ORGANOMETALLICS

Volume 4, Number 6, June 1985

Reactions of Derivatives of Bis(pentamethylcyclopentadienyl)vanadium with Nitric Oxide and the Crystal Structure of Paramagnetic $[(\eta\text{-}C_5(CH_3)_5)_2VBr(NO)][(\eta\text{-}C_5(CH_3)_5)VBr_2(NO)]$

Frank Bottomley,* James Darkwa, and Peter S. White

Department of Chemistry, University of New Brunswick, Fredericton, New Brunswick, Canada E3B 5A3

Received September 24, 1984

Reaction of Cp^*_2VI ($Cp^* = \eta^5\text{-}C_5(CH_3)_5$) with NO gave $(C_5(CH_3)_5)_2VI(NO)$, a 19-electron complex showing a single ν(NO) absorption band at 1710 cm^{-1} and a 24-line ESR spectrum. The complex is believed to have a linear {VNO} group and planar but displaced $C_5(CH_3)_5$ rings. The reaction between $Cp^*_2VBr_2$ and NO gave the salt $[Cp^*_2VBr(NO)][Cp^*VBr_2(NO)]$ which was characterized by X-ray diffraction. The cation is diamagnetic (18 electrons) with ν(NO) at 1755 cm^{-1}; the 16-electron anion has ν(NO) at 1715 cm^{-1}, a magnetic moment of 2.55 μ_B and an eight-line ESR spectrum with A_{iso} = 71.35 G, showing that the two unpaired electrons are localized on the vanadium atom. Only two electrons take part in V–NO π-bonding; therefore the ν(NO) frequencies and the VNO structural parameters are very similar in the cation and anion (V–N = 1.746 (16) and 1.741 (17) Å, N–O = 1.165 (23) and 1.134 (21) Å, and V–N–O = 175.0 (1.4) and 165.6 (1.8)°, respectively). The V–Br and V–Cp* distances are longer in the cation than in the anion (V–Br = 2.559 (3) vs. 2.483 (5) and 2.441 (4) Å and V–Cp* = 2.005 and 2.020 vs. 1.972 Å, respectively). The nitrosyls described were thermally unstable in solution; above −30 °C they gave green compounds which showed no ν(NO) absorption bands.

Introduction

In a recent paper we reported on the reactions of Cp_2V ($Cp = \eta^5\text{-}C_5H_5$) and its derivatives with nitrogen monooxide (nitric oxide, NO).[1,2] The most interesting complexes obtained from these reactions were $(C_5H_5)_2VX(NO)$ (X = Br, I), 19-electron nitrosyls showing fluxionality of the {VNO} group. A major problem in the investigation of these complexes was that they polymerized and also decomposed thermally in solution to the oxygen-bridged tetramer $[(CpVX)_2(CpV(NO))_2(\mu\text{-}O)_4]$. In the belief that substitution of Cp* ($Cp^* = \eta^5\text{-}C_5(CH_3)_5$) for Cp would lead to an enhanced stability of these complexes,[3,4] we prepared $(C_5(CH_3)_5)_2VI(NO)$. The properties of this complex were sufficiently different from those of $(C_5H_5)_2VI(NO)$ that we were prompted to investigate the reactions of other Cp* derivatives of vanadium with NO. With V(II) derivatives such as Cp^*_2V and $Cp^*_2V(CO)$ the substitution of Cp* for Cp proved no advantage; similar intractable mixtures of products as before[1] were obtained. With the halo derivatives Cp^*_2VX and $Cp^*_2VX_2$ (X = Cl, Br, I) it soon became apparent that the order of stability of the nitrosyl products was I > Br > Cl, as was also found in the work with Cp_2VX and Cp_2VX_2. In fact the chloro derivatives were oxidized to oxo-bridged polymers by NO, with concomitant production of N_2O.[5] We have therefore concentrated our work on the iodo and bromo derivatives, and the results are reported here.

Results and Discussion

Reaction of Cp_2^*VI with NO. In a 1:1 mole ratio this reaction gave only one product, yellow monomeric $(C_5(CH_3)_5)_2VI(NO)$. Unlike $(C_5H_5)_2VI(NO)$, which was fluxional and also polymerized,[1,2] $(C_5(CH_3)_5)_2VI(NO)$ did not have a fluxional {VNO} group; only one ν(NO) frequency appeared in the infrared spectrum in CH_2Cl_2 solution, at 1710 cm^{-1}. As a Nujol mull a doublet appeared (1695 and 1704 cm^{-1}), presumably due to crystal lattice effects. The ESR

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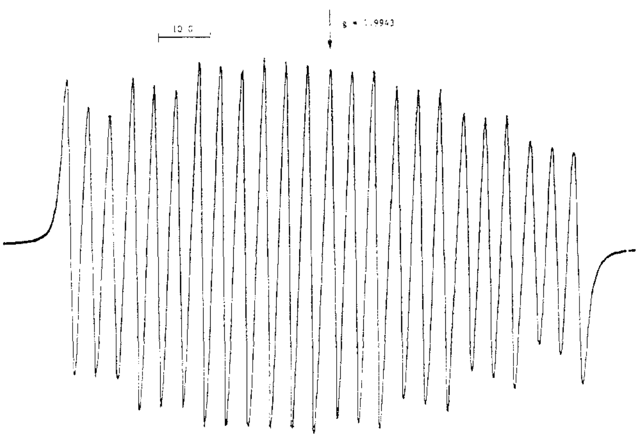

Figure 1. The electron spin resonance spectrum of $(C_5(CH_3)_5)_2VI(NO)$ at 20 °C.

spectrum in CH_2Cl_2 solution at 20 °C showed a simple 24-line spectrum resulting from hyperfine coupling of the unpaired electron in this formally 19-electron complex to both the ^{51}V ($I = {}^7/_2$) and ^{14}N ($I = 1$) nuclei (Figure 1). The observed isotropic coupling constants were 4.02 G for ^{14}N and 12.26 G for ^{51}V with $g = 1.9943$. The assignment was confirmed by a computer simulation which yielded the coupling constants $A_{iso}(^{14}N) = 4.10$ G and $A_{iso}(^{51}V) = 12.55$ G. The small A_{iso} for ^{51}V indicates a low-spin density on vanadium of the odd electron.[6] This is in agreement with the molecular orbital model for $Cp_2MX(NO)$ complexes derived by Lauher and Hoffmann.[7] The antibonding orbital accommodating the 19th electron is almost completely localized on the Cp ring and NO ligand, with little metal contribution. The hyperfine coupling to ^{13}C of the $C_5(CH_3)_5$ rings predicted by this model was not observed because of the low natural abundance of ^{13}C[8] and the fluxionality of the rings (see below).

The ESR spectrum shows that the odd electron resides in an orbital which is antibonding with respect to NO and to Cp*.[7] This fact should give rise to one or more of four possible distortions of the $Cp^*_2VI(NO)$ molecule. These are (A) bending of the {VNO} group as occurs[9] in nitrosyls of groups 8–10 of the periodic table,[34] (B) a linear {VNO} group but with short V–N and long N–O bond distances, as occurs in $CpW(NO)_2(P(OPh)_3)$,[10] (C) a normal linear {VNO} group with a nonplanar $C_5(CH_3)_5$ ring, as occurs in $Cp(\eta^3\text{-}C_5H_5)W(CO)_2$,[11] and (D) planar $C_5(CH_3)_5$ groups, but with the ring centers displaced with respect to the V atom, as occurs in $(C_5H_5)_2MoR(NO)$ (R = CH_3,[12] $\eta^1\text{-}C_5H_5$[13]) and $(C_5H_5)(p\text{-}FC_6H_4C_5H_4)MoI(NO)$.[14] For cases A and B, a low $\nu(NO)$ stretching frequency in the infrared spectrum would be expected. The observed value 1710 cm^{-1} is higher than those for either of the forms of $Cp_2VI(NO)$ (1590 or 1670 cm^{-1}),[1] despite the increased basicity of Cp* compared to Cp, and also higher than those in the 19-electron $CpW(NO)_2(P(OPh)_3)$ (1653, 1613 cm^{-1})[10] or the 20-electron $(C_5H_5)_2MoX(NO)$ (1600–1650 cm^{-1}).[15] Therefore the infrared spectrum is strongly against possibilities A or B. A nonplanar $C_5(CH_3)_5$ ring (C) is less likely than for C_5H_5 because of the increased basicity and steric crowding of $C_5(CH_3)_5$. We therefore favor D, a linear {VNO} group with normal V–N and N–O distances and one displaced but planar $C_5(CH_3)_5$ ring, as in $(C_5H_5)_2MoR(NO)$.[12–14] The $C_5(CH_3)_5$ rings will be fluxional in the sense that the normal to the ring plane through the V atom precesses around the center of the ring.

In the solid state $(C_5(CH_3)_5)_2VI(NO)$ was thermally stable though very air sensitive. In CH_2Cl_2 solution it decomposed slowly at temperatures above −30 °C to give a green material which showed no $\nu(NO)$ absorptions in the infrared spectrum. The first visible signs of the decomposition appeared after 24 h at room temperature. The complex was only sparingly soluble in solvents other than CH_2Cl_2.

When Cp^*_2VBr was treated with NO a green product which showed several $\nu(NO)$ absorptions in the infrared spectrum was obtained. However these absorptions all disappeared on repeated recrystallization.

Reaction of $Cp^*_2VBr_2$ with NO. This reaction proceeded smoothly to give in 70% yield the pale orange salt $[Cp^*_2VBr(NO)]^+[Cp^*VBr_2(NO)]^-$ whose structure was determined by X-ray diffraction (see below). As for other $Cp^*_nVX_n(NO)$ complexes, the salt was thermally unstable in CH_2Cl_2 solution giving the usual green solid showing no $\nu(NO)$ absorptions in the infrared spectrum. This green product was the only other identifiable product of the reaction of $Cp_2^*VBr_2$ with NO, suggesting that the reaction proceeds via the simple equation:

$$2Cp^*_2VBr_2 + 2NO \rightarrow [Cp^*_2VBr(NO)][Cp^*VBr_2(NO)] + \text{“}Cp^*Br\text{”} \quad (1)$$

The salt showed two $\nu(NO)$ absorptions in the infrared spectrum, at 1748 and 1760 cm^{-1} (Nujol mull) or 1715 and 1755 cm^{-1} (CH_2Cl_2 solution). The ESR spectrum was a sharp eight-line signal with a large $A_{iso}(^{51}V)$ of 71.35 G ($g = 2.0140$) indicating that the unpaired electrons are localized on the vanadium ($I = {}^7/_2$) with no coupling to the nitrosyl ligand. The magnetic moment at room temperature was 2.55 μ_B (uncorrected for any diamagnetism). The electron count of the cation is formally 18, and it will be diamagnetic; that of the anion is 16. The $[Cp^*VBr_2(NO)]^-$ anion is a pseudooctahedron and will have four electrons in the remnants of the three t_{2g} orbitals; two unpaired electrons are therefore expected. The somewhat low magnetic moment (compared to the spin-only value of 2.83 μ_B[16]) is at least partially due to the lack of a correction for the diamagnetism of the cation. The two paired electrons will be involved in π-back-bonding to the nitrosyl ligand leaving the two unpaired electrons localized on the vandium, in agreement with the ESR spectrum. In both the cation and anion only two electrons take part in back donation to the nitrosyl, thus accounting for the closeness of the $\nu(NO)$ frequencies. The vibration at low frequency (1715 cm^{-1}) will be due to the anion, which is, so far as we are aware, the first example of a paramagnetic nitrosyl with an even number of electrons.

The observation of an ESR signal for a d^2 complex at room temperature is unusual. Spin–orbit coupling of the $^3A_{2g}$ ground state of a trigonally distorted octahedron to a low-lying ^3E_g excited state lowers the spin-lattice relaxation time, and ESR measurements at low temperature are required.[17a] In the case of $[Cp^*VBr_2(NO)]^-$ the sym-

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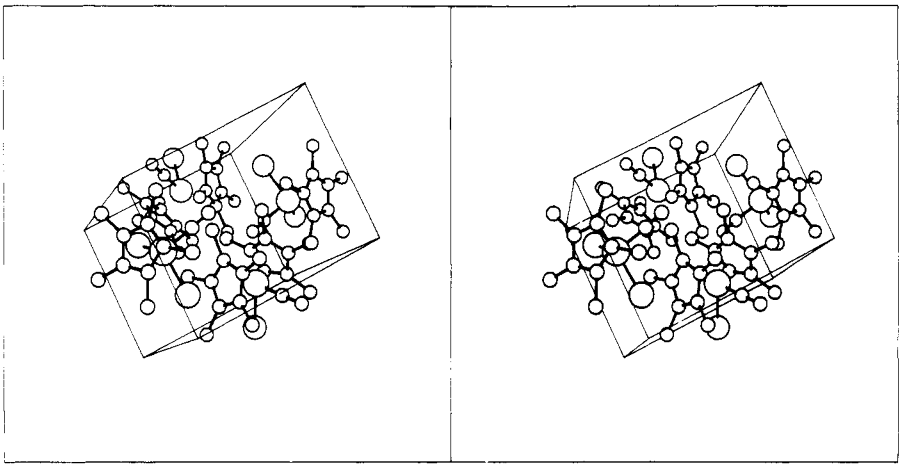

Figure 2. The unit cell of $[Cp^*_2VBr(NO)][Cp^*VBr_2(NO)]$. This is a stereoscopic drawing (PLUTO[32]).

Table I. Important Bond Distances (Å) and Angles (deg) in the Cation $[Cp^*_2VBr(NO)]^+$ (ESDs in Parentheses)[a]

V-N	1.746 (16)	V-N-O	175.0 (1.4)
V-Br	2.559 (3)	N-V-Br	86.4 (0.5)
V-Cp^a(1)	2.005	Cp^a-V-Cp^a	141.9
V-Cp^a(2)	2.020		
N-O	1.165 (23)		

[a] Cp^a is the centroid of the $C_5(CH_3)_5$ ring.

Table II. Important Bond Distances (Å) and Angles (deg) in the Anion $[Cp^*VBr_2(NO)]^-$ (ESDs in Parentheses)[a]

V-N	1.741 (17)	V-N-O	165.6 (1.8)
V-Br(2)	2.483 (5)	N-V-Br(2)	100.8 (0.6)
V-Br(3)	2.441 (4)	N-V-Br(3)	98.3 (0.5)
V-Cp^a	1.972	N-V-Cp^a	115.1
N-O	1.134 (21)	Br(2)-V-Br(3)	101.4 (0.2)
		Br(2)-V-Cp^a	119.1
		Br(3)-V-Cp^a	118.7

[a] Cp^a is the centroid of the $C_5(CH_3)_5$ ring.

metry is very much reduced (C_s) and the simple crystal field approximation does not apply; we have observed eight-line ESR spectra at room temperature for other d^2 complexes of vanadium having low symmetry, e.g., $Cp_2V(NCO)$.[1] The observation of a g value greater than 2.0023 for a vanadium complex is also unusual. However Cp_2VBr_2 and Cp_2VClBr also have g values greater than 2.0023.[17b]

Reaction of $Cp_2^*VI_2$ with NO gave a nitrosyl complex of empirical formula $Cp^*_4V_2I_8(NO)_2$ which is still under investigation.

Structure of $[Cp^*_2VBr(NO)][Cp^*VBr_2(NO)]$. The structure consists of well-separated cations and anions (Figure 2). The closest distance between a bromo ligand of one ion and a vanadium of the other is 5.5 Å, so there is no bridging between the ions. The geometries of the cation and anion are shown in Figures 3 and 4, respectively, the important distances and angles in Tables I and II. A more complete list of individual distances and angles is available with the supplementary material. The cation has the usual pseudotetrahedral structure about the vanadium atom (regarding the center of the Cp* ring as a single ligand), and the anion is a piano stool.

The {VNO} groups have essentially identical geometries in the cation and anion, despite the different formal electron counts[9] ($\{VNO\}^2$ in the cation and $\{VNO\}^4$ in the anion). This is because only two of the four available electrons in the anion participate in π-bonding, and π-bonding is crucial in determining the geometry of the {MNO} group.[9,18] The only significant difference (and even that is of marginal significance) is the VNO angle, 175.0 (1.4)° in the cation and 165.6 (1.8)° in the anion. However both angles are close to 180°, and as Kettle[19] has noted, there is no requirement for V–N–O to be linear in ions of such low symmetry (C_s). The two electrons participating in π-back-bonding in the anion will occupy one of the two π^*-orbitals of NO, and bending in the plane perpendicular to the major axis of this orbital will not affect this π-bonding. The same argument is true for the cation, though

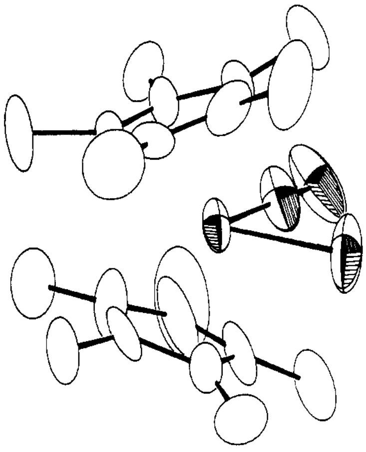

Figure 3. Geometry of the cation $[Cp^*_2VBr(NO)]^+$.

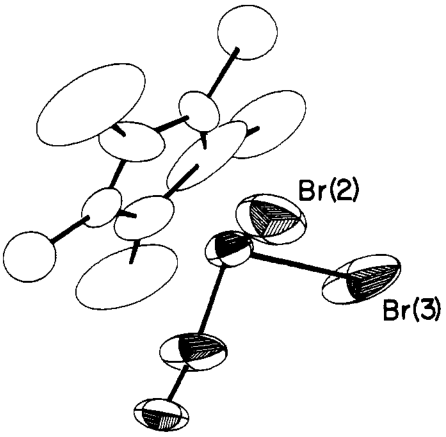

Figure 4. Geometry of the anion $[Cp^*VBr_2NO)]^-$.

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here movement of the oxygen atom out of the BrVN plane is restricted by the steric bulk of the $C_5(CH_3)_5$ rings. The V–N distances, 1.746 (16) and 1.741 (17) Å, are longer than observed in $\{VNO\}^4$ complexes, which average 1.68 Å,[20-23] again reflecting the number of electrons available for π-bonding.

Because of the different number of electrons surrounding the vanadium and the different coordination numbers (18 and 8 in the cation and 16 and 6 in the anion, respectively), the V–Br distances are shorter in the anion (2.441 (4) and 2.483 (5) Å) than in the cation (2.559 (3) Å). The same applies to the V–Cp^a distances, where these are defined as the distances between the respective V atoms and the centroid of the η^5-$C_5(CH_3)_5$ rings. The V–Cp^a distances in the cation, 2.005 and 2.020 Å, are longer than in the anion, 1.972 Å. The V–Cp^a distances lie in the range recently found for four $Cp^*{}_2V$ derivatives, 1.92–2.06 Å.[4,24] The Cp^aVCp^a angle in the cation, 141.9°, is the same as in $Cp^*{}_2V(CN)(C_6H_{11}NC)$ (142.1°[4]), which is the only other $Cp^*{}_2V(III)$ derivative which has been structurally characterized. The Cp* rings in the cation are staggered with respect to one another (see Figure 3). The only comparable complex containing a V–Br bond to be structurally characterized is $Cp_2VBr(C_2(CN)_4)$, but the *R* value was so high that no parameters were given;[25] V–Br in the five-coordinate V(V) anion $[VOBr_4]^-$ is 2.412 (1) Å.[26]

Experimental Section

General Data. All experiments were carried out under argon or vacuum using standard vacuum line techniques. Solvents were predried, stored over methyl lithium and distilled under vacuum. The complexes $Cp^*{}_2V$,[27] $Cp^*{}_2VI$,[4] and $Cp^*{}_2VI_2$[4] were prepared by the methods in the literature cited. The preparation of the starting materials $Cp^*{}_2VBr$ and $Cp^*{}_2VBr_2$, which have not been described previously, is given below. Nitrogen monoxide (99%) was purified by passage through silica gel at −78 °C. All other chemicals were reagent grade. Volumes of gaseous reactants and products were measured by using calibrated bulbs and gaseous products were separated by a Toepler pump using traps at different temperatures and a Cu/CuO bed at 300 °C. Instruments used were a Perkin-Elmer 683 infrared spectrophotometer (spectra measured as Nujol or Fluorolube mulls or in solution between KBr plates), an Alpha Scientific electromagnet with a Cahn electrobalance to measure magnetic moments by the Faraday method, and a locally modified version of the Varian E-4 ESR spectrometer. Microanalyses and molecular weight determinations (by osmometry) were by the Analytische Laboratorien, Engelskirchen, West Germany.

Preparation of Bis(pentamethylcyclopentadienyl)-bromovanadium. A solution of $Cp^*{}_2V$ (1.13 g, 3.52 mmol) in ether (30 cm^3) was cooled to −30 °C. Bromine (0.26 g, 1.62 mmol) was dissolved in ether (20 cm^3), precooled to −30 °C and added dropwise while being stirred. Yellow-brown $Cp^*{}_2VBr_2$ precipatated. When the mixture was warmed to room temperature with vigorous stirring, the solid disappeared, leading to a dark blue solution. After the solution was stirred for 3 h, the solvent was removed and the resultant solid extracted with hexane. When the hexane solution was cooled to −78 °C, blue crystals of $Cp^*{}_2VBr$ were obtained: yield 0.91 g, 65%. Anal. Calcd for $C_{20}H_{30}BrV$: C, 59.8; H, 7.5. Found: C, 59.4; H, 7.8. The product had very similar properties to the $(\eta^5\text{-}C_5(CH_3)_4(CH_2CH_3))_2VBr$ prepared by Köhler et al.[28]

Preparation of Bis(pentamethylcyclopentadienyl)dibromovanadium. A solution of $Cp^*{}_2V$ (0.95 g, 2.95 mmol) in ether (30 cm^3) was cooled to −30 °C. Bromine (0.47 g, 2.95 mmol) was dissolved in ether (20 cm^3), precooled to −30 °C, and added dropwise to the $Cp^*{}_2V$ solution while being stirred. Yellow brown $Cp^*{}_2VBr_2$ precipitated during reaction and was removed by filtration, keeping the solution at −30 °C. The product was washed well with cold ether: yield 1.40 g, 98%. Anal. Calcd for $C_{20}H_{30}Br_2V$: C, 49.9; H, 6.3. Found: C, 50.3; H, 6.3.

Reaction of Bis(pentamethylcyclopentadienyl)iodovanadium with Nitrogen Monoxide. Preparation of Bis(pentamethylcyclopentadienyl)iodonitrosylvanadium, $(C_5(CH_3)_5)_2VI(NO)$. A solution of $Cp^*{}_2VI$ (1.10 g, 2.45 mmol) in toluene (40 cm^3) was incubated with NO (2.40 mmol) at 20 °C. Upon addition of the gas the deep green solution slowly turned brown precipitating a golden colored solid in 1 h; stirring continued for 24 h. No gaseous products were found. The solid was isolated by filtration and washed several times with hexane to remove unreacted starting material. Recrystallization from a mixture of CH_2Cl_2–hexane (1:3) produced pure $(C_5(CH_3)_5)_2VI(NO)$ with $\nu(NO)$ at 1704 and 1695 cm^{-1} in Nujol mull and 1710 cm^{-1} in CH_2Cl_2 solution: yield 0.82 g, 69% (after recrystallization) based on NO used. Anal. Calcd for $C_{20}H_{30}INOV$: C, 50.2; H, 6.3; N, 2.9 Found: C, 49.7; H, 6.3; N, 2.8.

Reaction of Bis(pentamethylcyclopentadienyl)dibromovanadium with Nitrogen Monoxide. Preparation of [Bis(pentamethylcyclopentadienyl)bromonitrosylvanadium] [(Pentamethylcyclopentadienyl)dibromonitrosylvanadate]. A suspension of $Cp^*{}_2VBr_2$ (0.93 g, 1.93 mmol) in toluene (75 cm^3) was incubated with NO (1.90 mmol). The brown suspension gradually turned to a light orange suspension in a green solution. The orange product was isolated by filtration after 24 h and recrystallized from CH_2Cl_2–hexane (2:1). Slow diffusion of hexane into the CH_2Cl_2 gave crystals of $[Cp^*{}_2VBr(NO)][Cp^*VBr_2(NO)]$ suitable for X-ray structural determination (yield 0.43 g, 55%). The complex showed $\nu(NO)$ at 1760 and 1748 cm^{-1} in Nujol and Fluorolube mulls and 1755 and 1715 cm^{-1} in CH_2Cl_2 solution in the infrared spectrum; magnetic moment, μ_{eff} = 2.55 μ_B (20 °C, uncorrected). Anal. Calcd for $C_{30}H_{45}Br_3O_2N_2V_2$: C, 44.6; H, 5.6; N, 3.5. Found: C, 43.8; H, 5.6; N, 3.2%.

Determination of the Crystal Structure of $[Cp^*{}_2VBr(NO)][Cp^*VBr_2(NO)]$. Collection and Reduction of Intensity Data. Crystals were obtained by layering a solution of $[Cp^*{}_2VBr(NO)][Cp^*VBr_2(NO)]$ in CH_2Cl_2 with hexane and storing this at −30 °C for 3 weeks. The crystals were coated with air-free "Apiezon" grease and mounted in sealed tubes under argon. The space group and symmetry were determined by using precession photographs. Cell dimensions were determined at 20 °C from 12 Friedel pairs of reflections accurately centered on a Picker FACS-1 4 circle computer-controlled diffractometer, with which instrument the intensity data were measured.

Crystal data: $[Cp^*{}_2VBr(NO)][Cp^*VBr_2(NO)]$, $C_{30}H_{45}Br_3N_2O_2V_2$, M_r = 807.3; monoclinic, $P2_1$; a = 10.353 (2) Å, b = 19.160 (8) Å, c = 8.401 (3) Å, β = 92.68 (2)°, V = 1664.6 Å^3; Z = 2; D_{calcd} = 1.61 Mg m^{-3}; Mo Kα radiation, λ = 0.71073 Å; μ = 4.08 mm^{-1}, crystal dimensions 0.40 × 0.30 × 0.25 mm; 2254 independent reflections to $2\theta_{max}$ = 45°, of which 1544 were judged as observed ($I > 3\sigma(I)$) using an ω–2θ scan; final R (= $\sum\Delta|F|/\sum|F|$) = 0.069, R_w (= $(\sum w(\Delta F)^2/\sum wF^2)^{1/2}$) = 0.068; maximum residual intensity 0.83 e Å^{-3}, minimum residual intensity 1.20 e Å^{-3}. Because of the low value of μ no absorption correction was made; no significant change in the intensity of the standards was observed during collection of the data.

Structure Solution and Refinement. Preliminary positions for the vanadium atoms were found using the MULTAN-80 package.[29] The positions of these atoms were used in the phasing of a Fourier synthesis and the positions of all non-hydrogen atoms

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Table III. Positional Parameters of the Non-Hydrogen Atoms of the $[Cp^*{}_2VBr(NO)]^+$ Cation

atom	x	y	z
V(1)	0.4725 (2)	0.2477	0.8922 (3)
Br(1)	0.3998 (2)	0.1765 (2)	1.1298 (2)
N(1)	0.541 (1)	0.3056 (9)	1.033 (2)
O(1)	0.595 (2)	0.3450 (9)	1.118 (2)
C(11)	0.554 (2)	0.1703 (9)	0.702 (2)
C(12)	0.617 (2)	0.232 (1)	0.686 (2)
C(13)	0.689 (2)	0.246 (1)	0.826 (3)
C(14)	0.664 (2)	0.191 (1)	0.940 (2)
C(15)	0.581 (2)	0.140 (8)	0.860 (2)
C(16)	0.487 (2)	0.126 (1)	0.573 (2)
C(17)	0.643 (2)	0.271 (1)	0.536 (3)
C(18)	0.782 (2)	0.304 (2)	0.847 (4)
C(19)	0.732 (2)	0.181 (1)	1.093 (2)
C(20)	0.554 (3)	0.071 (1)	0.916 (4)
C(21)	0.267 (1)	0.2507 (7)	0.756 (2)
C(22)	0.249 (2)	0.274 (1)	0.907 (3)
C(23)	0.319 (1)	0.334 (1)	0.939 (9)
C(24)	0.385 (2)	0.3497 (8)	0.798 (2)
C(25)	0.349 (2)	0.3017 (8)	0.682 (2)
C(26)	0.195 (2)	0.192 (1)	0.669 (4)
C(27)	0.143 (2)	0.245 (1)	1.014 (3)
C(28)	0.305 (2)	0.376 (1)	1.083 (2)
C(29)	0.450 (2)	0.416 (1)	0.770 (3)
C(30)	0.358 (3)	0.310 (2)	0.504 (2)

Table IV. Positional Parameters of the Non-Hydrogen Atoms of the $[Cp^*VBr_2(NO)]^-$ Anion

atom	x	y	z
V(2)	0.0412 (3)	0.4563 (2)	0.4740 (3)
Br(2)	−0.0167 (2)	0.3400 (2)	0.3617 (4)
Br(3)	0.0691 (3)	0.4296 (2)	0.7575 (3)
N(2)	0.204 (2)	0.461 (1)	0.431 (2)
O(2)	0.305 (1)	0.4789 (7)	0.405 (2)
C(31)	−0.164 (2)	0.504 (1)	0.439 (4)
C(32)	−0.108 (2)	0.507 (1)	0.292 (2)
C(33)	−0.001 (2)	0.547 (1)	0.309 (2)
C(34)	0.011 (2)	0.5712 (9)	0.455 (3)
C(35)	−0.096 (4)	0.547 (2)	0.545 (2)
C(36)	−0.293 (3)	0.459 (2)	0.450 (6)
C(37)	−0.159 (5)	0.473 (2)	0.129 (4)
C(38)	0.086 (3)	0.566 (2)	0.186 (5)
C(39)	0.109 (5)	0.622 (2)	0.516 (9)
C(40)	−0.154 (7)	0.561 (3)	0.697 (4)

determined by successive Fourier, difference Fourier, and partial refinement techniques. The structure was refined by a standard least-squares technique, minimizing the function $\sum w(\Delta F)^2$ with a weighting scheme of the form $w = 1/(\sigma(F)^2 + kF^2)$, with σ based on counting statistics. Scattering factors were taken from ref 30 and were corrected for both the real and imaginary parts of the anomalous dispersion where appropriate. Final refinement was with all atoms except H having anisotropic thermal parameters. The hydrogen atoms were allowed to ride on the carbon atoms with a fixed C–H distance of 1.08 Å, sp^3 hybridization at the C atom and a fixed thermal parameter of 0.08. The SHELX-76 program package was used for the refinement;[31] diagrams were by PLUTO[32] and ORTEP.[33] Since $P2_1$ is a polar space group, refinement using the other enantiomorph was performed. The final R (0.076) was significantly higher.

The positional parameters for the non-hydrogen atoms of $[Cp^*{}_2VBr(NO)][Cp^*VBr_2(NO)]$ are given in Table III (for the cation) and Table IV (for the anion). Tables of hydrogen atom positions, thermal parameters, equations of some mean planes, comprehensive lists of bond distances and angles, and a table of $|F_o|$ and $|F_c|$ are available as supplementary material for this paper.

Acknowledgment. We thank Professor Jeffrey Petersen of West Virginia University for the computer simulation of the ESR of $Cp^*{}_2VI(NO)$, Professor Colin Mailer of the Physics Department, University of New Brunswick, for assistance with the ESR spectra, and the Natural Sciences and Engineering Research Council of Canada for financial support.

Registry No. $[Cp^*{}_2VBr(NO)][Cp^*VBr_2(NO)]$, 95615-98-8; $Cp^*{}_2VBr_2$, 95615-99-9; $Cp^*{}_2VBr$, 95616-00-5; $Cp^*{}_2VI(NO)$, 95616-01-6; $Cp^*{}_2V$, 74507-60-1; $Cp^*{}_2VI$, 89710-28-1; $Cp^*{}_2VI_2$, 89710-29-2; NO, 10102-43-9.

Supplementary Material Available: Figures of the geometry and numbering scheme and tables of hydrogen atom positions, thermal parameters, mean planes, bond distances and angles, and observed and calculated structures for both the anion and cation (22 pages). Ordering information is given on any current masthead page.

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