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Highly Oxidizing Organometallics: Physicochemical Characterization of (Methylcyclopentadienyl)vanadium(IV) Trichloride and Related Vanadium(III) and Titanium(III) Derivatives

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The compound (MeCp)VCl_3 (1) (Cp = η-C_5H_5) may be synthesized in high yield and purity from $(MeCp)_2VCl_2$ and $SOCl_2$. Compound 1 crystallizes in the space group $P\bar{1}$ with cell dimensions a = 6.860 (2) Å, b = 11.037 (4) Å, c = 6.832 (2) Å, α = 97.37 (3)°, β = 118.77 (2)°, γ = 80.73 (3)°, and Z = 2; R_w = 0.087, R = 0.069 for 1860 Mo Kα data with $I > 2.85\sigma(I)$. Vanadium-chlorine bond lengths range from 2.187 (4) to 2.208 (4) Å and the mean V-Cp distance is 1.93 (1) Å. Compound 1 undergoes a reversible reduction at +425 mV (Ag/AgCl), which may be compared with (MeCp)$VOCl_2$ (+270 mV) and (MeCp)$TiCl_3$ (-355 mV). Compound 1 shows a well-resolved paramagnetically shifted ^{1}H NMR spectrum. In comparison with the ^{1}H NMR signals of isoelectronic [Cp_2Co][(MeCp)$TiCl_3$], those observed for 1 indicate more covalent M-Cp interactions in 1 than in [Cp_2Co][(MeCp)$TiCl_3$]. Magnetic susceptibility measurements on solid [Cp_2Co][(MeCp)VCl_3] indicate a zero field splitting value of 8 cm^{-1}.

Introduction

High oxidation state organometallic complexes have attracted considerable recent attention. Part of the expanding activity in this area reflects the growing interest in bare main group ligands such as O,[1] N,[2] S_x,[3] and P_x.[4] Additionally, this topic is growing in interest because of the recently recognized role of high-valent organic complexes in various catalytic reactions. High oxidation state organometallics are also of interest since their stoichiometric simplicity facilitates interpretation of physicochemical data, which in turn leads to new approaches to organometallic synthesis and molecular catalysis.

One of the surprising properties of high oxidation state organometallic compounds is that they are generally not strong oxidants. This reflects the fact that most such compounds are derived from second- and third-row metal ions, which have relatively low ionization potentials. The muted oxidizing power of many high oxidation state organometallics may also be attributed to the potent π-donor properties[5] of oxo or sulfido coligands. The compound (RCp)VCl_3 (RCp = η^5-C_5H_5 or $CH_3C_5H_4$) is a rare example of a high oxidation state organometallic complex of a *first*-row metal that contains electronegative ligands which are *relatively poor* π donors.

Research into cyclopentadienyl vanadium complexes has been dominated by the better known Cp_2VX_2 series.[6] Studies of monocyclopentadienyl derivatives began in 1960 when Fischer and co-workers reported the synthesis of $CpVCl_3$ (Cp = C_5H_5) and its derivative $CpVOCl_2$.[7] Since that time only a few related studies have appeared, one describing an improved synthesis of $CpVCl_3$[8] and one describing C_5Me_5 analogues including $[(C_5Me_5)VI_2]_2O$.[9] Nieman and Teuben[10] have recently described complexes of the type $CpVCl_2(PR_3)_2$ (R = Me, Et) and related vanadium(II) derivatives, but this research did not involve a vanadium(IV) complex.

This report summarizes our reinvestigation of the (RCp)VCl_3 system. We have found that (RCp)VCl_3 is a rare example of a highly oxidizing organometallic free radical. The properties of (MeCp)VCl_3 are discussed relative to those of (MeCp)$VOCl_2$ and (MeCp)$TiCl_3$.

Results

Preparation and Basic Reactivity. The synthesis of air-sensitive (MeCp)VCl_3 (1) generally followed the two previously published syntheses of $CpVCl_3$,[7,8] although minor modifications of the procedure resulted in dramatic increases in the yield of the MeCp derivative. Microanalytical and NMR data suggested that the purity of the compound isolated by recrystallization was greater than 95%. Further purification could only be effected via a somewhat inefficient sublimation. Compound 1 is soluble in most nonpolar organic solvents. In the presence of coordinating solvents such as THF or CH_3CN, however, 1 readily undergoes ligand redistribution giving $(MeCp)_2VCl_2$ and solvent adducts of VCl_4 (eq 1). This redistribution process was monitored by EPR, and the final products were analyzed by cyclic voltammetry.

$$2(\mathrm{MeCp})\mathrm{VCl}_3 \xrightarrow[\text{excess L}]{} (\mathrm{MeCp})_2\mathrm{VCl}_2 + \mathrm{VCl}_4(\mathrm{L})_2 \quad (1)$$

Compound 1 reacts only slowly with molecular oxygen under mild conditions. When briefly exposed to a humid atmosphere, however, toluene solutions of 1 rapidly gave an EPR-active species (g_{iso} = 1.988, $A(^{51}V)$ = 75 G), which persists for hours. After many hours, EPR-silent (MeCp)$VOCl_2$ forms together with a black precipitate exhibiting a broad $g \sim 1.974$ EPR signal. The addition of small amounts of (wet) NaOH, benzoyl peroxide, or CH_3CN to solutions of 1 followed by exposure to O_2 was found to rapidly give blue solutions of (MeCp)$VOCl_2$. The synthesis of (MeCp)$VOCl_2$ is most efficiently carried out by treating 1 with KO_2, NO, or O_2/NaOH. Unlike 1, the

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[1] Herberhold, M.; Kremnitz, A.; Razari, A.; Schöllhorn, H.; Thewalt, U. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 601. Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 56. Van Asselt, A.; Burger, B.; Gibson, V. C.; Bercaw, J. E. *J. Am. Chem. Soc.* **1986**, *108*, 5347.

[2] Shapley, P. A.; Wepsiec, J. P. *Organometallics* **1986**, *5*, 1515 and references therein.

[3] Draganjac, M.; Rauchfuss, T. B. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 742.

[4] Scherer, D. J. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 924.

[5] Griffith, W. P. *Coord. Chem. Rev.* **1970**, *5*, 459. Huffman, J. C.; Moloy, K. G.; Marsella, J. A.; Caulton, K. J. *J. Am. Chem. Soc.* **1980**, *102*, 3009.

[6] Connelly, N. G. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1982; Vol. 3, p 672.

[7] Fischer, E. O.; Vigoreux, S.; Kuzel, P. P. *Chem. Ber.* **1960**, *93*, 701.

[8] Thiele, K. H.; Oswald, L. *Z. Anorg. Allg. Chem.* **1976**, *423*, 231.

[9] Bottomley, F.; Darkwa, J.; Sutin, L.; White, P. S. *Organometallics* **1986**, *5*, 2165.

[10] Nieman, J.; Teuben, J. H. *Organometallics* **1986**, *5*, 1149.

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Table I. Proton NMR Chemical Shifts versus Temperature Data for (MeCp)VCl$_3$, [Cp$_2$Co][(MeCp)TiCl$_3$], and [Cp$_2$Co][(MeCp)VCl$_3$]

	(MeCp)VCl$_3$			[Cp$_2$Co][(MeCp)TiCl$_3$]			[Cp$_2$Co][(MeCp)VCl$_3$]		
temp, °C	2,5	3,4	Me	2,5	3,4	Me	2,5	3,4	Me
30.1	56.0	52.7	-24.9	29.9	28.7	8.5	148.7	135.6	-11.9
19.8	57.5	54.2	-25.9	30.5	29.1	8.6	153.6	140.1	-12.5
10.0	59.1	55.7	-26.9	31.0	29.5	8.65	158.3	144.3	-13.1
-0.2	60.9	57.4	-28.1	31.7	30.1	8.75	164.0	149.5	-13.8
-9.9	62.8	59.1	-29.3	32.3	30.7	8.85	169.9	154.9	-14.6
-20.1	64.9	61.1	-30.8	33.2	31.4	8.95	176.7	161.1	-15.5
-30.2	67.2	63.4	-32.5	34.1	32.1	9.05	184.0	168.0	-16.5
-40.0	70.0	66.0	-34.4	35.1	32.9	9.15	191.7	174.9	-17.5
-50.0	72.7	68.6	-36.3	36.1	33.7	9.21	199.9	182.5	-18.6
-60.1	75.8	71.5	-38.6	37.4	34.6	9.26	210.6	192.1	-20.1
-70.1	79.3	74.8	-41.1	38.8	35.6	9.28	222.4	203.3	-21.8
-80.0	82.9	78.3	-43.8	40.3	36.7	9.26	234.2	214.0	-23.5

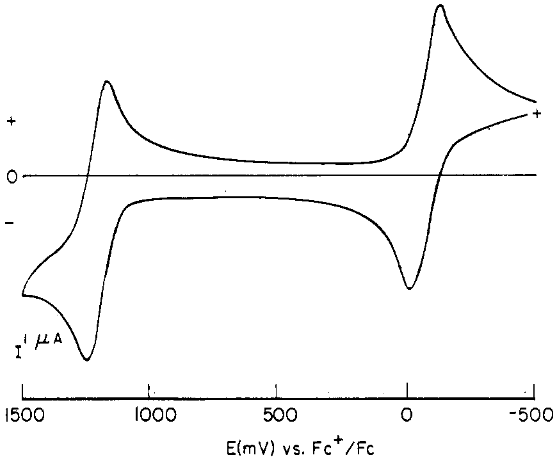

Figure 1. Cyclic voltammogram of (MeCp)VCl$_3$ in CH$_2$Cl$_2$ at 100 mV/s on a Pt working electrode (ca. 1 mM with 0.1 M TBAHFP).

oxide is fairly air-stable and sublimes well.

Reduction–Oxidation Properties. Due to the instability of 1 in coordinating solvents, dichloromethane was the solvent of choice for electrochemical studies. With rigorous exclusion of both oxygen and water, two redox couples were observed (Figure 1). Bulk electrolysis[11] and forced mass transport experiments confirmed that the electroneutral form of 1 predominates between a quasi-reversible oxidation at 1690 mV and a reversible reduction at 425 mV (versus Ag/AgCl[12]).

In contrast to the highly oxidizing nature of 1, (MeCp)TiCl$_3$ undergoes a reversible reduction at −355 mV and (MeCp)VOCl$_2$ at 270 mV. Cobaltocenium salts of one-electron reduced forms of 1, (MeCp)VOCl$_2$, and (MeCp)TiCl$_3$ were prepared through a reaction with cobaltocene. The isolated microcrystalline products of the composition [Cp$_2$Co]X, where X is the monoanion form of 1, (MeCp)VOCl$_2$, and (MeCp)TiCl$_3$, all showed electrochemical behavior corresponding to the superposition of the waves for cobaltocene and the respective MeCp compound.

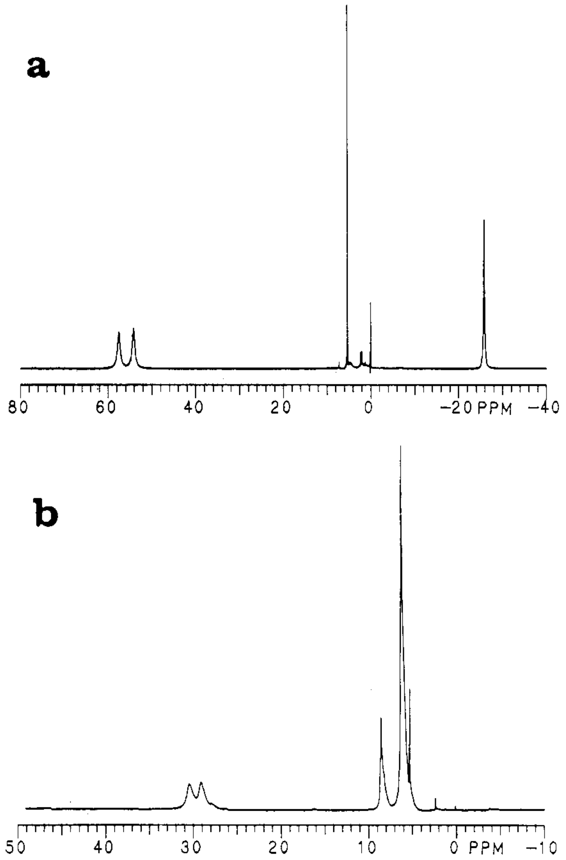

Figure 2. ^{1}H NMR spectra of CD$_2$Cl$_2$ solutions of (a) (MeCp)VCl$_3$ and (b) [Cp$_2$Co][(MeCp)TiCl$_3$] (200 MHz, 30 °C).

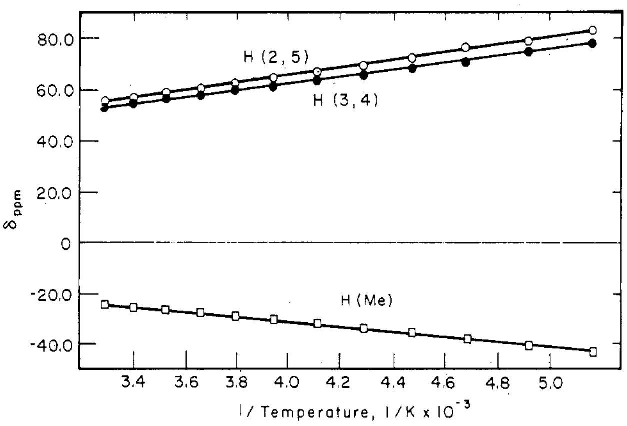

Figure 3. Plot of ^{1}H NMR shifts versus temperature for a CD$_2$Cl$_2$ solution of 1.

Proton NMR Studies. The ^{1}H NMR spectrum of 1 shows two CH$_3$C$_5$$H_4$ resonances shifted to low field and a

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[11] Solutions of 1 in 0.1 M TBAHFP·CH$_2$Cl$_2$ with aqueous Ag/AgCl reference electrodes undergo noticeable decomposition upon application of reductive currents after *ca.* 1 h. When the CH$_2$Cl$_2$ was "wet" (i.e., with the Ag/AgCl/H$_2$O reference system) 1 undergoes an autocatalytic decomposition initiated by voltammetric scans. The new species formed has a redox wave approximately 120 mV cathodic of the (MeCp)VCl$_3$$^{0/-}$ couple, corresponding roughly to (MeCp)VOCl$_2$.

[12] Most cyclic voltammograms were run with an aqueous Ag/AgCl reference electrode. Because under very anhydrous conditions variable dichloromethane/water junction potentials were observed, ferrocene was run in each experiment and the results standardized against ferrocene in "wet" dichloromethane at 480 mV. Scans performed with a ferrocenium/ferrocene reference electrode (dichloromethane/TBAHFP) allowed for reproducible CV behavior at the indicated potentials.

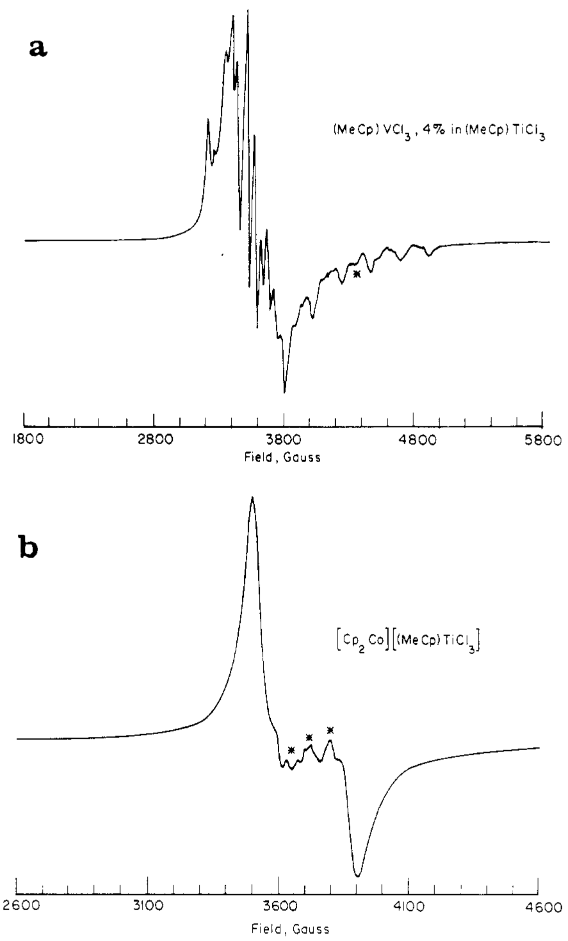

Figure 4. X-band EPR spectra of polycrystalline (MeCp)VCl_3 doped 4 mol % in (MeCp)$TiCl_3$ (a) and [CpCo][(MeCp)$TiCl_3$] (b), both at 3.4 K. Asterisked (*) features varied in intensity with sample rotation indicative of nonaveraging.

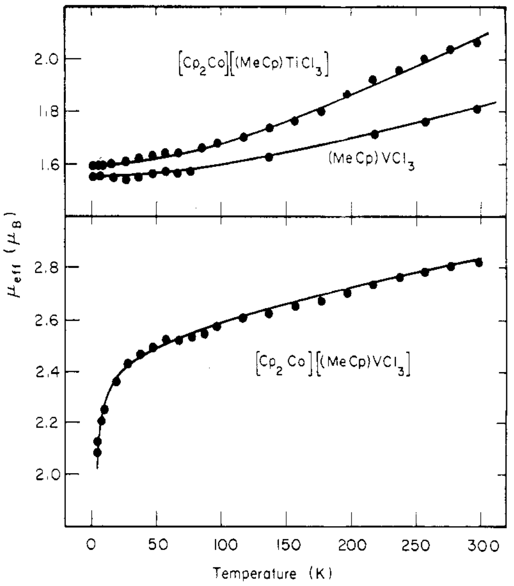

Figure 5. Plot of magnetic moment versus temperature for powder samples of (MeCp)VCl_3, $[Cp_2Co]$[(MeCp)$TiCl_3$], and $[Cp_2Co]$[(MeCp)VCl_3]. The solid line for $[Cp_2Co]$[(MeCp)VCl_3] represents the least-squares fit to eq 2 with D = 8.4 (2) cm^{-1}, g = 1.699 (5), and a TIP of 800(200) × 10^{-6} cgsu (see text).

$C\textit{H}_3C_5H_4$ resonance shifted to high field in the expected 2:2:3 ratio (Figure 2a). These resonances exhibit a pronounced temperature dependence, ranging from ca. 80 and −44 ppm at −80 °C to ca. 54 and −25 ppm at +30 °C, respectively (Figure 3). Chemical shift data measured at various temperatures are tabulated in Table I.

The ^1H NMR behavior of $[Cp_2Co]$[(MeCp)$TiCl_3$] was found to be dramatically different from that of the isoelectronic complex **1**. The $CH_3C_5\textit{H}_4$ resonances were observed at half the field of those in **1**, while the $C\textit{H}_3C_5H_4$ resonance was at a slightly *lower* field value (Figure 2b). The positions of these proton resonances ranged from ca. 38 and 9.33 ppm at −80 °C to ca. 29 and 8.5 ppm at 30 °C, respectively, in CD_2Cl_2.

The salt $[Cp_2Co]$[(MeCp)VCl_3] also exhibited a well-resolved NMR spectrum in CD_2Cl_2. The $CH_3C_5\textit{H}_4$ resonances occur at nearly three times lower field position than that for **1**, and the $C\textit{H}_3C_5H_4$ resonance occurs at only half as high a field. These resonances ranged from ca. 225 and −24 ppm at −80 °C to ca. 140 and −12 ppm at 30 °C, respectively.

The proton NMR spectrum of diamagnetic (MeCp)$VOCl_2$ displayed typical MeCp signals, while its cobaltocene reduction product exhibited one broad resonance attributable to Cp_2Co^+. Solutions of the salt exhibited a typical VO^{2+} EPR signal (g_{iso} = 1.975, $A(^{51}V)$ = 84.7 G) at room temperature.

Electron Paramagnetic Resonance Studies. Powder samples and toluene solutions of pure **1** showed no EPR signals at room temperature. Upon cooling, both types of samples exhibited a broad signal growing in at ca. g = 1.8, such that by 4 K a single feature at g = 1.865 was present. Magnetically dilute samples of **1** (4 mol % in (MeCp)$TiCl_3$) show reasonably well-resolved vanadium hyperfine signals (Figure 4a). A detailed simulation of this spectrum has not been accomplished, although g_z = 1.640 and A_z = 480 MHz accurately duplicate the parallel region of the spectrum.[13] The greatest success in full simulation has been obtained with values $2.0 > g_\perp \geq 1.8$ and $A_\perp \leq 100$ MHz ($g_x \neq g_y$).

The EPR spectrum of a powder sample of $[Cp_2Co]$[(MeCp)$TiCl_3$] consists of a broadened pseudoaxial signal at 4 K (Figure 4b). These signals are observed at $g_\parallel$ = 1.733 and $g_\perp$ = 1.938 and were invariant with sample rotation. A powder sample of $[Cp_2Co]$[(MeCp)VCl_3] gave no EPR signals down to 3.4 K.

Magnetism. The solution magnetic behavior of **1** was investigated at 295 K by means of the Evans method,[14] which gave an effective magnetic moment value of ca. 1.9 μ_B. This deviation from the spin-only value for one unpaired electron (μ = 1.73 μ_B) was confirmed for the solid state by means of SQUID measurements on powder samples between the temperatures of 300 (μ = 1.81 μ_B) and 5 K (μ = 1.57 μ_B) (Figure 5). Similar behavior was observed for $[Cp_2Co]$[(MeCp)$TiCl_3$] between 300 and 5 K, with a magnetic moment varying between 2.02 and 1.60 μ_B, respectively.

Susceptibility studies on powder samples of $[Cp_2Co]$[(MeCp)VCl_3] yielded a magnetic moment of 2.83 (300 K)–2.09 μ_B (5 K). Least-squares fitting of the molar magnetic susceptibility data (χ_M) to eq 2 for χ_M of a S =

$$\chi_M = \frac{1}{3}\left[C\frac{2e^{-x}}{1 + 2e^{-x}} + 2C\,\frac{(2/x)(1 - e^{-x})}{1 + 2e^{-x}} \right] \qquad (2)$$

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[13] Programs POW and QPOW are described in the following references: (a) Nilges, M. J. Ph.D. Thesis, University of Illinois, Urbana, IL, 1979. (b) Belford, R. L.; Nilges, M. J. *Computer Simulation of Powder Spectra*, EPR Symposium, 21st Rocky Mountain Conference; Denver, CO, Aug 1979. (C) Maurice, A. M. Ph.D. Thesis, University of Illinois, Urbana, IL, 1982.

[14] (a) Evans, D. F. *J. Chem. Soc.* **1959**, 2003. (b) Evans, D. F.; Fazakerley, G. V.; Phillips, R. F. *J. Chem. Soc. A* **1971**, 1931. (c) Crawford, T. H.; Swanson, J. *J. Chem. Educ.* **1971**, *48*, 382.

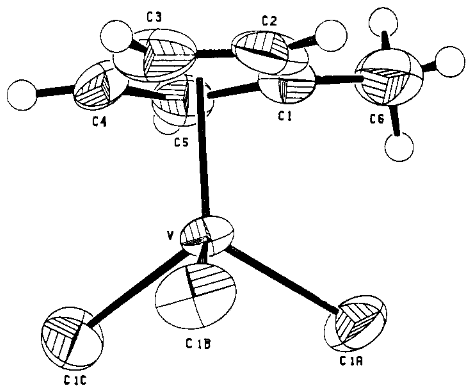

Figure 6. ORTEP drawing of the molecular structure of $(MeCp)VCl_3$. Thermal ellipsoids are drawn at a 40% probability level.

Table II. Metal-Chlorine Bond Lengths for Selected Compounds

compd	M-Cl, Å	ref
$(MeCp)VCl_3$	2.184 (4)-2.208 (4)	this work
$CpTiCl_3$	2.20-2.25	16
$(MeCp)_2VCl_2$	2.398 (2)	18
VCl_4[a]	2.138	19

[a] Bond distance in the gas phase as determined by electron diffraction.

1 (d^2) complex gave a value of 8 cm^{-1} for the axial zero field splitting parameter D (via $\tilde{H} = D\tilde{S}z^2$) and an isotropic g value of 1.735. In eq 2, $C = Ng^2\beta^2/kT$ and $x = D/kT$. A value of 800 × 10^{-6} cgsu was determined for temperature-independent paramagnetism (TIP) by means of an additive constant in the fitting.[15]

Solid-State Structure. The X-ray crystal structure of 1 conforms to that observed for other $CpML_3$ compounds, i.e., monomeric entities with a "piano-stool" configuration (see Figure 6). The dihedral angle between the MeCp and Cl_3 planes in 1 is less than 2°. The methyl group is nearly eclipsed with one of the chlorine ligands (torsion angle less than 2°). Compound 1 has a metal to MeCp-centroid distance of 1.928 (2) Å, which is comparable to that observed for $CpTiCl_3$[16] when corrected for differences in covalent radii.[17] The V-Cl distances in 1 are slightly shorter than in the titanium analogue (Table II) and significantly shorter than that found for $(MeCp)_2VCl_2$;[18] only in VCl_4 are the chlorine ligands more tightly bound.[19] The trend in V-Cl distances is explicable in terms of variations in the Cl-V π bonding.

Compound 1 crystallizes in a sheetlike structure although there are no bonding interactions between the individual molecules of 1. The closest intermolecular distances are all H···Cl contacts, ranging from 2.94 (1) to 2.81 (1) Å. The sum of chlorine and hydrogen van der Waals radii is 3 Å.

Electronic Characteristics. The observability of an NMR signal for a paramagnetic compound is dependent upon the availability of a mechanism(s) for reducing the electron spin lifetime (T_{1e}) to ca. 10^{-9} s, i.e., below that required for long-lived nuclear excited states. Consequently, the electron spin relaxation is so fast that the nuclear spins experience only an averaged electron magnetic field. One common mechanism for rapid spin-lattice relaxation is due to the presence of an orbitally degenerate ground state,[20] and thus orbital angular momentum. The bulk magnetic susceptibility measurements on the d^1 compounds 1 and $[Cp_2Co][(MeCp)TiCl_3]$ yielded greater than spin-only magnetic moments, indicating the presence of orbital angular momentum in the ground state.

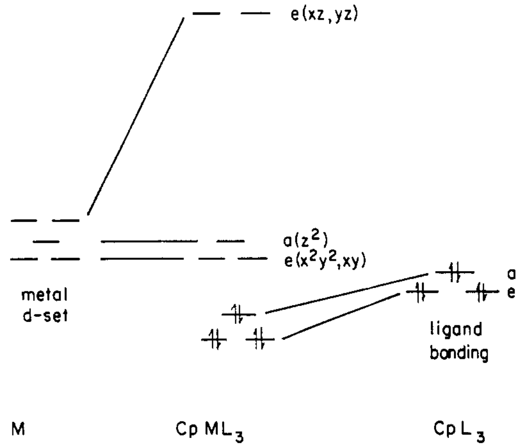

Figure 7. General electronic structure of the valence orbitals in $CpML_3$ compounds. Orbital designations are for an idealized C_{3v} molecular geometry. Complexes with a single unpaired d-shell valence electron receive a term symbol of ^2E_g.

Table III. Redox Couples for Selected Common Organic and Inorganic Compounds[a]

$E_{1/2}{}^{+/0}$	compd	$E_{1/2}{}^{0/-}$
1690	$(MeCp)VCl_3$	425
	$CpVCl_3$	~460
	$(MeCp)VOCl_2$	270
	$CpVOCl_2$	345
	$(MeCp)TiCl_3$	-355
	$V(CO)_6$	290
480	Cp_2Fe	
	TCNQ[b]	220

[a] Values are obtained in CH_2Cl_2/TBAHFP, referenced to Ag/AgCl. [b] TCNQ = tetracyanoquinodimethane.

Complexes of the type $CpML_3$ have an electronic configuration[21] similar to metallocenes[22] (Figure 7). The HOMO of a hypothetical d^1 metallocene would be the nonbonding e_{2g} orbital which is comprised of largely metal d_{xy} and $d_{x^2-y^2}$ orbitals. The resulting ground electronic state is $^2E_{2g}$.[21,23]

Although $[Cp_2Co][(MeCp)VOCl_2]$ is isoelectronic with 1, the electronic structure of its VO^{2+} core is considered as being composed of a largely metal-based *nondegenerate* d_{xy} HOMO, with a relatively large HOMO-LUMO gap of 10 000-15 000 cm^{-1}.[24] A nondegenerate ground state obviously does not experience an appreciable spin-lattice relaxation, and this explains the lack of ^1H NMR observability of $[Cp_2Co][(MeCp)VOCl_2]$.

Discussion

The electrochemical and magnetic resonance characteristics of $(MeCp)VCl_3$, $(MeCp)TiCl_3$, $(MeCp)VOCl_2$, and

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(15) Powder magnetic susceptibilities versus temperature data were analyzed through use of Program 66, DSTEPIT (Ver. 7.4) (QCPE, Department of Chemistry, Indiana University, Bloomington, Indiana, 47401), which optimized on selected variables in equations obtained from the following: O'Connor, C. J. In *Progress in Inorganic Chemistry*; Lippard, S. J., Ed.; Wiley: New York, 1982; Vol. 29, p 203.

(16) Engelhardt, L. M.; Papasergio, R. I.; Raston, C. L.; White, A. H. *Organometallics* **1984**, *3*, 18.

(17) Huheey, J. E. *Inorganic Chemistry*, 2nd ed.; Harper & Row: New York, 1978; p 232.

(18) Petersen, J. L.; Dahl, L. F. *J. Am. Chem. Soc.* **1975**, *97*, 6422.

(19) Morino, Y.; Uehara, H. *J. Chem. Phys.* **1966**, *45*, 4543.

(20) Wertz, J. E.; Bolton, J. R. *Electron Spin Resonance*; McGraw-Hill: New York, 1972; Chapter 12.

(21) Ammeter, J. H. *J. Magn. Res.* **1978**, *30*, 299.

(22) Burdett, J. K. *Molecular Shapes*; Wiley: New York, 1980; Chapter 9.

(23) Duggan, D. M.; Hendrickson, D. N. *Inorg. Chem.* **1975**, *14*, 955.

(24) Syamal, A. *Coord. Chem. Rev.* **1975**, *16*, 309.

Table IV. Comparison of Electron Delocalization Schemes for $(MeCp)VCl_3$ and $[Cp_2Co][(MeCp)TiCl_3]$

	Cp backbone ^1H spin density			Cp methyl ^1H spin density		
model	predicted	obsd		predicted	obsd	
contact[a]			linearity[b]			linearity
V	β	β	+0.9998	α	α	−0.9992
Ti		β	+0.9920		β	+0.9533
dipolar[c]			$(\delta_{calcd}/\delta_{obsd})_{av}$[d]			$(\delta_{calcd}/\delta_{obsd})_{av}$
V	β	β	+0.151	β	α	−0.0843
Ti		β	+0.298		β	+0.321

[a] See text for contact mechanism discussion. [b] Shift versus temperature plot; calculated nuclear hyperfine splitting values for $(MeCp)VCl_3$ are as follows (MHz): $a_N(3,4) = 2.0(1)$, $a_N(2,5) = 2.1(1)$, $a_N(Me) = -1.2(1)$. Errors result from estimates of $g_\perp$ in EPR studies. [c] Structural parameters: M–H(2,3,4,5) = 2.85 Å, M–Cp centroid–H(2,3,4,5) = 47.8°; H(Me) = 3.73 Å, 52.9°. [d] Calculated versus observed shifts at 20 °C; for $g_\parallel < g_\perp$, $0° \leq \theta \leq 54.7°$ yields a density of β, and $54.7° \leq \theta \leq 90°$ α.

their reduced derivatives provide valuable insight into their properties. In particular, *the (RCp)VX$_3$ compounds comprise the most strongly oxidizing class of neutral organometallic compounds known.*[25] The oxidative capability of 1 substantially exceeds both TCNQ and $V(CO)_6$ (Table III).[26] The oxidizing ability of 1 is especially remarkable in comparison to $(MeCp)TiCl_3$, which is 780 mV more difficult to reduce. It is interesting that $(MeCp)VOCl_2$ is a *poorer* oxidant than $(MeCp)VCl_3$ by about 150 mV. This difference is attributable to the superior π-donor properties of the oxide ligand compared to those of the chloride ligand.

Paramagnetic ^1H NMR spectroscopy has provided a convenient probe of the electronic properties of the complexes of this study. Unpaired spin density may transfer from the metal to the Cp ligand via dipolar or contact mechanisms. In the case of a low degree of covalency between the metal and the Cp ligand, dipolar shifts will result, yielding α spin density on both ring and methyl *Cp protons*. In the limiting case of a high degree of covalency between the metal and Cp ligand, contact shifts result via spin polarization of the π-bonding ligand orbitals and electron–electron correlation to lead to net α spin density in the *Cp π system* (indirect delocalization). Numerical analysis of shift versus temperature data (see Experimental Section) for 1 and $[Cp_2Co][(MeCp)TiCl_3]$ (Table IV) indicates that different mechanisms are responsible for electron delocalization. A contact shift mechanism yields the correct spin density on both sets of ligand protons for 1[27] and is supported by the high degree of linearity in shift versus temperature data. This implies that the ground state (Ψ_{grd}) of 1 is not a purely vanadium-based atomic orbital (Ψ_e) but an admixture with ligand-based orbitals (Ψ_L) as in eq 3.

$$\Psi_{grd} = \Psi_e + (1 - x)\Psi_L \qquad (0 < x < 1) \qquad (3)$$

This polarization mechanism for 1 ($x \ll 1$) is analogous to the configuration interaction observed in complexes such as the ferrocenium cation, wherein metal- and ligand-based orbitals are highly mixed.[23,28] As with the deep blue color of Cp_2Fe^+, a ligand-to-metal charge transfer (or hole transition) could account for the deep purple color of 1. Further, the smaller energy separation between metal and ligand orbitals in 1 relative to $[Cp_2Co][(MeCp)TiCl_3]$ ($x \sim 1$) is consistent with the electrochemical results, which indicate a much lower energy acceptor orbital in 1 than in $(MeCp)TiCl_3$. This model further provides an explanation for the pale green color of $[Cp_2Co][(MeCp)TiCl_3]$. Additionally, the magnetic moment for $[Cp_2Co][(MeCp)TiCl_3]$ indicates somewhat increased spin–orbit coupling compared to 1, which in turn may be indicative of a more metal-localized orbital.

To conclude, the covalency of the V···MeCp interaction, combined with the moderate π-donor abilities of Cl, gives rise to the highly oxidizing nature of $(MeCp)VCl_3$, a situation presently unique among the first-row Cp metal halides. Studies of related high-valent organoniobium and organochromium compounds would be of interest.

Experimental Section

Synthesis. All reactions and characterizations were conducted under an inert atmosphere by using standard Schlenk line techniques or a Vacuum Atmospheres Dri-Lab. In both cases dried and oxygen-free nitrogen were used. Solvents were distilled from appropriate drying agents under nitrogen (toluene, Na; hexanes, CaH_2; and CH_2Cl_2, P_4O_{10}). The compound $(MeCp)_2VCl_2$ was prepared in ~50% yield from VCl_3 (Cerac) and either Na(MeCp) or K(MeCp) in tetrahydrofuran (THF). The highest yields were obtained via batchwise (thirds) addition of the M(MeCp) solution to the refluxing solution of vanadium trichloride. Thionyl chloride (Aldrich) was used as received. Cobaltocene,[29] $(MeCp)TiCl_3$,[30] and tetra-*n*-butylammonium hexafluorophosphate[31] (TBAHFP) were prepared according to published literature methods.

$(MeCp)VCl_3$ (1). Excess $SOCl_2$ (100 g) was cooled to 0 °C, and 10 mmol of $(MeCp)_2VCl_2$ (2.80 g) was added with stirring. The reaction mixture was maintained at 0 °C for 1 h and then allowed to warm to room temperature over a period of 5 h. The solvent was then removed under vacuum and the reaction residue slurried in 20 mL of toluene and filtered by using a Schlenk filter. The residue was again washed with 3 × 10 mL of toluene and the solvent removed from the filtrate under vacuum. The residue was slurried in 5 mL of toluene, cooled to −78 °C, and filtered by cannula. The black crystalline solid was dried in vacuo for a 75% yield (1.7 g, 7.2 mmol) of >95% purity. ^1H NMR (C_6D_6, 293 K): δ 55.1 (2 H, fwhh = 149), 50.8 (2 H, fwhh = 147), −24.5 (3 H, fwhh = 49). [fwhh = full width (Hz) at half-height of NMR resonance.] MS (EI): *m/e* 235 (M). Anal. Calcd for $C_6H_7VCl_3$: C, 30.48; H, 2.98; Cl, 44.99. Found: C, 31.11; H, 3.10; Cl, 44.15.

High-purity $(MeCp)VCl_3$ (used in the magnetic susceptibility, EPR, and NMR measurements) was obtained by sublimation in

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(25) Morse, D. B.; Rauchfuss, T. B.; Wilson, S. R., manuscript in preparation.

(26) All compounds were examined as part of this study under identical conditions. Kotz, J. C. In *Topics in Organic Electrochemistry*; Fry, A. J., Britton, W. E., Eds.; Plenum: New York, **1986**; Chapter 3.

(27) Past studies have indicated that the methyl protons may have non-zero overlap with the ring π-bonding network, and so direct delocalization from the carbon π-orbitals to the CH_3 protons cannot be ruled out; this yields the same result as with spin-polarization through the Cp framework. (a) Cramer, R. E.; Drago, R. S. *J. Am. Chem. Soc.* **1970**, *92*, 66. (b) Horrocks, W. Dew, Jr.; Johnston, D. L. *Inorg. Chem.* **1971**, *10*, 1835.

(28) Sohn, Y. S.; Hendrickson, D. N.; Gray, H. B. *J. Am. Chem. Soc.* **1971**, *93*, 3603.

(29) King, R. B. *Organometallic Syntheses*; Academic: New York, 1965; Vol. 1.

(30) Lucas, C. R.; Green, M. L. H. *Inorg. Synth.* **1976**, *16*, 238.

(31) Fry, A. J.; Britton, W. E. In *Laboratory Techniques in Electroanalytical Chemistry*; Kissinger, P. T., Heineman, W. R., Eds.; Marcel Dekker: New York, 1984; Chapter 13.

dynamic vacuum at 60 °C onto a water-cooled probe in ca. 50% yield. Anal. Calcd for $C_6H_7VCl_3$: C, 30.48; H, 2.98; Cl, 44.99. Found: C, 30.34; H, 3.02; Cl, 44.85.

(MeCp)VOCl$_2$. (MeCp)VCl$_3$ (0.5 mmol, 120 mg) was dissolved in 10 mL of toluene, a single chip of NaOH was added, and the flask was flushed with dry O_2 for 1 min. After 1 h, the solvent was removed under vacuum, and the product was sublimed onto a cold finger under dynamic vacuum at 35 °C. Yield: 80% (90 mg, 0.4 mmol). ^{1}H NMR (CDCl$_3$): δ 6.81 (2 H), 6.46 (2 H), 2.52 (3 H). MS (EI): *m/e* 216 (M). Anal. Calcd for $C_6H_7VOCl_2$: C, 33.22; H, 3.25; Cl, 32.68. Found: C, 33.29; H, 3.44; Cl, 32.70.

[Cp$_2$Co][(MeCp)VCl$_3$]. A solution of Cp$_2$Co (80 mg, 0.42 mmol) in 10 mL of CH_2Cl_2 was added dropwise to a stirred solution of (MeCp)VCl$_3$ (100 mg, 0.42 mmol) in 10 mL of CH_2Cl_2. After 1 h, the solution was concentrated to 2 mL, and the crude product was precipitated with the rapid addition of 20 mL of toluene. After the residue was washed with 5 mL of toluene, the brown residue was extracted with two 2-mL portions of CH_2Cl_2 and filtered. The filtrate was evaporated to dryness and the product dried in vacuo. Yield: 90% (160 mg, 0.38 mmol). ^{1}H NMR (CDCl$_3$, 295 K): δ 156 (2 H, fwhh = 385), 142 (2 H, fwhh = 300), 5.5 (10 H, fwhh = 45), −12.6 (3 H, fwhh = 84). Anal. Calcd for $C_{16}H_{17}Cl_3CoV$: C, 45.16; H, 4.03; V, 11.97. Found: C, 45.37; H, 3.90; V, 11.80.

[Cp$_2$Co][(MeCp)TiCl$_3$]. A procedure analogous to that used for [Cp$_2$Co][I] was employed, wherein equal volume solutions of (MeCp)TiCl$_3$ (130 mg, 0.56 mmol) and Cp$_2$Co (110 mg, 0.58 mmol) in CH_2Cl_2 were mixed. The solvent was removed from the green solution under vacuum, and the residue was washed twice with 10 mL of toluene. The remaining material was dissolved in 3 mL of CH_2Cl_2 and filtered, rinsing with 2 mL of CH_2Cl_2. The solvent was removed to yield the cobaltocenium salt of the highly air-sensitive titanium anion in 77% yield (181 mg). ^{1}H NMR (CD$_2$Cl$_2$, 293 K): δ 30.5 (2 H, fwhh = 157), 29.1 (2 H, fwhh = 161), 8.6 (3 H, fwhh = 50), 6.2 (10 H, fwhh = 48). Anal. Calcd for $C_{16}H_{17}Cl_3CoTi$: C, 45.49; H, 4.06; Ti, 11.35. Found: C, 45.02; H, 4.16; Ti, 10.99.

[Cp$_2$Co][(MeCp)VOCl$_2$]. A procedure analogous to that for [Cp$_2$Co][1] was used, but the precipitated product was first extracted into CH_2Cl_2 (10 mL), filtered, reprecipitated with toluene (10 mL), and washed with toluene (2 × 5 mL). Yield: 20% (35 mg). ^{1}H NMR (CDCl$_3$): δ 5.69. EPR (CH$_2$Cl$_2$): g_{iso} = 2.975, $A(^{51}V)$ = 84.7 G.

Physical Measurements. Nuclear magnetic resonance spectra were acquired on a Varian XL-200 200-MHz FT-NMR at approximately 0.15 M sample concentrations, while electron paramagnetic resonance spectra were obtained by means of either a Varian E-9 X-band EPR spectrometer equipped with a quartz nitrogen-flow low-temperature Dewar or a Bruker ER-200D X-band EPR spectrometer equipped with an Oxford Instruments liquid-helium cryostat. Evans magnetic moment determinations were made by measuring the methyl resonance of toluene-filled capillaries. Variable-temperature magnetic susceptibility experiments were performed at 10 kG on a S.H.E. VTS-50 series 800 SQUID susceptometer.

Microanalyses were carried out by the University of Illinois Microanalytical Laboratory, mass spectra determination by the University of Illinois Mass Spectrometry Center, and X-ray crystallography by the School of Chemical Sciences Crystallography Center. Electrochemical studies were carried out on a BioAnalytical Systems BAS-100 electrochemical analyzer equipped with a three-electrode cell using Pt working and counter electrodes. Original computer programs were written for the analysis of paramagnetic ^{1}H NMR data (PNMRC, FORTRAN) and for the plotting of cyclic voltammetry scans (BASPLOT, BASIC).

Crystallography. The solid state X-ray structure of (MeCp)VCl$_3$ was determined from a crystal grown by slow evaporation of a 1:1 toluene/hexane solution. The opaque black prismatic crystal selected was mounted under an inert atmosphere by using a trace of grease in a 0.3-mm thin-walled tapered glass capillary. Data collection was performed at 25 °C on a Syntex P2$_1$ automated four-circle diffractometer with graphite-monochromated molybdenum radiation ($\lambda(K\bar{\alpha})$ = 0.71073 Å).

The best available crystal was twinned. However, the diffuse scatter was minimal and the diffraction pattern was intense so a unique set of 15 reflections was carefully selected and centered to determine cell parameters. Crystal and experimental data are listed in Table V, and the atomic coordinates are listed in Table VI. The data were corrected for Lorentzian and polarization effects and numerically corrected for absorption. The structure was solved by direct methods (SHELX); correct positions for vanadium and chlorine atoms were deduced from an *E* map. Subsequent least-squares difference Fourier calculations located the carbon atoms. Non-hydrogen atoms were refined with anisotropic thermal coefficients, and hydrogen atoms were included as fixed contributions in "idealized" positions (d(C–H) = 0.95 Å). Selected bond distances and angles are listed in Table VII.

Table V. Crystal, Experimental, and Refinement Data for (MeCp)VCl$_3$ (1)

Crystal Data

cryst system: triclinic
space group: $P\bar{1}$ (C_i^1)
a = 6.860 (2) Å
b = 11.037 (4) Å
c = 6.832 (2) Å
V = 446.7 (3) Å^3
α = 97.37 (3)°
β = 118.77 (2)°
γ = 80.73 (3)°
Z = 2
cryst faces: $(1\bar{5}\bar{1})$, $(\bar{1}51)$, (010), $(0\bar{1}0)$, (100), (001), $(21\bar{3})$, (213)

Refinement Data

size (mm from center)	0.10, 0.10, 0.11, 0.11, 0.15, 0.22, 0.24, 0.26
scan mode	$\omega/2\theta$
scan range	$3.0 < 2\theta < 53.0°$ for $\pm k,\pm k,+l$
std intensities	3/100 (no decay)
unique intensities	1860 (2107 collected)
"obsd" intensities	904 ($I > 2.58\sigma(I)$)
internal consistency	R_i = 0.024
absorpn correctn	numerical (μ = 19.07 cm^{-1}; transmissn factors 0.719–0.503)
refined parameters	92 (max shift error 0.001)
agreement factors	R = 0.069, R_w = 0.087, E = 1.96
final diff map	0.73 e/Å^3 in vicinity of vanadium atom
temp	25 °C

Table VI. Positional Parameters for (MeCp)VCl$_3$ (1)

atom	x/a	y/b	z/c
V	0.4600 (3)	0.2317 (2)	0.3514 (3)
ClA	0.3705 (6)	0.2486 (3)	0.6223 (5)
ClB	0.2747 (5)	0.3950 (3)	0.1645 (6)
ClC	0.2457 (6)	0.0893 (3)	0.1350 (6)
C1	0.763 (2)	0.290 (1)	0.338 (2)
C2	0.724 (2)	0.173 (1)	0.241 (2)
C3	0.754 (2)	0.096 (1)	0.408 (4)
C4	0.810 (2)	0.164 (2)	0.598 (2)
C5	0.814 (2)	0.281 (2)	0.567 (2)
C6	0.768 (3)	0.397 (2)	0.245 (4)

Table VII. Selected Distances and Angles for (MeCp)VCl$_3$ (1)

	Distances (Å)		
V–ClA	2.193 (4)	V–ClB	2.187 (4)
V–ClC	2.208 (4)	V–Cp(centroid)	1.93 (1)
	Angles (deg)		
ClA–V–ClB	103.3 (1)	ClA–V–ClC	98.7 (1)
ClA–V–Cp	117.8 (5)	ClB–V–ClC	100.8 (1)
ClB–V–Cp	116.4 (5)	ClC–V–Cp	116.9 (5)

Evaluation of Paramagnetic NMR Data. The interpretation and evaluation of data from proton paramagnetic NMR is based upon the account by La Mar et al.[32] The observed effect of unpaired electrons on the nuclear energy levels of a proton in an applied magnetic field arises from the interaction between the magnetic moment (field) of the proton and the magnetic moment (field) of the electrons. The total spin Hamiltonian includes the primary hyperfine components: (Fermi) contact, (pseudocontact)

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[32] *NMR of Paramagnetic Molecules*; LaMar, G. N., Horrocks, W. D., Holm, R. H., Eds.; Academic: New York, 1973.

dipolar, and orbital interactions. The contact term is represented by a partial Hamiltonian

$$\mathcal{H}_{\rm con} = a_N \mathbf{S}\cdot\mathbf{I}$$

where a_N is the electron–nuclear hyperfine coupling constant and **S·I** the product of electron and nuclear spin tensors. The dipolar term may be represented by

$$\mathcal{H}_{\rm dip} = g\beta\hbar\gamma_N\left\{\frac{3(\mathbf{r}\cdot\mathbf{S})(\mathbf{r}\cdot\mathbf{I})}{r^5} - \frac{\mathbf{S}\cdot\mathbf{I}}{r^3}\right\}$$

where the electron spin tensor interacts according to its position relative to the nucleus (**r**) and the inverse of its distance from the nucleus (r). The orbital term may likewise be represented by

$$\mathcal{H}_{\rm orb} = 2\hbar\gamma_N\beta\sum l\mathbf{I}/r^3$$

in which an electron's orbital angular momentum (l) couples with the nuclear spin as a function of distance.

These three terms are combined by using simplifications based on averaging conditions (electronic relaxation time $T_{1e} \ll$ rotational correlation time (t_c); i.e., where spin level populations are not affected by variations in the applied magnetic field. The two following equations result for a molecule with axial symmetry:

$$(d\nu/\nu)^{\rm con} = -a_N\beta S'(S'+1)(g_\parallel + 2g_\perp)/9\hbar\gamma_N kT$$

$$(d\nu/\nu)^{\rm dip} = \beta^2 S'(S'+1)(3\cos^2\theta - 1)(g_\parallel{}^2 - g_\perp{}^2)/9kTr^3$$

In these expressions $d\nu$ is the frequency difference between the resonant positions of a diamagnetic model and its paramagnetic analogue, ν is the ^{1}H resonance frequency at the applied field, S' is the effective spin number, θ is the angle formed by the primary magnetic axis and the nucleus of interest with the metal as origin, and r is the metal–proton distance. Under the conventions used in this derivation, positive spin density (β spin) is indicated by a positive a_N value and a low-field (high-frequency) shift for the observed nucleus. Under isotropic conditions, the above equations simplify to

$$(d\nu/\nu)^{\rm iso} = -g\beta S(S+1)a_N/3\hbar\gamma_N kT$$

Values of a_N in units other than ergs may be obtained through the usual relationships between g, β, $\mathcal{H}$, and $\hbar$.[33]

The predominant mechanism involved in paramagnetic shifts was qualitatively analyzed by comparing observed and calculated contributions from contact and dipolar processes. The observed variations in proton NMR chemical shift with temperature were used with electronic g values to calculate nuclear hyperfine splitting values, a_N, under contact-only circumstances.[34] Dipolar shifts were estimated by using the crystallographically determined metal-to-proton structural parameters of (MeCp)VCl$_3$ and CpTiCl$_3$ and observed g values to calculate shift versus temperature data. The relation for a dipolar case

$$(d\nu/\nu)^{\rm iso} = (d\nu/\nu)^{\rm con} + (d\nu/\nu)^{\rm dip}$$

was used to estimate contact shift contributions based on the dipolar predictions. These results were reviewed on the basis of goodness-of-fit (linear and/or second-order polynomial) for the contact values, and the predictive quality of the dipolar calculations (ratio of calculated to observed shifts). Studies of the origin of paramagnetic line widths were beyond the scope of the present investigation.

Acknowledgment. This research was supported by the National Science Foundation through NSF DMR 83-16981 (to T.B.R.). D.B.M. gratefully acknowledges financial assistance in the form of a University of Illinois Fellowship; T.B.R. is a fellow of the Camille and Henry Dreyfus Foundation. Mass spectrometry facilities were supported in part by a grant from the National Institute of General Medical Sciences (Grant No. GM 27029).

Registry No. 1, 111005-01-7; [Cp$_2$Co][1], 111005-00-6; (MeCp)VOCl$_2$, 111005-02-8; [Cp$_2$Co][(MeCp)TiCl$_3$], 111005-04-0; [Cp$_2$Co][(MeCpVOCl$_2$], 111005-06-2; (MeCp)$_2$VCl$_2$, 59139-01-4; Cp$_2$Co, 1277-43-6; (MeCp)TiCl$_3$, 1282-31-1; CpVCl$_3$, 34767-30-1; CpVOCl$_2$, 1293-64-7; V(CO)$_6$, 14024-00-1; CpFe, 81714-34-3; TCNQ, 1518-16-7.

Supplementary Material Available: Stereoscopic packing diagram of (MeCp)VCl$_3$, tables of thermal parameters, "idealized" hydrogen positions, bond distances and angles for MeCpVCl$_3$, and cyclopentadienyl plane for MeCpVCl$_3$, listing of the FORTRAN program PNMRC used in assessment of paramagnetic shift versus temperature, and a table of magnetic data for (MeCp)VCl$_3$, [Cp$_2$Co][(MeCp)TiCl$_3$], and [Cp$_2$Co][(MeCp)VCl$_3$] (13 pages); tables of final observed and calculated structure factor amplitudes for (MeCp)VCl$_3$ (4 pages). Ordering information is given on any current masthead page.

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(33) (a) Oshawa, Y.; DeArmond, M. K.; Hanck, K. W.; Moreland, C. G. *J. Am. Chem. Soc.* **1985**, *107*, 5383. (b) Khramtsov, V. V.; Weiner, L. M.; Gogolev, A. Z.; Grigor'ev, I. A.; Starichenko, V. F.; Volodarsky, L. B. *Magn. Reson. Chem.* **1986**, *24*, 199.

(34) The effects of concentration (high field shift) and bulk magnetic susceptibility (low field shift) were evaluated as cancelling and small; errors in chemical shift determination were greater than this error. Kohler, F. H. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1980**, *35B*, 187.