupling between the V(III) and Fe(III) centers. The temperature dependence of the susceptibility down to 4.5 K indicates that the ground state is antiferromagnetic. Collectively, these measurements indicate the solid consists of Cp_2Fe^+ and $CpVBr_3^-$ subunits.

Solution ^1H NMR spectroscopy indicates that full charge transfer is not achieved in solution, however. A single broad $(C_5H_5)_2Fe$ signal is observed at 6.41 ppm downfield of TMS (Cp_2Fe, δ 4.16; $[Cp_2Fe]PF_6$, δ 35), as well as a single $(C_5H_5)VBr_3$ signal at δ 61 ($CpVBr_3$, δ 54; $CpVBr_3^-$, ca. δ 150). The position of each NMR resonance can be shifted by the presence of an excess of either reagent. For example, the addition of an excess of Cp_2Fe drives the $CpVBr_3^{\delta-}$ resonance to lower fields. We conclude that in solution there is facile reversible electron transfer between the donor Cp_2Fe and the acceptor $CpVBr_3$ (eq 1).[8]

$$Cp_2Fe + CpVBr_3 \rightleftarrows Cp_2Fe^+ + CpVBr_3^- \qquad (1)$$

Preparation and Properties of $CpVI_3$. The addition of I_2 to $CpV(CO)_4$ in CH_2Cl_2 results in the formation of $CpVI_3$, which was isolated in 75% yield. This black, air-sensitive and thermally sensitive material is prone to loss of I_2. Single crystals of $CpVI_3$, however, are thermally stable at room temperature over a period of months. Previously, this reaction had been reported to give $CpVI_2$.[9] More recently Herberhold prepared the C_5Me_5 derivative

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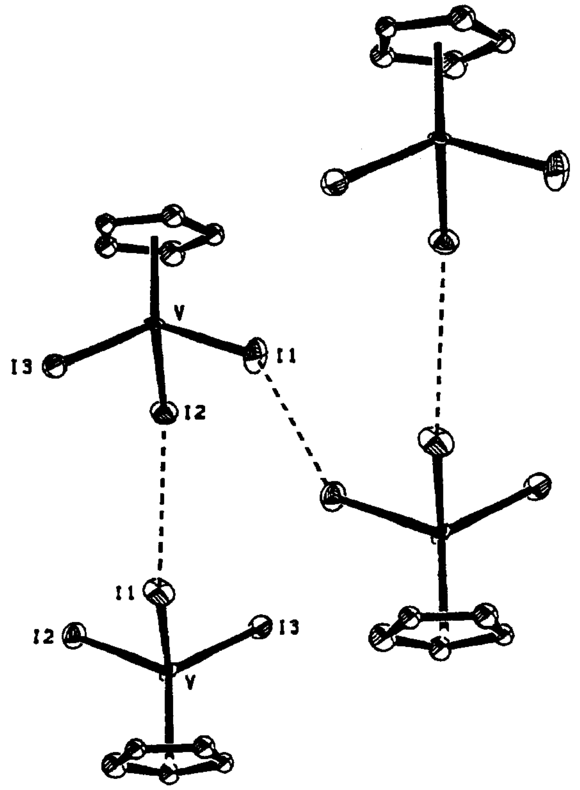

Figure 1. Solid-state packing arrangement for $CpVI_3$ at −78 °C.

Table I. Selected Bond Distances (Å) and Angles (deg) for $CpVI_3$ (−75 °C)[a]

V–I1	2.562 (5)	V–I3	2.544 (1)
V–I2	2.601 (5)	V–Cp[b]	1.926 (6)
I1–V–I2	99.5 (1)	I1–V–Cp	115.6 (1)
I1–V–I3	101.6 (1)	I2–V–Cp	116.5 (3)
I2–V–I3	101.0 (1)	I3–V–Cp	119.5 (2)

[a] The C–C distances are all 1.420 (9–20) Å. [b] Cp refers to the center of the cyclopentadienyl ring.

Cp^*VI_3 but characterized it on the basis of its mass spectrum only.[10] We have examined both the solid- and solution-state properties of $CpVI_3$.

The compound $CpVI_3$ was structurally characterized by X-ray diffraction at −75 °C (198 K). The best refinement was achieved in the polar space group $Pn2_1a$. The molecules are not well separated in the lattice but are interconnected in a chain motif via a series of long (3.824 (4) Å) I···I contacts (Figure 1). The van der Waals radius of iodide (I^-) is 2.15 Å.[11] Two iodides of each $CpVI_3$ unit are involved in the linear polymer, which has the connectivity $[I–V–I\cdots I–V–I\cdots I–V–I]_n$. The "bridging" iodides have slightly longer bonds to vanadium (2.601 (5) and 2.562 (2) Å) vs the "terminal" iodides, 2.544 (1) Å (Table I). At room temperature (298 K), the I···I contact elongates to 3.869 (2) Å.

Magnetic susceptibility measurements indicate that $CpVI_3$ is not a simple d^1 complex (Figure 2). At high temperatures the magnetic moment is indicative of an $S = {}^1/_2$ spin system, but by ca. 20 K the susceptibility response assumes a spin-pairing profile.

Cyclic voltammetry of CH_2Cl_2 solutions prepared from high-quality samples of $CpVI_3$ exhibit a reversible reduction wave at $E_{1/2}$ = 425 mV (vs Ag/AgCl). This value is notably lower than that observed for $CpVBr_3$ despite the decreased amount of π-donation of iodide or bromide. The electrochemistry of $CpVI_3$ is also distinct from that for I_2.[12] The oxidation of $CpVI_3$ is electrochemically irreversible, whereas the chloride and bromide analogues undergo quasi-reversible oxidation to vanadium(V).

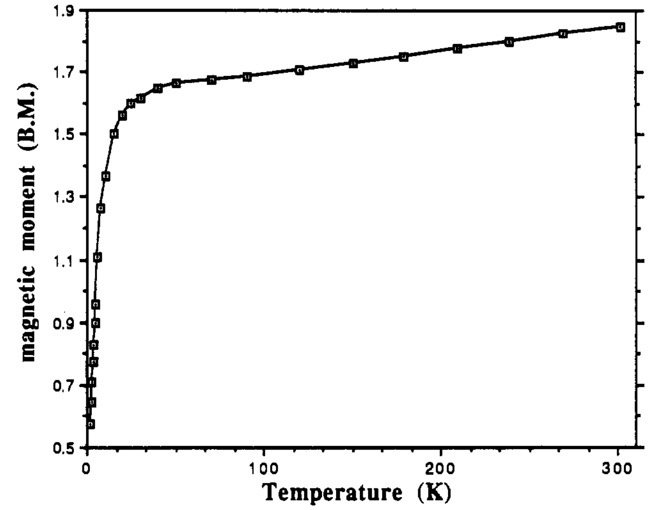

Figure 2. Magnetic susceptibility data (effective magnetic moment) at 10 kG for $CpVI_3$.

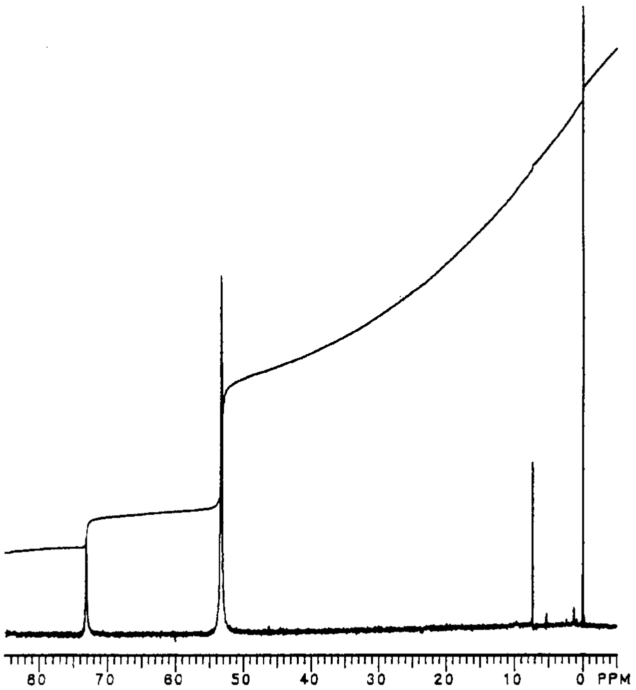

Figure 3. ^1H NMR spectrum of $CpVI_3$ (200 MHz, $CDCl_3$/TMS, 19 °C).

The ^1H NMR spectroscopy of $CpVI_3$ is unlike that for any other $CpMX_3$ complex reported to date (Figure 3). A typical spectrum displays *two* isotropically shifted signals at δ 73 and 53 in a 1:4.5 integrated ratio (the product from thermal decomposition of $CpVI_3$, "$[CpVI_2]_2$", exhibits a resonance at δ 105). The integration-weighted average position of these signals is approximately at the shift expected by extrapolation of the shifts for $CpVCl_3$ and $CpVBr_3$. Variable-temperature, -solvent ($CDCl_3$ and toluene-d_8), and -concentration (18 and 1.5 mM) studies were carried out to determine the cause of this peculiar spectrum. The positions of these signals are *not* concentration dependent, but they are solvent dependent. In contrast, the integrated ratio of these resonances is nearly independent of solvent at fixed concentration

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but somewhat dependent upon concentration. The ^{1}H NMR data for $CpVI_3$ are indicative of molecular association phenomena. The MeCp derivative of $CpVI_3$ was prepared, and similar spectra were obtained.

Discussion

Our results indicate that $CpVBr_3$ is the most highly oxidizing organometallic complexes known. With a reduction potential of 510 mV (vs Ag/AgCl; $Cp_2Fe^{+/0}$ under the same conditions, 500 mV), $CpVBr_3$ oxidizes ferrocene to give the salt$[Cp_2Fe^+][CpVBr_3^-]$. In solution, $CpVBr_3^-$ is involved in rapid reversible electron exchange with Cp_2Fe^+. The substitution of bromide for chloride in the $CpVX_3$ class increases the oxidative potential of the complex by ca. 50 mV, about twice the effect in substituting Cp for MeCp. The anodic shift in reduction potentials on changing from $CpVCl_3$ to $CpVBr_3$ is attributed to the weaker π-donor ability of bromide. When a very strong π-donating ligand such as oxide is added to the coordination sphere of these vanadium compounds, the subtle differences between the properties of chloride and bromide are overshadowed (the d^0 complexes $CpVOBr_2$ and $CpVOCl_2$ display the same reduction potential, 345 mV).

We have also established that the product of $CpV(CO)_4$ and I_2 is the vanadium(IV) complex $CpVI_3$. The $E_{1/2}$ for $CpVI_3$ is roughly equal to that for $(MeCp)VCl_3$. On the basis of ^{1}H NMR results, we believe that $CpVI_3$ aggregates in solution concomitant with the formation of polyiodide anions. Compounds of the type Cp^*CrI_x clearly display associative behavior.[13] Additionally, the chemistry of the binary vanadium halides is known to be quite complex, involving equilibria between I_2, VI_2, VI_3, and even gaseous VI_4.[14] Bottomley and co-workers isolated a species proposed to be $[(C_5Me_5)V(NO)]_2(\mu\text{-}I_8)$.[15]

Magnetic measurements show that in the solid-state $CpVI_3$ undergoes spin pairing at low temperatures. The temperature dependence of μ_{eff} resembles in profile that for $[Cp_2Co^+][(MeCp)VCl_3^-]$.[4] A localized model for this spin-pairing mechanism is not possible since $CpVI_3$ is an odd-electron entity. The structural data show a linear chain structure where already at 198 K there are significant I···I contacts. We propose that at lower temperatures the I···I contacts are strengthened such that by 20 K V^{IV} has oxidized its own iodide ligands.

It is remarkable to us that compounds of the simple composition $CpVX_3$ have such rich and varied chemistry. The structure of "$CpVI_3$" in solution remains unknown.

Experimental Section

Syntheses. All reactions and characterizations were conducted under an inert atmosphere by using standard Schlenk line techniques and a Vacuum Atmospheres Dri-Lab. Dried and oxygen-free nitrogen was used. Solvents were distilled from appropriate drying agents under nitrogen (toluene, Na; hexanes, Na/K; $CDCl_3$, P_4O_{10}).

$CpVBr_3$. A solution of 0.5 mL of Br_2 (10 mmol) in 20 mL of CH_2Cl_2 was added dropwise to a solution of $CpV(CO)_4$ (405 mg, 1.8 mmol) in 30 mL of CH_2Cl_2. After 1 h, the solvent was removed in vacuo and the residue was extracted with 60 mL of toluene. The filtrate was evaporated, and the resulting solid was washed twice with 1 mL of toluene followed by 30 mL of hexanes. The microcrystalline solid was dried in vacuo for a yield of 525 mg (83%). Anal. Calcd for $C_5H_5Br_3V$: C, 16.88; H, 1.42; V, 14.32. Found: C, 17.04; H, 1.42; V, 14.40. ^{1}H NMR ($CDCl_3$/TMS, 291 K): δ 54.5 (fwhh = 95 Hz).

$CpVI_3$. A solution of I_2 (446 mg, 1.8 mmol) in 20 mL of CH_2Cl_2 was added to a solution of $CpV(CO)_4$ (250 mg, 1.1 mmol) in 20 mL of CH_2Cl_2. After 1 h, the solvent was removed under vacuum. The crude solid was then extracted with 25 mL of toluene. The filtrate was then reduced in volume and the product was precipitated by addition of a 10-fold excess of hexanes. The solid was dried in vacuo for a yield of 75% (410 mg). Anal. Calcd for $C_5H_5I_3V$: C, 12.09; H, 1.01. Found: C, 12.25; H, 0.96.

Table II. Crystallographic Data for $(C_5H_5)VI_3$

chem formula = $C_5H_5I_3V$
fw = 496.75
space group: $Pn2_1a$ (No. 33)
a = 11.847 (4) Å
b = 11.304 (3) Å
c = 7.532 (1) Å
$\alpha = \beta = \gamma = 90°$
V = 1008.7 Å^3
$Z = 4$
T = −75 °C
λ = 0.71073 Å (Mo Kα)
ρ_{obs} = 3.271 g/cm^3
μ = 99.76 cm^{-1}
transm coeff = 0.315-0.108
R = 0.039
R_w = 0.048

Table III. Atomic Coordinates for Non-Hydrogen Atoms in $(C_5H_5)VI_3$

	x	y	z
I1	0.0790 (2)	0.0767 (5)	0.1925 (2)
I2	0.0773 (1)	0.4252 (5)	0.1891 (2)
I3	−0.13406 (5)	0.2501 (6)	0.50259 (9)
V	0.0729 (1)	0.2496	0.4122 (2)
C1	0.1160 (5)	0.2321 (10)	0.7038 (8)
C2	0.1751	0.1432	0.6085
C3	0.2519	0.2000	0.4916
C4	0.2403	0−.3241	0−.5146
C5	0.1563	0.3439	0.6458

$CpVI_3$ thus obtained slowly liberated I_2 and developed ^{1}H NMR characteristics attributable to $[CpVI_2]_2$ unless stored with a small piece of solid iodine. Alternatively, the crude reaction mixture can be extracted with toluene, the filtrate reduced in volume by half, and cooled to −25 °C. Large crystals thus obtained showed no decomposition at room temperature over a period of many months.

$(MeCp)VI_3$. This complex was synthesized according to the procedure for the C_5H_5 analogue. The ease of preparation of $(MeCp)VI_3$ depends greatly on the purity of the $(MeCp)V(CO)_4$ starting material. ^{1}H NMR ($CDCl_3$/TMS, 293 K): δ −4.5 (Me_a), 74.5 (CH_a), −10.0 (Me_b), 57 (CH_b).

Physical Measurements. Microanalyses were performed by the University of Illinois Microanalytical Laboratory, and ^{1}H NMR measurements were recorded with a Varian XL-200 200-MHz FT-NMR instrument. Electrochemical studies were carried out at ca. 1 mM in CH_2Cl_2 on a Bioanalytical Systems BAS-100 instrument equipped with a three-electrode cell using Pt working and counter electrodes and ca. 0.1 M $[^nBu_4N][PF_6]$ (TBAHFP) supporting electrolyte. Inert-atmosphere voltammograms were performed in a Dri-Lab box, utilizing a $[Cp_2Fe][PF_6]$–Cp_2Fe–TBAHFP (CH_2Cl_2) reference electrode ($[Cp_2Fe^+]$ = $[Cp_2Fe]$ = 0.5 mM) and potentials standardized to the Ag/AgCl reference system by using Cp_2Fe as an internal reference. Variable-temperature magnetic susceptibility experiments were performed on a SHE Industries VTS-50 Series 800 SQUID susceptometer; a value of -208.85×10^{-6} cgsu for the mole unit of $CpVI_3$ was used for diamagnetic correction. X-ray analysis was performed by the School of Chemical Sciences Crystallography Center.

Crystallography. The structure was determined from a crystal grown by slow cooling to −25 °C of a concentrated toluene solution. The opaque prismatic crystal selected (0.1 × 0.2 × 0.3 mm) was cut from a larger crystal and was mounted by using oil (Paratone-N, Exxon) to a thin glass fiber at −25 °C. Data collection was performed at −75 °C on an Enraf-Nonius CAD4 automated κ-axis diffractometer using graphite-monochromated molybdenum radiation (λ(Kα) = 0.71073 Å).

Crystallographic data are contained in Table II. From 2790 measured intensities, 1416 were processed in the orthorhombic model $Pn2_1a$ (conventionally $Pna2_1$), resulting in 1202 observed reflections with $I > 2.58\sigma(I)$. Total crystal exposure time was 19.07 h. The data were corrected for Lorentzian, anomalous dispersion, and polarization effects and were numerically corrected for absorption. A second shell was collected to confirm diffraction symmetry.

The structure was solved by direct methods (SHELX-86); correct positions for iodine and vanadium atoms were deduced from an E map. Subsequent least-squares difference Fourier calculations revealed positions for the carbon atoms. Carbon atoms were idealized, and hydrogen atoms were included as fixed contributors in "idealized" positions. Atomic coordinates are given in Table III. In the final cycle of least-squares refinement, vanadium and iodine atoms were refined with anisotropic thermal coefficients, carbon atoms were refined with isotropic thermal coefficients, and a group isotropic thermal parameter for the hydrogen atoms and an isotropic extinction parameter were refined. The highest peaks in the final difference Fourier map ($+1.56 > e/Å^3 > -2.85$) were in the vicinity of the iodine atoms. No apparent systematic errors were observed; R = 0.039, and R_w = 0.048.

Refinement with the centric model $Pnma$ with 1269 intensities processed resulted in 1057 observed reflections. No new features are ob-

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served in the final difference Fourier map, but a short C3–C3′ distance (1.35 (1) Å) is present; $R = 0.044$, and $R_w = 0.054$.

Acknowledgment. This work was performed with the financial support of the Department of Energy (Grant DOE-DE-ACO2-76ERO1198). D.B.M. gratefully acknowledges the support of 3M Corp. and Roger Adams Fellowships.

Registry No. $CpVBr_3$, 60530-27-0; $CpVI_3$, 131322-14-0; $(MeCp)VI_3$, 131297-75-1; $CpV(CO)_4$, 12108-04-2; $(MeCp)V(CO)_4$, 63339-27-5.

Supplementary Material Available: Tables of magnetic susceptibility data, crystal data and refinement, and position and thermal parameters (6 pages); a table of final and observed structure factors (4 pages). Ordering information is given on any current masthead page.

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Synthesis and Structures of Rhodium Isocyanide Complexes Containing an η^2-Hydrotris(3,5-dimethylpyrazolyl)borate Ligand

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Received August 10, 1990

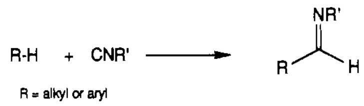
Complexes of the general type $HB(Pz^*)_3Rh(CNR)_2$ (Pz^* = 3,5-dimethylpyrazol-1-yl, R = neopentyl, 2,6-xylyl, methyl) were prepared by reaction of an isocyanide and $K[HB(Pz^*)_3]$ with $[RhCl(C_2H_4)_2]_2$ in benzene. The complexes with R = neopentyl (**1a**) and R = 2,6-xylyl (**1b**) have been structurally characterized. Complex **1a** crystallizes in the monoclinic space group $P2_1/c$ with $a = 12.882$ (5) Å, $b = 12.740$ (6) Å, $c = 18.836$ (7) Å, $\beta = 101.11$ (3)°, $V = 3033$ (4) Å^3, and $Z = 4$. Complex **1b** crystallizes in the triclinic space group $P\bar{1}$ with $a = 10.179$ (4) Å, $b = 13.415$ (4) Å, $c = 14.792$ (9) Å, $\alpha = 67.06$ (3)°, $\beta = 75.61$ (4)°, $\gamma = 75.47$ (3) °, $V = 1775$ (3) Å^3, and $Z = 2$. The $HB(Pz^*)_3$ ligand in both **1a** and **1b** is bidentate, with the noncoordinated pyrazole ring lying roughly cofacial with the square plane formed by the metal, two-coordinated isocyanides, and two-coordinated pyrazole rings with $HB(Pz^*)_3$. A comparison of the infrared and NMR spectra of **1a** in solution (C_6D_6) and the solid state (KBr pellet) with the corresponding solution and solid-state spectra of $H_2B(Pz^*)_2Rh(CNR)_2$ (**2**) (R = neopentyl) indicates that complex **1a** remains square planar in solution and possesses a rapidly fluxional bidentate $HB(Pz^*)_3$ ligand. Complex **1a** reacts with HBF_4 to give the metal hydride salt $[HB(Pz^*)_3Rh(H)(CNR)_2]BF_4$ (**3**) (R = neopentyl), which has been structurally characterized. Complex **3** crystallizes in the monoclinic space group $P2_1/c$ with $a = 12.028$ (9) Å, $b = 26.234$ (6) Å, $c = 12.298$ (14) Å, $\beta = 100.13$ (5)°, $V = 3820$ (8) Å^3, and $Z = 4$, displaying an octahedral geometry in which the $HB(Pz^*)_3$ ligand is tridentate.

Introduction

Since its original synthesis by Trofimenko,[1] hydrotris(pyrazolyl)borate ($HB(Pz)_3$) has been widely used as a ligand in the synthesis of novel transition-metal complexes.[2] The $HB(Pz)_3$ ligand is normally tridentate and has been considered to be both sterically and electronically similar to the cyclopentadienyl anion (Cp).[3] Complexes containing the $HB(Pz)_3$ ligand often display fluxional behavior which can vary depending on the hapticity and coordination environment of the $HB(Pz)_3$ ligand.[4]

Recently, Ghosh and Graham reported that the complex $HB(Pz^*)_3Rh(CO)_2$ (Pz^* = 3,5-dimethylpyrazol-1-yl) was capable of forming metal alkyl hydrides of the type $HB(Pz^*)_3Rh(H)(R)(CO)$ (R = alkyl) upon photolysis in alkane solution.[5] They also presented infrared spectral evidence suggesting that $HB(Pz^*)_3Rh(CO)_2$ exists in solution as a mixture of isomers in which the $HB(Pz^*)_3$ ligand is either bidentate or tridentate.[6] Recently, they have also obtained a crystal structure for the related complex $HB(F_6\text{-}Pz^*)_3Rh(CO)_2$ ($F_6\text{-}Pz^*$ = 3,5-bis(trifluoromethyl)pyrazo-1-yl), which shows bidentate coordination of the $HB(F_6\text{-}Pz^*)_3$ ligand.[7]

We prepared the isocyanide complexes $HB(Pz^*)_3Rh(CNR)_2$ (**1a–c**), analogous to our previously studied $(C_5Me_5)Rh(CNR)_2$,[8] in the hope that they would be active as catalysts for hydrocarbon functionalization[9] (eq 1). X-ray crystal structures were obtained



(1)

for two analogues, both of which show that the $HB(Pz^*)_3$ ligand is bound in the uncommon bidentate mode.[10] Infrared and NMR spectral data are presented which indicate that the structures of these complexes in solution contain a fluxional bidentate $HB(Pz^*)_3$ ligand.

Results

Complexes **1a–c** are prepared by slow addition of the appropriate isocyanide to a benzene solution of $[RhCl(C_2H_4)_2]_2$, during which time the original orange suspension of the rhodium dimer becomes black. The black intermediate(s) has (have) not been

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