Table VI. Peak Potentials[a] for the Couples $[Fe_4S_4(SPh)_{4-n}X_n]^{2-/3-}$

	E_p, V	$E_{pc} - E_{pa}$, mV	i_{pc}/i_{pa}	concn, M
$[Fe_4S_4(SPh)_4]^{2-}$	−1.05	86	0.95	1.6×10^{-3}
$[Fe_4S_4(SPh)_2Cl_2]^{2-}$	−0.95	100	0.87	1.2×10^{-3}
$[Fe_4S_4Cl_4]^{2-}$	−0.87	109	0.89	1.0×10^{-3}
	In CH_3CN			
$[Fe_4S_4(SPh)_4]^{2-}$	−0.90	72	0.96	5×10^{-4}
$[Fe_4S_4(SPh)_2Cl_2]^{2-}$	−0.85	168	0.88	1.7×10^{-3}
$[Fe_4S_4Cl_4]^{2-}$	−0.72	133	0.89	1.2×10^{-3}

[a] Solutions were 0.1 M in tetra-*n*-butylammonium perchlorate. Potentials are reported vs. a saturated calomel electrode. In all measurements the scan rate was 200 mV/s.

same 5–10-mV increments (Table VI). The values for the 2^-–3^- couples for the $[Fe_4S_4(SPh)_4]^{2-}$ and $[Fe_4S_4Cl_4]^{2-}$ clusters in *N*-methyl-2-pyrrolidinone vs. SCE electrode at −1.04 and −0.85 V, respectively,[34] compare very favorably with corresponding values we have obtained in DMF at −1.05 and −0.87 V. The deviations of the anodic–cathodic peak separations ($|E_{pa} - E_{pc}|$) from the theoretical 0.059 mV may indicate the absence of strict electrochemical reversibility. However, the cathodic to anodic peak current ratios, (i_{pc}/i_{pa}) (Table VI) are all very close to 1 and suggest effective chemical reversibility.

Mixed chloro mercaptido "cubanes" of the type $[Fe_4S_4(SR)_{4-n}X_n]^{2-}$ have been reported previously[34] as species present in $[Fe_4S_4(SR)_4]^{2-}/C_6H_5COCl$ reaction mixtures. Possible difficulties encountered in the isolation of any such species are apparent in the statement: "...the roughly statistical distribution of species presumably precludes isolation of a pure salt of any one such species...".[34]

The utility of $[Fe_4S_4(SPh)_2Cl_2]^{2-}$ as a precursor for the synthesis of "mixed" mercaptido clusters of the types $[Fe_4S_4(SR)_2(SR')_2]^{2-}$ or $[Fe_4S_4(SR)_2(L)_2]^{n-}$ is at present under investigation.

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Registry No. I, 80765-11-3; II, 80939-30-6; III, 80765-12-4; $(Ph_4P)_2[Fe_4(SPh)_6Br_4]$, 80789-26-0; $(Ph_4P)_2[Fe_4S_4(SPh)_4]$, 80765-13-5; $[Fe_4(S\text{-}p\text{-tol})_6Cl_4]^{2-}$, 80765-08-8; $(Ph_4P)_2Fe(SPh)_4$, 57763-34-5; BzSSSBz, 6493-73-8; BzSH, 100-53-8; SCl_2, 10545-99-0; PhCOCl, 98-88-4.

Supplementary Material Available: Tables of observed structure factors for $(Ph_4P)_2[Fe_4(SPh)_6Cl_4]$ (32 pages), final atomic positional and thermal parameters for the phosphorus and carbon atoms of the cations and the anion, weighted least-squares planes and dihedral angles (38 pages). Ordering information is given on any current masthead page.

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Syntheses and Electronic Structures of Decamethylmetallocenes

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Abstract: The syntheses of the $(Me_5Cp)_2M$ (M = Mg, V, Cr, Co, and Ni) and $[(Me_5Cp)_2M]PF_6$ (M = Cr, Co, and Ni) compounds are described. In addition, a preparative route to a novel, dicationic decamethylmetallocene, $[(Me_5Cp)_2Ni](PF_6)_2$, is reported. Physical measurements indicate that all the above compounds are D_{5d} or D_{5h} decamethylmetallocenes with low-spin electronic configurations. The decamethylvanadocene cation is apparently coordinatively unsaturated. A paramagnetic acetonitrile complex, $[(Me_5Cp)_2V(NCCH_3)]PF_6$, and a diamagnetic dicarbonyl derivative, $[(Me_5Cp)_2V(CO)_2]PF_6$, of the cation can be prepared, but pure $[(Me_5Cp)_2V]PF_6$ has not been isolated. Cyclic voltammetry studies verify the reversibility and the one-electron nature of the $(Me_5Cp)_2M \rightleftharpoons [(Me_5Cp)_2M]^+$ (M = Cr, Fe, Co, and Ni) and $[(Me_5Cp)_2Ni]^+ \rightleftharpoons [(Me_5Cp)_2Ni]^{2+}$ redox reactions and show that the neutral decamethylmetallocenes are much more easily oxidized than their metallocene counterparts due to the electron-donating properties of the methyl groups. Magnetic susceptibility and EPR studies indicate the following ground-state assignments for the paramagnetic decamethylmetallocenes: ${}^4A_{2g}[e_{2g}{}^2a_{1g}{}^1]$ for the 15-electron compounds $(Me_5Cp)_2V$ and $[(Me_5Cp)_2Cr]^+$, ${}^3E_{2g}[e_{2g}{}^3a_{1g}{}^1]$ for the 16-electron compounds $(Me_5Cp)_2Cr$ and $[(Me_5Cp)_2Mn]^+$, ${}^2E_{2g}[e_{2g}{}^3a_{1g}{}^2]$ for the 17-electron compound $[(Me_5Cp)_2Fe]^+$, ${}^2E_{1g}[e_{2g}{}^4a_{1g}{}^2e_{1g}{}^1]$ for the 19-electron compounds $(Me_5Cp)_2Co$ and $[(Me_5Cp)_2Ni]^+$, and ${}^3A_{2g}[e_{2g}{}^4a_{1g}{}^2e_{1g}{}^2]$ for the 20-electron compound $(Me_5Cp)_2Ni$. The UV–visible absorption spectra of the 15-, 18- and 20-electron decamethylmetallocenes are also reported. Assignments are proposed for the absorptions due to d–d transitions, and a ligand-field analysis is used to derive the ligand-field splitting parameters Δ_1 and Δ_2 and the Racah electron repulsion parameter *B*. Comparison of these parameters with those previously reported for the isoelectronic Cp_2M compounds shows the net ligand-field splitting and *B* are larger in the permethylated compounds. The increased value of *B* indicates greater electron density at the metal center.

Since the discovery[1] and structural characterization[2,3] of ferrocene (η^5-$(C_5H_5)_2Fe$ or Cp_2Fe) in the early 1950s, at least one cyclopentadienyl derivative of every main group and transition metal, as well as most f-block metals, has been prepared and characterized.[4-6] A large number of monoalkyl- and monoaryl-substituted cyclopentadienyl metal compounds have also been

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prepared, but extensive study of peralkylcyclopentadienyl metal compounds was not practical until the recent development of convenient and efficient synthetic routes to pentamethylcyclopentadiene and alkyltetramethylcyclopentadienes.[7-9] A number of studies have now appeared demonstrating some dramatic differences between the structure and chemistry of cyclopentadienyl- and (pentaalkylcyclopentadienyl)metal compounds.[10-21] In general, these differences can be attributed to the relative steric bulk of the Me_5Cp^- ligand or to its lack of a reactive ring carbon-to-hydrogen bond. The latter feature has proven especially useful in studies of early transition-metal cyclopentadienyl derivatives where a common mode of reactivity involves insertion of the metal into a C–H bond of C_5H_5.[22-26]

The steric effects of complete ring alkylation have proven particularly influential in the structure and chemistry of uranium(IV) and thorium(IV) cyclopentadienyl derivatives. Complexes of these metals containing four Cp^- rings (Cp_4M; M = U, Th),[27,28] three Cp^- rings (Cp_3MCl; M = U, Th),[29,30] and one Cp^- ring ($CpUCl_3$(1,2-dimethoxyethane))[31] can be isolated, depending on reaction conditions and stoichiometry. The missing member of this series, Cp_2UCl_2, disproportionates to tris- and mono(cyclopentadenyl) derivatives in donor solvents[32] and authentic Cp_2UCl_2 has not yet been isolated.

With pentamethylcyclopentadienide or ethyltetramethylcyclopentadienide ($EtMe_4Cp^-$), monomeric uranium(IV) and thorium(IV) compounds containing one peralkylated ring ((Me_5Cp)$ThCl_3$;[6] ($EtMe_4Cp$)UCp_2Cl[33]) and two peralkylated rings (($Me_5Cp)_2MCl_2$; M = Th and U;[18] ($EtMe_4Cp)_2UCl_2$[17]) have been prepared, but complexes containing three peralkylated rings have proven elusive.[6]

A third possible consequence of complete alkylation of the Cp^- ring is the effect on the electron donor/acceptor properties of the ring and the electronic structures of the metal derivatives. Evidence for such an effect was described in our earlier studies of decamethylmanganocene.[34] Magnetic studies of decamethylmanganocene showed that permethylation of the Cp^- ring results in an exclusively low-spin $^2E_{2g}$ electronic configuration, in contrast to other manganocenes where high-spin $^6A_{1g}$ states are thermally populated.[35] In spite of the fact that Me_5Cp^- is a much bulkier ligand than Cp^-, the metal-to-ring carbon distances in $(Me_5Cp)_2Mn$ are about 0.3 Å shorter than those in high-spin manganocenes. Manganocenes with the low-spin configuration are inert toward ring displacement and hydrolysis. The permethylated complex does undergo reversible one-electron oxidation and reduction to give low-spin 16- and 18-electron derivatives for which no analogues exist in other manganocenes.

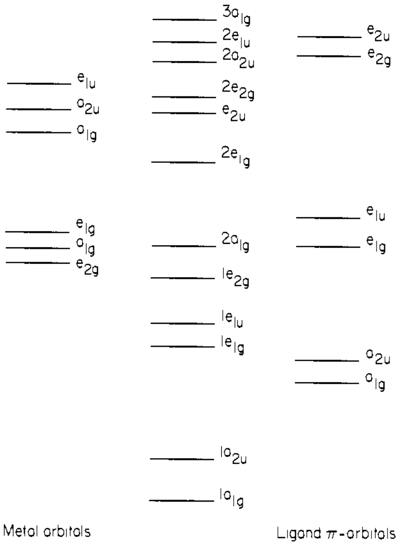

Figure 1. Molecular orbital diagram for ferrocene after ref 37.

These results indicate that the ligand-field strength of the Cp^- ring is significantly enhanced by the complete replacement of the hydrogens with electron-donating methyl groups. In this paper we describe studies that determine the nature, scope, and magnitude of such an effect via a systematic comparison of the chemistry and electronic structures of the metallocenes and the decamethylmetallocenes containing the first transition series metals V, Cr, Fe, Co, and Ni. Magnetic studies show the decamethylmetallocenes possess the same ground electronic configurations as their metallocene counterparts. Comparison of UV-visible spectra (and derived parameters) of the d^3, d^6, and d^8 metallocenes and decamethylmetallocenes is used to determine the effects of ring peralkylation on the ligand-field splitting. Before describing these results, we will briefly review the salient features of bonding in metallocenes with D_{5d} symmetry.[36-38]

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Review of Electronic Structure. The molecular orbital diagram shown in Figure 1 is useful in describing the ground-state electronic configurations of the first transition series metallocenes and in accounting for the optical and UV–photoelectron spectra of these molecules.[37,38] The principal bonding between the metal and the rings results from interaction of metal 3d and ligand π orbitals of e_{1g} symmetry to generate strongly bonding ($1e_{1g}$) and strongly antibonding ($2e_{2g}$) molecular orbitals. Overlap of the other metal 3d orbitals with ligand π orbitals is much weaker, so the molecular $2a_{1g}$ and $1e_{2g}$ levels retain a high degree of metal character. Although some controversy remains regarding the absolute ordering of the $2a_{1g}$ and $1e_{2g}$ molecular orbitals,[38,39] the ordering shown here ($\epsilon(2a_{1g}) > \epsilon(1e_{2g})$) provides for the most straightforward interpretation of the d^3, d^6, and d^8 metallocene electronic spectra and will be used in the following discussions.

UV–photoelectron and UV–visible studies of the first transition series metallocenes establish that the splitting of the $2a_{1g}$ and $1e_{2g}$ molecular orbitals, $\Delta_1 = (\epsilon(2a_{1g}) - \epsilon(1e_{2g}))$, is rather small (ca. 4000–7000 cm^{-1}) compared to the spin-pairing energy, so 15-electron species adopt a high-spin ${}^4A_{1g}[e_{2g}{}^2a_{1g}{}^1]$ rather than a low-spin ${}^2E_{2g}[e_{2g}{}^3]$ electronic configuration. The splitting of the $2e_{1g}$ and $2a_{1g}$ orbitals ($\Delta_2 = \epsilon(2e_{1g}) - \epsilon(2a_{1g})$) is much greater (ca. (17–20) × 10^3 cm^{-1}), and 16- through 19-electron metallocenes generally have low-spin electronic configurations with electrons paired in the $2a_{1g}$, $1e_{2g}$ manifold when possible. The exceptions to this rule are the high-spin 17-electron complexes Cp_2Mn and $(MeCp)_2Mn$.[35]

Experimental Section

General. Reagent grade tetrahydrofuran (THF) was predried over CaH_2. Hexane, pentane, toluene, 1,4-dioxane, 1,2-dimethoxyethane (DME), and THF were purified by distillation from sodium benzophenone ketyl. Acetone was purified by distillation from anhydrous K_2CO_3. Spectroscopic grade acetonitrile was distilled from P_2O_5 and freeze–thaw degassed for optical and electrochemical studies. For EPR studies, spectroscopic grade toluene and methylcyclohexane were distilled from sodium. Deuterated solvents for NMR studies were vacuum distilled from the appropriate desiccant (CaH_2 for C_6D_6 and THF-d_8, P_2O_5 for CD_3CN) and then freeze–thaw degassed. All solvents were stored under argon.

1,2,3,4,5-Pentamethylcyclopentadiene,[7] sodium pentamethylcyclopentadienide,[10] $NiBr_2 \cdot 2DME$,[40] and decamethylferrocene[41] were prepared by literature procedures. Chromous acetate, $[Cr(OAc)_2]_2 \cdot 2H_2O$,[42] and commercially available $CoCl_2 \cdot 6H_2O$ were dehydrated by heating to 120 °C in vacuo. Ferrocenium hexafluorophosphate was prepared according to the procedure described by Pinsky.[43] Ferrocenium tetrafluoroborate was prepared by adding solid $NaBF_4$ (1 equiv) to a filtered aqueous solution of $(Cp_2Fe)FeCl_4$. Upon cooling (5 °C), crystalline $(Cp_2Fe)BF_4$ deposited. This was filtered in air, washed with water (2 × 1 mL) and then with THF (2 × 10 mL), and dried under vacuum. All other chemicals were reagent grade and were used without further purification.

Air-sensitive solids were stored and manipulated in a Vacuum Atmospheres inert-atmosphere box equipped with a modified drytrain. Air-sensitive solutions and dry, deoxygenated solvents were transferred with 18-gauge stainless steel cannulae connected by polyethylene tubing. Unless otherwise noted, all reactions were carried out in dry, deoxygenated solvents under an argon atmosphere by using standard Schlenk-tube techniques. Solutions for NMR, EPR, and optical studies were prepared and transferred to appropriate cells inside an inert atmosphere box.

Infrared spectra were recorded as KBr pellets or mulls (Nujol or Kel-F) between CsI plates with a Perkin-Elmer 283 spectrophotometer. Proton NMR spectra and magnetic susceptibility measurements by the Evans NMR method were recorded on a Varian A-60 spectrometer. Proton-decoupled ^{13}C NMR spectra were obtained at 25 MHz in the pulsed Fourier transform mode with a Nicolet TT-23 spectrometer. All chemical shifts are reported in ppm (δ) with reference to tetramethylsilane. Optical spectra were recorded on a Cary-17 spectrophotometer with a nitrogen-purged sample compartment.

Variable-temperature bulk magnetic susceptibility measurements were made on a PAR Model 155 vibrating sample magnetometer calibrated with $HgCo(SCN)_4$. Field strength was monitored with a rotating coil gaussmeter. Temperature was measured with a calibrated GaAs diode.

X-band EPR spectra of decamethylmetallocenes in frozen toluene or methylcyclohexane solution (~0.1 M) or diluted in diamagnetic decamethylmetallocenes at 10–15 K were obtained by using a Varian E-12 spectrometer employing an Air Products Helitran cooling system mounted in the room-temperature cavity. The cavity frequency was measured with a Hewlett-Packard transfer oscillator and frequency counter and the magnetic field with a proton NMR gaussmeter.

Cyclic voltammograms were recorded in the three-electrode configuration with a platinum disk working electrode, a platinum wire auxiliary electrode, and a $Ag/AgNO_3$ (CH_3CN) reference electrode inside an inert atmosphere box. All potentials were referenced to the saturated calomel electrode (SCE) by measuring the ferrocene/ferrocenium couple under identical conditions.

Mass spectra were recorded on an AEI-MS 12 mass spectrometer equipped with a direct inlet system. Elemental analyses were performed by the Microanalytical Laboratory of the University of California, Berkeley. Melting points were determined on a Thomas-Hoover Unimelt apparatus and are uncorrected.

Preparation of Complexes. Bis(pentamethylcyclopentadienyl)vanadium(II). A suspension of $VCl_3 \cdot 2THF$ in THF (50 mL) was prepared from VCl_3 (3.11 g; 19.8 mmol) and Zn dust (0.65 g; 9.9 mmol) by using the method described by Kohler and Prössdorf.[44] The stirred suspension was added through a cannula to a solution of Me_5CpNa (4.00 g; 25.3 mmol) in THF (100 mL), and the mixture was refluxed for 7 h to yield a dark purple solution. Solvent was removed under reduced pressure, and the product was heated under vacuum (60 °C; 10^{-3} torr) for 6 h to remove oily contaminants. The residue was then extracted with pentane (50 mL), filtered, and washed with pentane until washings were colorless (3 × 20 mL). Solvent was again removed in vacuo to give a red, microcrystalline solid. Sublimation (100 °C; 10^{-5} torr) followed by recrystallization from pentane gave $(Me_5Cp)_2V$ as air-sensitive, dark red prisms (2.60 g; 65%).

(Acetonitrile)bis(pentamethylcyclopentadienyl)vanadium(III) Hexafluorophosphate. Acetonitrile (40 mL) was added through a cannula to a mixture of $(Me_5Cp)_2V$ (0.20 g; 0.62 mmol) and $(Cp_2Fe)PF_6$ (0.20 g; 0.60 mmol). The ferrocenium salt dissolved instantly with stirring, yielding a deep blue solution. Over a period of 30 min, the decamethylvanadocene dissolved and reacted to give a dark green solution of the product. Solvent was removed under vacuum, and the resulting solid was washed with hexane (5 × 10 mL) to remove Cp_2Fe and then dried under vacuum to yield the crude product as an air-sensitive, dark green powder (0.22 g; 96%). Olive green needles were obtained by crystallization from acetonitrile/toluene (2/1, v/v).

Dicarbonylbis(pentamethylcyclopentadienyl)vanadium(III) Hexafluorophosphate. Carbon monoxide was passed over a stirred solution of $[(Me_5Cp)_2V(NCCH_3)]PF_6$ (0.40 g; 0.79 mmol) in acetone (50 mL) for 1.5 h, and the color changed from dark green to yellow. The solution was concentrated to ca. 10 mL, and hexane (10 mL) was added slowly until the solution became cloudy. Upon cooling (−30 °C, 12 h), the product crystallized as bright yellow prisms. The solid was filtered, washed with hexane (2 × 10 mL), and dried under vacuum (0.38 g; 78%).

Bis(pentamethylcyclopentadienyl)chromium(II). Solid $Cr_2(OAc)_4$ (2.15 g; 6.32 mmol) was added against an argon counterstream to a solution of Me_5CpNa (4.00 g; 25.28 mmol) in THF (50 mL). The mixture was stirred for 8 h at room temperature to yield a white solid suspended in a dark red solution. Decamethylchromocene was isolated from this mixture as red air-sensitive prisms (2.6 g; 64%), following the procedure described above for $(Me_5Cp)_2V$.

Bis(pentamethylcyclopentadienyl)chromium(III) Hexafluorophosphate. Tetrahydrofuran (40 mL) was added to a mixture of $(Me_5Cp)_2Cr$ (0.94 g; 2.92 mmol) and $(Cp_2Fe)PF_6$ (0.92 g; 2.78 mmol). The chromium compound dissolved rapidly with stirring, but the ferrocenium salt dissolved only slowly. After stirring for 8 h at room temperature, the ferrocenium salt was no longer visible and the product had deposited as a yellow precipitate. This was collected by filtration, washed with THF (3 × 10 mL), and dried under vacuum to give a green-yellow solid (1.20 g; 90%). Crystallization from a concentrated acetone solution yielded

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Table I. Physical, Analytical, and Infrared Data for Decamethylmetallocenes

compound	melting point, °C	mass spectrum,[a] p^+	infrared,[b] cm^{-1}	anal. calcd (found)
$(Me_5Cp)_2V$	299–300	321 (100)	587 (w), 463 (m), 422 (w), 233 (w)	C, 74.74 (74.90); H, 9.41 (9.15)
$[(Me_5Cp)_2V(NCCH_3)]PF_6$			459 (m), 442 (w), $\nu_{CN} = 2270$ (s)	C, 52.07 (52.24); H, 6.55 (6.31); N, 2.76 (2.75); P, 6.11 (5.93)
$[(Me_5Cp)_2V(CO)_2]PF_6$			515 (m), 454 (w), $\nu_{CO} = 1989$ (s), 1954 (s), 1975 (w), 1902 (w)	C, 50.58 (50.69); H, 5.79 (5.84); P, 5.93 (5.79)
$(Me_5Cp)_2Cr$	296–297	322 (100)	585 (m), 418 (m), 235 (w)	C, 74.49 (74.34); H, 9.09 (9.09)
$[(Me_5Cp)_2Cr]PF_6$			525 (m), 440 (w), 432 (w)	C, 51.39 (51.50); H, 6.47 (6.39); P, 6.63 (6.63)
$(Me_5Cp)_2Co$	294–296	329 (100)	586 (m), 429 (w), 320 (w), 232 (w)	C, 72.93 (73.06); H, 9.18 (9.11)
$[(Me_5Cp)_2Co]PF_6$			590 (w), 448 (m), 362 (m), 255 (w)	C, 50.54 (50.79); H, 6.37 (6.35); P, 6.53 (6.42)
$(Me_5Cp)_2Ni$	296–297	328 (100)	587 (w), 385 (m), 320 (w)	C, 72.98 (73.03); H, 9.19 (9.07)
$[(Me_5Cp)_2Ni]PF_6$			472 (w), 225 (w)	C, 50.66 (50.41); H, 6.38 (6.27); P, 6.53 (6.68)
$[(Me_5Cp)_2Ni](PF_6)_2$			468 (w), 432 (m), 328 (m), 248 (m)	C, 38.80 (38.63); H, 4.88 (4.88); P, 10.01 (9.81)
$(Me_5Cp)_2Mg$	289–292	294 (308)	587 (w), 560 (m), 517 (s), 427 (m), 283 (m), 210 (w)	C, 81.49 (82.65); H, 10.26 (10.15)

[a] 70 eV. Only parent ion reported. *m/e* (relative abundance). [b] Absorptions between 600 and 200 cm^{-1} reported. Between 4000 and 600 cm^{-1} infrared spectra are superimposable with characteristic absorptions at 2989 (m), 2940 (m), 2895 (s), 2850 (m), 2750 (w), 1470 (m), 1448 (m), 1422 (m), 1373 (m), 1355 (w), 1065 (m), 1023 (w), and 722 (w) cm^{-1}. The PF_6^- salts also show bands at 874 (s), 845 (s), 725 (m), 552 (s), and 530 (m) cm^{-1}.

pure $[(Me_5Cp)_2Cr]PF_6$ as orange-yellow prisms.

Bis(pentamethylcyclopentadienyl)cobalt(III) Hexafluorophosphate. A solution of Me_5CpH (8.00 g; 58.7 mmol) in THF (200 mL) was cooled to −78 °C (dry ice/ethanol) and treated with *n*-butyllithium (24.5 mL; 2.4 M in hexane). Upon warming to room temperature (ca. 1 h), white Me_5CpLi precipitated from a yellow solution. Solid anhydrous $CoCl_2$ (3.81 g; 29.3 mmol) was added against an argon counterstream and the mixture immediately turned brown. After being stirred at room temperature for 12 h, the dark brown solution was treated with solid NH_4PF_6 (5.00 g; 30.7 mmol), resulting in a mildly exothermic reaction and evolution of gas. After being stirred an additional 12 h at room temperature, the mixture was filtered. The resulting brown solid was washed with THF (3 × 20 mL) and H_2O (5 × 20 mL) and dried under vacuum to give a green powder. The aqueous wash and all subsequent steps were performed in air. The green solid was extracted into acetone and filtered, and the solution was concentrated to ca. 20 mL. Addition of hexane (100 mL) gave a yellow precipitate which was filtered, washed with hexane (2 × 10 mL), and dried in air to yield $[(Me_5Cp)_2Co]PF_6$ as a bright yellow air-stable powder (3.8 g; 28%). Crystallization from a concentrated acetone solution gave yellow prisms.

Bis(pentamethylcyclopentadienyl)cobalt(II). Tetrahydrofuran (30 mL) was added to a mixture of $[(Me_5Cp)_2Co]PF_6$ (2.75 g; 5.80 mmol) and Na/Hg amalgam (17.0 g; 0.83% Na; 6.4 mmol of Na). After stirring for 12 h, all of the Co(III) starting material had reacted to give a clear brown solution which was decanted from the Hg through a cannula into a Schlenk tube. Solvent was removed in vacuo and the product was sublimed (10^{-5} torr/100 °C) and then crystallized from hexane to yield $(Me_5Cp)_2Co$ as dark brown, air-sensitive prisms (1.60 g; 84%).

Bis(pentamethylcyclopentadienyl)nickel(II). Pentamethylcyclopentadiene (8.00 g; 58.7 mmol) in THF (35 mL) was deprotonated with *n*-butyllithium (25.0 mL; 2.37 M in hexane) at −78 °C, as described in the preparation of $[(Me_5Cp)_2Co]PF_6$. Solid $NiBr_2 \cdot 2DME$ (9.06 g; 29.4 mmol) was added against an argon counterstream to the Me_5CpLi suspension at room temperature, and the mixture was stirred for 1 day at room temperature to yield a dark brown solution. Following the procedure described in the isolation of $(Me_5Cp)_2V$, we obtained $(Me_5Cp)_2Ni$ as dark green prisms (5.5 g; 57%). Several sublimations were required to separate the product from a yellow, pentane-soluble but involatile impurity.

Bis(pentamethylcyclopentadienyl)nickel(III) Hexafluorophosphate. Decamethylnickelocene (1.40 g; 4.25 mmol) and $(Cp_2Fe)PF_6$ (1.30 g; 3.93 mmol) were allowed to react in THF in the manner described above in the preparation of $[(Me_5Cp)_2Cr]PF_6$ to give $[(Me_5Cp)_2Ni]PF_6$ as a brown powder (1.67 g; 90%). Crystallization from acetone afforded dark brown prisms. The BF_4^- salt was prepared similarly from $(Cp_2Fe)BF_4$ and $(Me_5Cp)_2Ni$.

Bis(pentamethylcyclopentadienyl)nickel(IV) Bis(hexafluorophosphate). Tetrahydrofuran (30 mL) was added to a mixture of solid $(Me_5Cp)_2Ni$ (0.83 g; 2.52 mmol) and solid $HgCl_2$ (0.68 g; 2.51 mmol). The solids dissolved rapidly and an orange precipitate separated from a pale green solution. The mixture was stirred for 1 h and then filtered. The orange precipitate was washed with THF (2 × 10 mL) and dried under vacuum. Subsequent reactions were performed in air. The product (1.46 g) was dissolved in 0.1 M aqueous HCl (10 mL) to give an orange solution and a metallic precipitate. The solution was filtered and then treated with solid NH_4PF_6 (1.5 g). A yellow-brown solid immediately precipitated. This was filtered and then extracted with warm (40 °C) 0.1 M aqueous HCl (10 × 30 mL). The solvent volume was reduced under vacuum to ca. 10 mL, and the product crystallized as orange prisms which were collected on a fritted disk filter, washed with cold H_2O (2 × 5 mL), and dried in air (0.60 g; 38%). Recrystallization from warm 0.1 M HCl gave an analytically pure sample.

Solid $[(Me_5Cp)_2Ni](PF_6)_2$ decomposes slowly (over a period of a week) in air, under vacuum, or under an argon atmosphere to a paramagnetic dark brown material. The complex decomposes instantly in $(CH_3)_2CO$ or CH_3CN solution but is stable for several days in acidic aqueous solution. The PF_6^- salt was not sufficiently soluble in aqueous solution to allow determination of the ring-carbon chemical shift in the ^{13}C NMR spectrum although the methyl carbon atom resonance was observed at δ 9 after 26 000 pulses. For determination of the complete ^{13}C NMR spectrum, a sample of the orange precipitate from the $HgCl_2/(Me_5Cp)_2Ni$ reaction (0.3 g) was dissolved in a minimum volume of 0.1 M HCl (1 mL), filtered, treated with a deficiency (0.5 equiv) of NH_4PF_6 to precipitate $[(Me_5Cp)_2Ni]PF_6$ and any paramagnetic impurities, and then filtered again. The resulting solution was diamagnetic, as determined by the Evans NMR method. The optical spectrum of a diluted aliquot of this solution was identical with that of the pure PF_6^- salt. The concentrated solution of $[(Me_5Cp)_2Ni]Cl_2$ was then transferred to a coaxial NMR tube with C_6D_6 in the inner capillary to provide a deuterium lock and reference for the ^{13}C chemical shifts.

Bis(pentamethylcyclopentadienyl)magnesium(II). A solution of *i*-PrMgCl in THF (66 mL; 1.2 M; 79.2 mmol) was transferred with a syringe into a flask containing Me_5CpH (10.0 g; 73.4 mmol). Toluene (125 mL) was added through a cannula and the mixture was stirred at 80 °C for 6 h to give an orange solution. 1,4-Dioxane (70 mL) was added and a small quantity of a white solid, $MgCl_2 \cdot 1,4$-dioxane, precipitated. The mixture was stirred at 80 °C for 36 h. During this time additional white solid precipitated. The solution was cooled to room temperature and filtered, and the resulting white solid was washed with toluene (2 × 20 mL). The solution was reduced under vacuum to an orange oil which was freed of volatile liquids by evacuation overnight at 70 °C. The flask was then fitted with a water-cooled probe and $(Me_5Cp)_2Mg$ was sublimed (4.45 g; 41%). Resublimation gave an analytically pure sample. The product crystallizes from hexane as colorless prisms.

Analytical, mass spectral, and infrared data for these compounds are given in Table I.

Results and Discussion

Synthesis and Characterization. The synthesis of the decamethylmetallocenes frequently requires modifications of the commonly used routes to the metallocenes and the 1,1′-dimethylmetallocenes. For example, the reaction $MCl_3 + 3Na^+RCp^- \rightarrow (RCp)_2M + RCp + 3NaCl$ (R = H or Me) has been used in the preparation of vanadocenes and chromocenes[35a] where 1 equiv of cyclopentadienide serves to reduce the trivalent metal salts. However, the hydrocarbon-soluble products derived from the reaction of 3 equiv of Me_5CpNa with VCl_3 or $CrCl_3$ in THF are intractable oils containing only small amounts of the desired products. The isolation of pure decamethylmetallocenes from these reaction mixtures is complicated by the presence of the pentamethylcyclopentadiene dimer,[45] a colorless solid whose volatility and solubility properties are quite similar to those of the desired products. These results suggest that efficient routes to neutral decamethylmetallocenes require the use of divalent metal starting materials.

Kohler and Prössdorf[44] have reported the preparation of $(RCp)_2V$ (R = H or Me) from the reaction of $VCl_2 \cdot 2THF$ with 2 equiv of Na^+RCp^- in THF. We find that $(Me_5Cp)_2V$ may also be prepared by this route. Me_5CpLi may be substituted for Me_5CpNa, but with a significant reduction in yield. We have also obtained nearly quantitative yields of $(Me_5Cp)_2V$ from the reaction of Me_5CpNa with $VCl_2 \cdot (pyridine)_4$[46] in THF.

Kohler and Prössdorf also describe the synthesis of $(RCp)_2Cr$ from the reaction of a cyclopentadienide with $CrCl_2 \cdot THF$.[44] We find that readily available $Cr_2(OAc)_4$ reacts with 4 equiv of $(Me_5Cp)Na$ in THF to afford $(Me_5Cp)_2Cr$ in good yield.

The modest yield obtained in the synthesis of $[(Me_5Cp)_2Co]PF_6$ merits comment. Both Cp_2Co and $(MeCp)_2Co$ are obtained in high yield from the reaction of the cyclopentadienide with $CoCl_2$[35a] in THF, but anhydrous cobaltous salts (e.g., $CoCl_2$, $CoBr_2$, and $Co(OAc)_2$) react with $MeCp_5^-$ (as the Li^+, Na^+, or Mg^{2+} salts) in THF to give a complex mixture of products, most of which are insoluble in nonpolar solvents.[47] Isolation of pure $(Me_5Cp)_2Co$ from the crude reaction mixture is complicated by the presence of other volatile-hydrocarbon soluble products, but oxidation of the reaction mixture with NH_4PF_6 affords the air-stable $[(Me_5Cp)_2Co]PF_6$ as a yellow precipitate in 28% yield. Subsequent reduction of the cation with Na/Hg in THF gives $(Me_5Cp)_2Co$ in high yield. Subsequent to the completion of this work, Koelle and Khouzami[48] reported that the reaction of $CoBr_2 \cdot 1,2$-dimethoxyethane with Me_2CpLi in a refluxing mixture of THF and diethyl ether gives, after oxidation with $FeCl_3$ and treatment with PF_6^-, $[(Me_5Cp)_2Co]PF_6$ in 85% yield. Their success is probably due to replacement of diethyl ether for some of the THF in the solvent mixture; however, the THF/ether ratio was not specified. These workers used K/Hg to reduce $[(Me_5Cp)_2Co]PF_6$ to $(Me_5Cp)_2Co$.

Decamethylnickelocene is obtained in moderate yield from the reaction of $NiBr_2 \cdot 2DME$ with Me_2CpLi in THF. Again, Koelle and Khouzami report that much higher yields (90%) are realized when this reaction is performed in a refluxing THF/diethyl ether mixture.[48]

The neutral decamethylmetallocenes are very soluble in aromatic and aliphatic hydrocarbon solvents as well as THF, diethyl ether, and dichloromethane, but are only slightly (ca. 10^{-3} M) soluble in acetone or acetonitrile. They melt in the range 290–300 °C and are volatile, subliming at temperatures greater than 70 °C (10^{-5} torr). With the exception of $(Me_5Cp)_2Fe$, the neutral compounds are air sensitive both as solids and in solution.

Table II. Metallocene and Decamethylmetallocene Electrochemical Data

metallocenes	$E_{1/2}{}^a$	reference	decamethylmetallocenes	$E_{1/2}{}^{a,b}$	reference
$(Cp_2Cr)^+$	-0.55^c	50c	$[(Me_5Cp)_2Cr]^+$	-1.04	this work
$(Cp_2Fe)^+$	0.41	this work	$[(Me_5Cp)_2Fe]^+$	-0.12	this work, 48
$(Cp_2Co)^+$	-0.91	48	$[(Me_5Cp)_2Co]^+$	-1.47	this work
$(Cp_2Ni)^+$	-0.09	52	$[(Me_5Cp)_2Ni]^+$	-0.65	this work
$(Cp_2Ni)^{2+}$	0.77	52	$[(Me_5Cp)_2Ni]^{2+}$	0.31	this work

[a] Half-wave potentials for the reaction $[(R\text{-}Cp)_2M]^{n+} + e^- \rightleftarrows [(R\text{-}Cp)_2M]^{(n-1)+}$ given in volts with reference to the saturated calomel electrode. [b] Determined by cyclic voltammetry in CH_3CN solution with 0.1 *M* $[(n\text{-}Bu)_4N]BF_4$ electrolyte. [c] The reversibility of this wave in CH_3CN solution is questionable.[50c]

Like the first transition series metallocenes, the permethylated compounds undergo facile one-electron oxidation to isolable monocationic derivatives. The $[(Me_5Cp)_2M]PF_6$ salts (M = Cr, Mn, Co, and Ni) are obtained in nearly quantitative yield via the reaction of $(Me_5Cp)_2M$ with 1 molar equiv of $(Cp_2Fe)PF_6$ in THF.[49] Decamethylcobaltocene and decamethylchromocene are *very* strong reducing agents (see Table II); both are oxidized by proton sources such as H_2O and NH_4^+. In contrast, Cp_2Cr^+ has been prepared only by oxidation of Cp_2Cr with allyl iodide[50a] or carbon tetrachloride.[50b] The reaction of chromocene with $(Cp_2Fe)PF_6$ results in extensive decomposition.[50c]

The $[(Me_5Cp)_2M]PF_6$ compounds are very soluble in acetone, acetonitrile, and dichloromethane, sparingly soluble in THF and diethyl ether, and insoluble in aromatic and aliphatic hydrocarbon solvents. The cationic Fe, Co, and Ni compounds are air-stable solids. The Cr(III) complex decomposes *very* slowly in air. This contrasts with $[Cp_2Cr]I$, which is reported to be very air sensitive.[50a] The cationic Cr and Ni compounds are air sensitive in solution.

The cyclic voltammograms of $[(Me_5Cp)_2M]PF_6$ (M = Cr, Fe, Co, Ni) in dry, oxygen-free acetonitrile show that each complex is reduced in a reversible step with a peak separation close to 59 mV, the theoretical value for a reversible one-electron process.[51] Half-wave potentials for these couples are reported in Table II. Values for the Fe, Co, and Ni derivatives are in good agreement with those determined in CH_2Cl_2 solution by Koelle and Khouzami.[48]

The reduction potentials of the decamethylmetallocene cations are in general cathodically shifted by about 500 mV relative to the corresponding metallocene–metallocenium couples. Along similar lines, a UV–PES study of the $(Me_5Cp)_2M$ compounds in the gas phase showed that the more localized the orbital is on the ligand, the greater the lowering of the ionization energy (1–1.5 eV) in the peralkylated derivatives as compared to the corresponding ionization energies of the Cp_2M compounds.[34e] The enhanced stability of the decamethylmetallocene cations is again attributed to the electron-donating properties of the substituent methyl groups.

As Koelle and Khouzami found, the cyclic voltammogram of $[(Me_5Cp)_2Ni]PF_6$ in acetonitrile exhibits *two* reversible, one-electron waves at −0.65 and 0.31 V vs. SCE, which correspond to the $[(Me_5Cp)_2Ni]^+/(Me_5Cp)_2Ni$ and $[(Me_5Cp)_2Ni]^{2+}/[(Me_5Cp)_2Ni]^+$ redox couples, respectively.[48] Formally, this may be viewed as a Ni(II), Ni(III), Ni(IV) system analogous to the $[(B_9C_2H_{11})_2Ni]^{2-/1-/0}$ complexes isolated by Hawthorne et al.[52a] Van Duyne[52b] and Hawthorne[52a] have independently reported electrochemical evidence for the existence of $(Cp_2Ni)^{2+}$ in dry acetonitrile, but to date neither its isolation nor its characterization in solution has been reported.

In acetone or acetonitrile solution, $[(Me_5Cp)_2Ni]PF_6$ reacts with Ce(IV), O_2, Ag^+, or H_2O_2 to give an amorphous, green, paramagnetic solid. However, treatment of a THF solution of $(Me_5Cp)_2Ni$ with 1 molar equiv of $HgCl_2$ results in immediate precipitation of an orange solid. This dissolves in 0.1 M aqueous HCl to yield colloidal Hg and a solution of $[(Me_5Cp)_2Ni]^{2+}$, which

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(47) Green and Pardy (ref 15) recently found that tri-*n*-butyl(ethyltetramethylcyclopentadienyl)tin reacts with $CoCl_2$ in THF solution to yield a toluene-soluble, red-brown oil. Chlorination of this oil afforded complexes of the stoichiometry $[(EtMe_4Cp)CoCl_2]_2$ and $[(EtMe_4Cp)_2Co_3Cl_6]$ ($EtMe_4Cp$ = η-ethyltetramethylcyclopentadienyl). These compounds dissolved in water to give blue solutions of the trichloro-bridged dimer, $[(EtMe_4Cp)_2Co_2(\mu\text{-}Cl_3)]^+$. Halbert et al. isolated the bridged dimer $(\mu\text{-}CO)(\mu\text{-}CH_2)(Me_5Cp)_2Co_2$ from the reaction of *n*-butyllithium with Me_5C_5H at room temperature, followed by addition of $CoCl_2$. Halbert, T. R.; Leonowicz, M. E.; Maydonovitch, D. J. *J. Am. Chem. Soc.* **1980**, *102*, 5101–5102. No decamethylcobaltocene was isolated from these reaction mixtures.

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(49) Koelle and Khouzami prepared $[(Me_5Cp)_2Ni]^+$ by oxidation of $(Me_5Cp)_2Ni$ with $FeCl_3$. $[(Me_5Cp)_2Ni]^{2+}$ was obtained by O_2 or Br_2 oxidation of $(Me_5Cp)_2Ni$; see ref 48.

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was subsequently isolated as the crystalline, orange-brown PF_6^- salt. The infrared spectrum of $[(Me_5Cp)_2Ni](PF_6)_2$ in the range 4000–700 cm^{-1} is similar to the spectra of the $[(Me_5Cp)_2M]PF_6$ compounds (see below). An Evans' NMR method measurement[53] shows that the complex is diamagnetic in solution. We conclude that $[(Me_5Cp)_2Ni]^{2+}$ is a planar, 18-electron decamethylmetallocene, isoelectronic with $[(Me_5Cp)_2Mn]^-$, $(Me_5Cp)_2Fe$, and $[(Me_5Cp)_2Co]^+$.

The decamethylnickelocene dication is a metastable complex. The solid PF_6^- salt slowly decomposes to a brown solid, even in the absence of air. In cold, acidic, aqueous solution the complex is stable for several days, but in neutral or basic solution it is rapidly reduced to the Ni(III) derivative. Dissolution of the dication in acetonitrile or acetone, or addition of these solvents to an aqueous solution of the complex, results in decomposition to the same green substance obtained in attempts to oxidize $(Me_5Cp)_2Ni^+$ in nonaqueous solvents.

The cyclic voltammogram of $(Me_5Cp)_2V$ in acetonitrile solution is complex and exhibits no reversible one-electron waves. Decamethylvanadocene is rapidly oxidized by $(Cp_2Fe)PF_6$ in THF, but the blue product polymerizes the solvent. In acetone, acetonitrile, or diethyl ether solution, $(Me_5Cp)_2V$ reacts with $(Cp_2Fe)PF_6$ to yield paramagnetic solvated V(III) complexes corresponding to the formulation $[(Me_5Cp)_2VS]PF_6$ (S = solvent). Attempts to remove the solvent from these compounds by heating under vacuum resulted in their decomposition to intractable materials. This behavior parallels that of $(Cp_2V)^+$, which is also isolated as a solvated species in the absence of a coordinating anion (such as Cl^- or Br^-[54,55]) and further demonstrates the coordinative unsaturation of metallocenes with a 14-electron configuration.[10] Like $(Cp_2V)^+$, the permethylated derivative reacts with CO (1 atm) to give the diamagnetic 18-electron dicarbonyl complex, $[(Me_5Cp)_2V(CO)_2]PF_6$.[56] As King has found in a comparison of cyclopentadienyl- and (pentamethylcyclopentadienyl)metal carbonyls, the CO stretching frequencies occur at substantially lower energy in the permethylated compound (ν_{CO} = 1990, 1936 cm^{-1}) than in the unsubstituted derivative (ν_{CO} = 2050, 2010 cm^{-1}).[57] We follow King in suggesting this effect is due to the influence of electron-donating methyl groups which increase electron density on the metal center, thereby enhancing the M–CO bond and weakening the C–O bonds.[41]

The D_{5d} metallocene structure has been established by X-ray crystallography for $(Me_5Cp)_2M$ (M = Mn, Fe, Co) and $[(Me_5Cp)_2M]PF_6$ (M = Cr, Mn, Fe, Co).[35c,36] Infrared spectra of the neutral transition-metal compounds are superimposable in the ranges 3000–2700 cm^{-1} (four bands), 1350–1500 cm^{-1} (five bands), and 1000–1100 cm^{-1} (two bands). Infrared spectra of the cationic complexes are similar, but more poorly resolved. Since these bands are insensitive to changes in metal ion oxidation state and even geometry (e.g., the "bent" $[(Me_5Cp)_2V(CO)_2]^+$ and $[(Me_5Cp)_2V(solvent)]^+$ complexes), they must represent primarily ligand vibrational modes for the η^5-bound Me_5Cp^- ligand. Below 600 cm^{-1}, where metal–ring vibrations are expected to occur, the infrared spectra vary from compound to compound. Specific infrared data in this region are listed in Table I.

A comparison of the ^1H and ^{13}C NMR data for diamagnetic Me_5Cp^- compounds (Table III) shows that the chemical shift of the ring carbon atom is very sensitive to the electronic effects induced by variation of the metal ion. Although ^{13}C chemical shift values are subject to a number of influences, we find that for the planar transition-metal compounds, the order of decreasing chemical shift, $\delta(Ni) > \delta(Co) > \delta(Fe) > \delta(Mn)$, follows the expected order of increasing metal to ring electron donation (i.e., Ni < Co < Fe < Mn).

Table III. ^1H and ^{13}C NMR Data for Diagmagnetic Me_5Cp^- Compounds[a]

		^{13}C[b]		
compound	^1H	ring C	methyl C	solvent
Me_5CpNa	2.01	105.1	11.8	THF-d_8
$(Me_5Cp)_2Mg$	1.93	110.1	9.6	C_6D_6
$[(Me_5Cp)_2V(CO)_2]PF_6$	2.00	107.4	9.3	$(CD_3)_2CO$
$Na[(Me_5Cp)_2Mn]$[34b]	1.83	72.4	8.5	THF-d_8
$(Me_5Cp)_2Fe$	1.70	78.4	9.6	C_6D_6
$[(Me_5Cp)_2Co]PF_6$	1.78	93.4	6.3	$(CD_3)_2CO$
$[(Me_5Cp)_2Ni]^{2+}$	2.20	118.3[c]	9.4[c]	D_2O

[a] All values in parts per million (δ) vs. tetramethylsilane. [b] Proton decoupled. [c] Values determined for the Cl^- salt in 0.1 M aqueous HCl.

Magnetic Susceptibility and EPR. Fifteen- and Twenty-Electron Systems. The magnetic properties of the metallocenes have been thoroughly investigated from both an experimental and a theoretical viewpoint.[38,58,59] The simplest behavior is found for systems with orbitally nondegenerate ground states, that is, compounds with 15-electron $^4A_{1g}$ (Cp_2V and Cp_2Cr^+) or 20-electron $^3A_{2g}$ (Cp_2Ni) configurations. No orbital contributions to the moment are expected, and furthermore, species with these configurations are not subject to Jahn–Teller distortions which can alter magnetic parameters (vide infra). Consequently, magnetic moments close to spin-only values are expected. Magnetic susceptibility measurements on vanadocenes and nickelocenes have confirmed these expectations. The complexes obey the Curie–Weiss law over a wide temperature range, and moments within experimental error of the spin-only values (2.87 μ_B for $S = 1$; 3.89 μ_B for $S = {}^3/_2$)[59] are found (Table IV).

Prins and co-workers observed that the Cp_2Ni magnetic susceptibility curve deviates from Curie–Weiss behavior below 70 K, and the susceptibility becomes essentially independent of temperature below 30 K.[60] They attributed this result to the influence of a large zero-field splitting on an otherwise nondegenerate triplet ground state. The magnitude of the zero-field splitting (25.6 cm^{-1}) was taken as conclusive evidence that the two unpaired electrons reside in a molecular orbital that is substantially metal rather than ligand in character, indicating a $^3A_{2g}$ $[e_{2g}{}^4a_{1g}{}^2e_{1g}{}^2]$ ground-state formulation. This ground state has also been assigned on the basis of UV–visible[61] and UV–PES[35g,h] studies of Cp_2Ni. The existence of a large zero-field splitting explains why no EPR signal is observed for Cp_2Ni.[62,63]

The χ_m^{-1} vs. T curve for $(Me_5Cp)_2Ni$ is very similar to that determined for Cp_2Ni by Prins. Above 20 K, χ_m^{-1} is proportional to temperature, yielding an effective moment (2.93 ± 0.1 μ_B) close to the spin-only value for an $S = 1$ molecule. A similar moment is observed in solution at room temperature (Table IV). Below 25 K, χ_m^{-1} becomes virtually independent of temperature. Magnetization data throughout the temperature range display a normal linear magnetic-field dependence, so ferromagnetism may be ruled out as an explanation for the unusual magnetic behavior observed at low temperatures.

As was found for Cp_2Ni, the $(Me_5Cp)_2Ni$ magnetic susceptibility data can be explained by use of a model that considers the influence of a large zero-field splitting on a nondegenerate, triplet ground state. Following the treatment of Prins et al.,[60] we assume the free electron value for $g_{\parallel}$ and by fitting the magnetic susceptibility data obtain $g_{\perp} = 1.74$ and $D = 30.5 \pm 1.0$ cm^{-1}. The values for D and μ_{eff} for $(Me_5Cp)_2Ni$ are close to those obtained for Cp_2Ni, so these compounds appear to have the same electronic

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Table IV. Magnetic Susceptibility Data for Metallocenes and Decamethylmetallocenes, $\chi_m = C/(T - \theta)$

compound	solid			solution		reference
	μ_{eff}[b]	θ	temp range[c]	μ_{eff}[b]	temp[c]	
$(Me_5Cp)_2V$	3.69 ± 0.1	0	5-64	3.78 ± 0.1	304	this work
Cp_2V	3.78 ± 0.2	6.5	14-430	3.78	298	71, 73
$[(Me_5Cp)_2Cr]PF_6$	3.73 ± 0.1	0	4.5-81	3.74 ± 0.1	304	this work
$(Cp_2Cr)I$	3.87		90-296			50a
$(Me_5Cp)_2Cr$	3.01 ± 0.1	0	6-81	2.90 ± 0.1	304	this work
Cp_2Cr	3.20 ± 0.16	17	90-295	3.10	298	72, 73
$(Me_5Cp)_2Co$	1.45 ± 0.1	0	5-130	1.56 ± 0.1	304	this work
Cp_2Co	1.75-2.04[d]		83-298	1.76	298	59, 73
$[(Me_5Cp)_2Ni]PF_6$	1.67 ± 0.1[e,f]	28	5-75	1.44 ± 0.1	304	this work
$[(Me_5Cp)_2Ni]BF_4$	1.62 ± 0.1	0	6-57			this work
$(Cp_2Ni)B(C_6H_5)_4$	1.82 ± 0.15		90-300			74
$(Me_5Cp)_2Ni$	2.93 ± 0.1[e]	−15	6-100	2.89 ± 0.1	304	this work
Cp_2Ni	2.89 ± 0.15[e]	6	70-300	2.86	298	73

[a] Measured in toluene or acetonitrile solution by the Evans NMR method.[53] [b] Values in μ_B [c] Temperature in K. [d] θ value uncertain because of curvature in χ_m^{-1} vs. T plot. [e] Moments and θ values obtained from the linear portion of the χ_m^{-1} vs. T curve. [f] Antiferromagnetic. Néel temperature = 18 K.

Table V. EPR Data for 15-Electron Metallocenes and Decamethylmetallocenes

compound	host	temp[a]	$g_\parallel$	$g_\perp$[b]	$A_\parallel$[c]	$A_\perp$[c]	ref
$(Me_5Cp)_2V$	toluene	19	2.001 (1)	3.973 (1)	24.0 (0.2)	16.0 (0.2)	this work
	toluene	300	$\langle g \rangle = 1.985$		$\langle A \rangle = 23.10$ (0.2)		this work
	$(Me_5Cp)_2Mg$	24	2.005 (2)	3.991 (1)	23.2 (0.2)	17.1 (0.2)	this work
Cp_2V	methylcyclohexane	77	1.990 (2)	4.004 (1)	36.7 (1.0)	21.5 (0.5)	61
	2-methyltetrahydrofuran	4	1.9888 (4)	4.0040 (6)	36.3 (0.2)	20.9 (0.2)	64
	Cp_2Mg	4	1.9882 (4)	4.0028 (6)	36.3 (0.2)	20.9 (0.2)	64
$[(Me_5Cp)_2Cr]PF_6$	$[(Me_5Cp)_2Co]PF_6$	9	2.001 (1)	4.02 (1)	*d*	253 (2)	this work
	$[(Me_5Cp)_2Co]PF_6$	300	2.004 (1)	4.03 (2)	*d*	*d*	this work
$[(Me_5Cp)_2Cr]^+$	$(Me_5Cp)_2Mg$[e]	17	1.99 (1)	4.01 (1)	*d*	*d*	this work
$(Cp_2Cr)^+$	Cp_2Mg[e]	4	2.002 (2)	3.954 (2)	*d*	*d*	64

[a] Temperatures in K. [b] This is a "half-field" resonance corresponding to a $\Delta m_s = 2$ transition. The true $g_\perp$ values are one-half of those reported. [c] In units of 10^{-4} cm^{-1}. [d] Hyperfine coupling not resolved. [e] Spectra of the neutral chromocenes cosublimed with Cp_2Mg or $(Me_5Cp)_2Mg$.

ground state. No EPR signal is observed for $(Me_5Cp)_2Ni$ in toluene solution at either 10 or 298 K, presumably because of the large magnitude of the zero-field splitting parameter.

Magnetic susceptibility and EPR studies for the 15-electron metallocenes Cp_2V and $(Cp_2Cr)^+$ indicate that they possess an orbitally nondegenerate $^4A_{2g}$ $[e_{2g}^2 a_{1g}^1]$ ground state. The magnetic moments of Cp_2V and $(Cp_2Cr)^+$ are close to the spin-only value for an $S = {}^3/_2$ system and are independent of temperature (Table IV). The EPR spectra of Cp_2V and $(Cp_2Cr)^+$ diluted in diamagnetic hosts consist of resonances near $g = 2$ ($g_\parallel$; $m_s = -{}^3/_2 \rightarrow m_s = -{}^1/_2$) and $g = 4$ ($g_\perp$; $m_s = -{}^3/_2 \rightarrow m_s = {}^1/_2$) (Table V). Vanadocene EPR spectra exhibit ^{51}V ($I = {}^7/_2$) hyperfine coupling on both resonances at low temperature.[61,63,65] Ammeter has shown that the g and A values for Cp_2V are essentially independent of the host matrix employed.[64] This situation is to be contrasted with that found for metallocenes with orbitally degenerate ground states (e.g., cobaltocene and low-spin manganocenes), whose EPR spectra show a pronounced host dependence.[64]

Bulk magnetic susceptibility measurements on $(Me_5Cp)_2V$ and $[(Me_5Cp)_2Cr]PF_6$ show simple Curie behavior in the temperature range 5–70 K. The magnetic moments obtained from these measurements are in agreement with the solution values at room temperature (Table IV) and are close to the spin-only value for $S = {}^3/_2$ molecules. These data imply a $^4A_{2g}$ ground state, an assignment that is confirmed by UV–photoelectron[34e] and EPR spectroscopy.

The EPR spectra of $(Me_5Cp)_2V$ and $[(Me_5Cp)_2Cr]^+$ diluted in diamagnetic host lattices exhibit resonances near $g = 2$ and $g = 4$ (Table V) and are quite similar to the spectra reported for Cp_2V and $(Cp_2Cr)^+$. Signals are observed both at room and liquid-helium temperature, although the room-temperature spectra are somewhat broadened. The g and A values are insensitive to changes in host matrix, a result that is in accord with a nondegenerate electronic configuration. Metal hyperfine coupling is resolved only on $g_\perp$ for the Cr derivative (^{53}Cr, $I = {}^3/_2$, 9.55% natural abundance) but is found on both $g_\parallel$ and $g_\perp$ for the vanadium compound (^{51}V, $I = {}^7/_2$, 99% natural abundance).

Table VI. Metal Orbital Mixing Coefficients for Vanadocene and Decamethylvanadocene

compd	C_0^2	C_σ^2	C_δ^2
Cp_2V[a]	0.22	0.78	0.65
$(Me_5Cp)_2V$[b]	0.25	0.75	0.53

[a] Calculated from EPR data in ref 61. [b] Calculated from $(Me_5Cp)_2V$ in toluene (19 K) EPR spectrum.

Prins and Van Voorst have derived expressions that allow determination of the metal orbital mixing coefficients C_0^2 (metal 4s), C_δ^2 (metal e_{2g}), and C_σ^2 (metal a_{1g}) for $^4A_{2g}$ metallocenes from the g and A values (see eq 2 of ref 61). Using these expressions (with a minor modification suggested by Ammeter[66]), we have calculated these parameters for Cp_2V and $(Me_5Cp)_2V$. In both cases, the most reasonable (i.e., positive) sets of mixing coefficients are obtained with the assumption of negative values for the hyperfine coupling constants. A comparison of the C_0^2, C_σ^2, and C_δ^2 values for vanadocene and decamethylvanadocene (Table VI) shows that C_0^2 and C_σ^2 are essentially the same in both compounds. However, C_δ^2 is substantially smaller in the peralkylated derivative, indicating that the overlap of the ring and metal e_{2g} orbitals in vanadocene is enhanced by complete alkylation of the rings.

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Table VII. EPR Data for 19-Electron Metallocenes and Decamethylmetallocenes

compound	host	temp[a]	g_x	g_y	g_z	A_x[b]	A_y[b]	A_z[b]	reference
$(Me_5Cp)_2Co$	toluene	14		$g_{iso} = 2.0$					this work
	methylcyclohexane	15		$g_{iso} = 1.8$					this work
	$(Me_5Cp)_2Fe$[c]	9	1.693 (3)	1.733 (8)	1.754 (1)	<6	111 (3)	65 (1)	this work
Cp_2Co	2-MeTHF	4	1.81 ($g_\perp$)		1.69				64
	Cp_2Fe	4	1.755	1.847 (3)	1.693 (2)		−135	−85.6	67d
	Cp_2Mg	4	1.637	1.627	1.638 (3)	−92.8	−111	−94.6	67d
$[(Me_5Cp)_2Ni]PF_6$	$[(Me_5Cp)_2Co]PF_6$	8	1.973 (1)	2.014 (1)	1.831 (2)				this work
$(Cp_2Ni)^+$	$(Cp_2Co)PF_6$	4	1.972 (1)	2.015 (1)	1.800 (8)				64, 67d
	$(Cp_2Co)BF_4$	4	1.865 (1)	1.915 (1)	1.744 (2)				64, 67d
	$(Cp_2Co)SbF_6$	4	1.642 (5)	1.692 (8)	1.700 (8)				64, 67d

[a] Temperatures in K. [b] In units of 10^{-4} cm^{-1}. [c] Calculated from Figure 3. Includes second-order shift. Signs for *A* values uncertain.

Sixteen- and Nineteen-Electron Complexes. Magnetic susceptibility,[58,59] EPR,[38] and UV-photoelectron[35h] studies have established that the 16-electron, low-spin 17-electron, and 19-electron metallocenes possess orbitally degenerate $^3E_{2g}$ $[e_{2g}{}^3\ a_{1g}{}^1]$, $^2E_{2g}$ $[e_{2g}{}^3\ a_{1g}{}^2]$, and $^2E_{1g}$ $[e_{2g}{}^4\ a_{1g}{}^2 e_{1g}{}^1]$ electronic configurations, respectively. Detailed calculations for the magnetic parameters of such systems prove to be more complex than the relatively simple treatment applied to metallocenes with nondegenerate ground states. For example, significant orbital contributions to the magnetic moment are expected, effects which would in general produce temperature-dependent moments that are greater than the spin-only value. Warren's ligand-field calculations indicate that increased delocalization of the unpaired (metal) electron over ligand π orbitals (a decrease of the orbital reduction factor, k') will serve to reduce the moments toward the spin-only value.[58] The systems under consideration are also subject to distortions from purely axial symmetry. Warren calculates that a large static C_{2v} distortion of these metallocenes will result in temperature-independent moments that are close to the spin-only values.[58] These theoretical considerations indicate that magnetic moments of orbitally degenerate metallocenes may be expected to lie within a rather large range of values (see Tables A–F of ref 58).

Two low-spin ground states are possible for 16-electron metallocenes: the orbitally degenerate $^3E_{2g}$ $[e_{2g}{}^3\ a_{1g}{}^1]$ configuration and the nondegenerate $^3A_{2g}[e_{2g}{}^2\ a_{1g}{}^2]$ configuration. Magnetic susceptibility studies of Cp_2Cr and $(MeCp)_2Cr$ gave moments (ca. 3.2 μ_B; Table IV) substantially larger than the spin-only value for $S = 1$ systems (2.87 μ_B), indicating a $^3E_{2g}$ ground-state assignment.[59] This assignment has also been proposed from a UV-PES study of the chromocenes.[35h] We previously noted that solid $[(Me_5Cp)_2Mn]PF_6$ obeys the Curie–Weiss law with an effective moment of 3.07 ± 0.1 μ_B (T = 4–65 K).[39] Bulk susceptibility measurements on $(Me_5Cp)_2Cr$ indicate simple Curie behavior with $\mu_{eff} = 3.01 \pm 0.1$ μ_B from 6 to 81 K. The solid-state and solution magnetic susceptibility data for both complexes are consistent with a triplet ground state, but the magnetic moments are only slightly greater than the spin-only value, so the choice between $^3A_{2g}$ and $^3E_{2g}$ ground-state assignments is ambiguous. However, a recent UV-photoelectron study of $(Me_5Cp)_2Cr$ and $[(Me_5Cp)_2Mn]^+$ (final state) has established that these complexes possess an orbitally degenerate $^3E_{2g}$ ground state in the gas phase.[34e]

No EPR spectra were observed for $(Me_5Cp)_2Cr$ and $[(Me_5Cp)_2Mn]^+$. The neutral chromium compound was run in toluene solution (10 or 298 K). Samples of $(Me_5Cp)_2Cr$ cosublimed with $(Me_5Cp)_2Mg$ do give strong EPR signals at liquid helium and room temperature, but these are due to the fortuitous presence of the oxidized derivative, $[(Me_5Cp)_2Cr]^+$ (see Table V). Similar negative results were found for Cp_2Cr.

Magnetic susceptibility measurements on the 19-electron metallocenes Cp_2Co and $(Cp_2Ni)^+$ have shown they are low-spin complexes with one unpaired electron (Table IV). The most recent measurements on Cp_2Co revealed that the moment is temperature dependent in the range 83–298 K, in accord with an orbitally degenerate ground state.[59] UV-PES and EPR studies of the 19-electron systems indicate that the unpaired electron resides in an orbital with substantial metal character, and a $^2E_{1g}$ $[e_{2g}{}^4\ a_{1g}{}^2\ e_{1g}{}^1]$ ground state has been assigned.

Ammeter and co-workers[64,67d] have examined the EPR spectra of Cp_2Co and $[Cp_2Ni]^+$ as well as an extensive series of ring-substituted derivatives. They find that EPR signals are observable only at very low temperatures due to the short relaxation times of the degenerate ground state. Molecules with a $^2E_{1g}$ ground state are expected to be unstable with respect to distortions from pure axial symmetry, either by an external (i.e., lattice effects) or an internal mechanism (i.e., Jahn–Teller distortions). This is found experimentally: the g values of cobaltocenes and nickelocenium systems (and the A values of cobaltocenes) are very sensitive to changes in the diamagnetic host and alkyl substitution on the ring.

Under pure axial symmetry, the g values for a $^2E_{1g}$ metallocene are $g_{\parallel} = 2(k' + 1)$; $g_{\perp} = 0$; so no EPR signal is expected. Experimentally, this is not the case: a fully anisotropic g tensor ($g_x \neq g_y \neq g_z$) is generally observed for cobaltocenes and nickelocenium compounds.[64,67] A theoretical treatment which considered the effect of a static C_{2v} distortion predicted $g_z \neq g_x = g_y$, and so is unsatisfactory. Ammeter and Swalen demonstrated that the anisotropy of the g tensor could result from *dynamic* Jahn–Teller coupling.[67b] This effect is a consequence of the breakdown of the Born–Oppenheimer approximation due to vibronic coupling of degenerate or near-degenerate electronic states. In this treatment, the g and A tensors are found to be a function of the orbital reduction factor (k'), a vibronic reduction factor (V), and α, a measure of the static distortion from fivefold symmetry.[67b] This analysis indicates that dynamic Jahn–Teller distortions predominate over static distortions but are gradually suppressed (relative to the static distortions) by increasing asymmetry of the guest molecule and/or host lattice.[64,67d]

Solid $(Me_5Cp)_2Co$ obeys the Curie law in the temperature range 6–130 K. The solid-state and solution magnetic data (Table IV) yield a moment (ca. 1.5 μ_B) that is significantly smaller than the spin-only value for an $S = {}^1/_2$ system (1.73 μ_B). The $\chi_m{}^{-1}$ vs. T curve for $[(Me_5Cp)_2Ni]PF_6$ (Figure 2) reveals a pronounced departure from simple Curie–Weiss behavior and is suggestive of an antiferromagnetic coupling. Above 30 K, the curve is linear, yielding an effective moment of 1.67 μ_B. $\chi_m{}^{-1}$ has a minimum at about 18 K, and then it monotonically increases with decreasing temperature to 4.2 K. In contrast, the $\chi_m{}^{-1}$ vs. T plot for the BF_4^- salt of $[(Me_5Cp)_2Ni]^+$ (Figure 2) follows the Curie law and yields a moment (1.62 μ_B) that is strikingly close to that obtained from the linear range of the $[(Me_5Cp)_2Ni]PF_6$ $\chi_m{}^{-1}$ vs. T plot. This result substantiates the contention that the unusual magnetic behavior of the PF_6^- salt has intermolecular rather than intramolecular origins.

The EPR spectra of $(Me_5Cp)_2Co$ and $[(Me_5Cp)_2Ni]^+$ are consistent with a $^2E_{1g}$ ground state. At 9 K, the spectrum of $[(Me_5Cp)_2Ni]PF_6$ diluted in $[(Me_5Cp)_2Co]PF_6$ exhibits three

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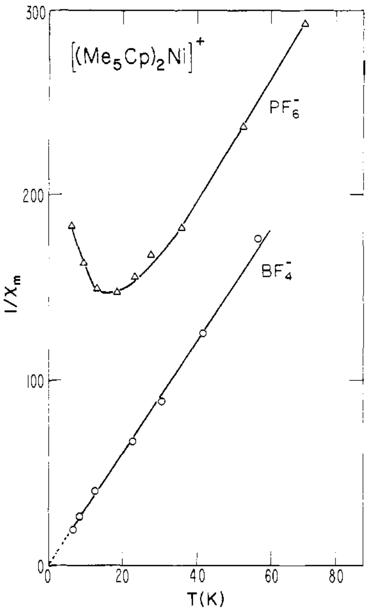

Figure 2. $1/\chi_m$ (mol/emu) vs. T plot for solid $[(Me_5Cp)_2Ni]PF_6$ and $[(Me_5Cp)_2Ni]BF_4$.

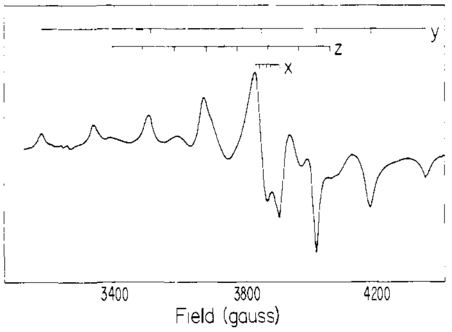

Figure 3. X-band EPR spectrum of $(Me_5Cp)_2Co$ diluted in $(Me_5Cp)_2Fe$ at 9 K with **g** and **A** tensors indicated.

resonances near $g = 2$ (Table VII). The g values are close to those reported for $(Cp_2Ni)^+$ diluted in $(Cp_2Co)^+$ matrices and the spectrum is nearly identical with that of $(Cp_2Ni)PF_6$ diluted in $(Cp_2Co)PF_6$. No EPR signal is observed for $[(Me_5Cp)_2Ni]^+$ at room temperature.

The EPR spectrum of $(Me_5Cp)_2Co$ was measured in several diamagnetic hosts. In toluene or methylcyclohexane glasses at 6 K, the spectrum exhibits a broad resonance centered near $g = 2$ and spread over a range of ca. 1200 G, with superimposed $^{59}Co(I = {}^7/_2)$ hyperfine coupling. The number of lines observed (>10) requires that the g tensor be anisotropic, but the spectra are not sufficiently well resolved to allow determination of the g and A values. Much better resolution is obtained in the EPR spectrum of $(Me_5Cp)_2Co$ diluted in $(Me_5Cp)_2Fe$. The spectrum and its assignment are shown in Figure 3. The assignment of the axes of the g and A tensors is tentative, but follows the general observation that $A_y > A_z > A_x$ for cobaltocenes. No EPR signal is observed for $(Me_5Cp)_2Co$ in any of these environments at room temperature. EPR data for $(Me_5Cp)_2Co$ and Cp_2Co in diamagnetic hosts are compared in Table VII. It is apparent that the g and A values of both compounds are extremely sensitive to changes in the host matrix, but in general the EPR parameters of Cp_2Co and $(Me_5Cp)_2Co$ in matrices of similar composition appear to be comparable.

The observation of an EPR signal for $(Me_5Cp)_2Co$ and $[(Me_5Cp)_2Ni]^+$ is evidence that the compounds are distorted from pure axial symmetry. The sensitivity of the $(Me_5Cp)_2Co$ EPR spectrum to changes in the host lattice reflects the influence of molecular environment on the nature and magnitude of the distortions. In diamagnetic decamethylmetallocene hosts, both complexes exhibit anisotropic g tensors ($g_x \neq g_y \neq g_z$). According to the arguments of Ammeter,[64] this is a consequence of Jahn–Teller distortions that are dynamic in nature. In this context, it is noteworthy that a single-crystal X-ray diffraction study of $(Me_5Cp)_2Co$ provides evidence for a static distortion from D_{5d} symmetry at room temperature.[36] The observed distortion is very similar to that found in a crystallographic study of $(Me_5Cp)_2Mn$, involving variation of the ring-carbon to ring-carbon distances from 1.412 (1) to 1.434 (1) Å. In $(Me_5Cp)_2Fe$, which has a nondegenerate $^1A_{1g}$ ground state, these distances remain constant at 1.419 (1) Å. Root-mean-square vibrational amplitudes for ring-carbon atoms in the neutral Fe and Co compounds are comparable, and this would seem to argue *against* the dynamic Jahn–Teller motion (in $(Me_5Cp)_2Co$) implied by the EPR investigation. However, it is possible that such motion is masked by the normal thermal vibrations at room temperature. Low-temperature crystallographic studies could test this idea.

Electronic Spectra. Having established the ground-state electronic configurations of the decamethylmetallocenes from the magnetic data, we turn now to an examination of their optical spectra, and in particular the ligand-field (d–d) transitions, since a complete assignment of the ligand-field spectrum can yield the 3d orbital splitting parameters, Δ_1 and Δ_2, and the Racah electron-repulsion parameters, B and C. Earlier, we ascribed the low-spin nature of $(Me_5Cp)_2Mn$ (vis-à-vis the high-spin complexes Cp_2Mn and $(MeCp)_2Mn$) to a substantial increase in the ligand-field strength of the Cp^- ring upon permethylation. Such an effect should be apparent from a comparison of the ligand-field parameters of isoelectronic metallocenes and decamethylmetallocenes. Furthermore, quantitative comparisons are possible.

With the strong field approach, ligand-field theory predicts three spin-allowed d–d transitions for metallocenes with an 18-electron, $^1A_{1g}$ ground state.[68] The one-electron transition $2a_{1g} \rightarrow 2e_{1g}$ gives rise to a single excited state of $^1E_{1g}$ symmetry. The one-electron transition $1e_{2g} \rightarrow 2e_{1g}$ yields two excited states of $^1E_{1g}$ and $^1E_{2g}$ symmetries. In order to differentiate between the two $^1E_{1g}$ states, we denote the former as $^1E_{1g}(a)$ and the latter, $^1E_{1g}(b)$. Three spin-forbidden transitions (singlet → triplet) are also predicted. These excited states have the same symmetry labels as the corresponding spin-allowed states, with the exception of the spin multiplicity. Sohn et al.[68] have given the transition energy expressions (including configuration interaction) for the spin-allowed and spin-forbidden d–d transitions (Table I of ref 68). With the energies of the three relatively weak (singlet) absorption bands observed in the optical spectra of Cp_2Fe, Cp_2Ru, and $[Cp_2Co]^+$, they used these expressions to calculate Δ_1, Δ_2, and B with the assumption $C = 4B$ (Table VIII).

The expectations for 15-electron ($^4A_{2g}$) and 20-electron ($^3A_{2g}$) metallocenes are similar. The one-electron transitions from the $2a_{1g}$ and $1e_{2g}$ levels to the $2e_{1g}$ level yield three spin-allowed excited states of $E_{1g}(a)$, E_{2g}, and $E_{1g}(b)$ symmetry.[61] Prins and Van Voorst[61] found three relatively weak absorption bands in the optical spectra of Cp_2V and Cp_2Ni. In accordance with a ligand-field assignment, these bands decreased in relative intensity and shifted to higher energy at low temperature. With consideration of configuration interaction between the $E_{1g}(a)$ and $E_{1g}(b)$ states, these authors derived transition energy expressions for the excited ligand-field states which permitted calculation of Δ_1, Δ_2, and B from the spectral data (Tables IX and X). As Sohn and coworkers[68] found for 18-electron metallocenes, only one ligand-field assignment scheme, $E_{1g}(b) > E_{2g} > E_{1g}(a)$, yielded physically reasonable (nonimaginary) B values. A reexamination of the Cp_2V and Cp_2Ni absorption spectra by Pavlik, Cerny, and Maxova[69]

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Table VIII. Ligand-Field Absorption Data and Parameters for 18-Electron Metallocenes and Decamethylmetallocenes[a]

transition	Cp_2Fe[b]	$(Me_5Cp)_2Fe$	$(Cp_2Co)^+$[b]	$[(Me_5Cp)_2Co]^+$	$[(Me_5Cp)_2Ni]^{2+}$
$^1A_{1g} \rightarrow {}^1E_{1g}(a)$	21.8 (36)	23.5 (121)	24.3 (140)	23.8 (330)	22.5 (455)
$\rightarrow {}^1E_{2g}$	24.0 (72)	30.5 (180)	26.4 (120)	29.5 (1430)	31.5 (60,000)[c]
$\rightarrow {}^1E_{1g}(b)$	30.8 (49)	34.5 (2970)[c]	33.3 (1200)	40.0 (1170)	42.5 (7800)[d]
$\rightarrow {}^3E_{1g}(a)$	18.9 (7)		21.8 (7)	12.7 (0.2)	
$\rightarrow {}^3E_{2g}$				18.5 (0.8)	
$\rightarrow {}^3E_{1g}(b)$				21.3 (8)	
Δ_1	7.1	11.2	7.2	14.1[e]	19.0
Δ_2	22.0	23.1	24.4	24.1[e]	21.5
B	0.39	0.42	0.40	0.63[e]	0.69

[a] All energies in $cm^{-1} \times 10^3$. Extinction coefficients are enclosed in parentheses. Δ_2 values calculated assuming $C/B = 4.0$. [b] Data and parameters from ref 68. Ferrocene spectrum measured in 2-methylbutane solution; $(Cp_2Co)ClO_4$ spectrum measured in aqueous solution. [c] Estimated energy of transition. [d] Assignment uncertain. [e] Δ_1, Δ_2 and B values calculated from singlet absorption spectrum. Analysis of spin-forbidden transitions yields $B = 0.68 \times 10^3$ cm^{-1} and $\Delta_1 = 13.9 \times 10^3$ cm^{-1}.

Table IX. Ligand-Field Spectral Data and Parameters for 20-Electron Metallocenes and Decamethylmetallocenes[a]

transition	Cp_2Ni[b]	$(Me_5Cp)_2Ni$	
$^3A_{2g} \rightarrow {}^3E_{1g}(a)$	14.38 (62)	15.9 (99)	
$\rightarrow {}^3E_{2g}$	16.90 (23)	18.5 (58)	
		I	II
$\rightarrow {}^3E_{1g}(b)$	23.45 (26)	25.0 (3250)[c]	26.5 (3250)[c]
Δ_1	4.60	4.8	4.9
Δ_2	13.92	15.4	15.6
B	0.57	0.58	0.69

[a] Energies in $cm^{-1} \times 10^3$. Extinction coefficients enclosed in parentheses. [b] Data from ref 69a (measured in n-heptane solution). Parameters from ref 38. [c] Estimated values.

revealed additional very weak absorption ($\epsilon < 1$) that were assigned to spin-forbidden d–d transitions.[38]

Warren and Gordon[59] have demonstrated that the $^3E_{2g}$, $^2E_{2g}$, and $^2E_{1g}$ electronic configurations determined for low-spin 16-, 17- and 19-electron metallocenes give rise to a large number of spin-allowed ligand-field excited states. Ligand-field bands observed in the spectra of Cp_2Cr, $[Cp_2Fe]^+$, and Cp_2Co were poorly resolved, and an unambiguous assignment was not possible.[38,59,68] Electronic spectra of the analogous $(Me_5Cp)_2M$ (M = Cr, Mn, Co) and $[(Me_5Cp)_2M]^+$ (M = Mn, Fe, Ni) complexes are also rather featureless and will not be discussed here.

The shoulders found at 23.8, 29.5, and 40.0 × 10^3 cm^{-1} in the spectrum of $[(Me_5Cp)_2Co]PF_6$ are assigned to the three spin-allowed ligand-field transitions, $^1A_{1g} \rightarrow {}^1E_{1g}(a)$, $^1E_{2g}$, and $^1E_{1g}(b)$. Spectra of concentrated solutions or thick single crystals of $[(Me_5Cp)_2Co]PF_6$ reveal three very weak absorptions at 12.7, 18.5, and 21.3 × 10^3 cm^{-1} which we assign to the three spin-forbidden ligand-field transitions. A weak, but sharp, peak is observed at 8.4 × 10^3 cm^{-1}. This band could not be rationalized in terms of a ligand-field assignment, so we suggest that it is due to a vibrational overtone.

The spectrum of $(Me_5Cp)_2Fe$ exhibits only two bands (23.5 and 30.5 × 10^3 cm^{-1}) whose intensity suggests a ligand-field assignment. Two shoulders at 34.5 and 36.0 × 10^3 cm^{-1} neither shift to lower energy nor decrease in intensity at 77 K (methylcyclohexane glass), so a charge-transfer assignment is indicated. Nonetheless, both shoulders are rather broad and fairly intense, so it is reasonable to propose that the third ligand-field band is hidden in this region. We therefore use 34.5 × 10^3 cm^{-1} as a minimum estimate for the energy of the $^1A_{1g} \rightarrow {}^1E_{2g}(b)$ transition in the calculation of ligand-field parameters for $(Me_5Cp)_2Fe$.

The spectrum of $[(Me_5Cp)_2Ni]^{2+}$ consists of a weak absorption at 22.5 × 10^3 cm^{-1}, intense peaks at 31.5 and 40.9 × 10^3 cm^{-1}, and a shoulder at ca. 42.5 × 10^3 cm^{-1}. The band at 22.5 × 10^3 cm^{-1} is assigned to the $^1A_{1g} \rightarrow {}^1E_{1g}(a)$ transition. *If* the shoulder at 42.5 × 10^3 cm^{-1} is due to the highest energy ligand-field state ($^1E_{1g}(b)$), then the intermediate $^1E_{2g}$ excited state must be masked by one of the intense charge-transfer transitions. To derive ligand-field parameters for the Ni(IV) complex, we have assumed that this transition lies under the absorption at 31.5 × 10^3 cm^{-1}.

The fourth member of the series of the $^1A_{1g}$ decamethylmetallocenes, $[(Me_5Cp)_2Mn]^-$, is too air sensitive to allow an accurate determination of its absorption spectrum. Spectra of $Na[(Me_5Cp)_2Mn]$ in THF solution invariably exhibit peaks attributable to $(Me_5Cp)_2Mn$.

For the 18-electron decamethylmetallocenes, the assignment of the observed ligand-field bands follows the pattern established for d^3, d^6, and d^8 Cp_2M compounds.[61,68] The lowest energy singlet absorption band corresponds to the $2a_{1g} \rightarrow 2e_{1g}$ one-electron transition ($^1A_{1g} \rightarrow {}^1E_{1g}(a)$) and the highest energy band is assigned to the $^1A_{1g} \rightarrow {}^1E_{1g}(b)$ transition. The parameters B and Δ_1 are then obtained directly from appropriate combinations of the transition energy expressions (Table VIII). This calculation confirms the ordering of the excited states, $^1E_{1g}(b) > {}^1E_{2g} > {}^1E_{1g}(a)$, since other assignments yield physically unrealistic (imaginary) values for B. The parameter Δ_2 was calculated with the assumption $C = 4B$.[38,68] The bands at 12.7, 18.5, and 21.3 × 10^3 cm^{-3} found in the spectrum of $[(Me_5Cp)_2Co]^+$ are assigned to the $^3E_{1g}(a)$, $^3E_{2g}$, and $^3E_{1g}(b)$ excited states, respectively. By a similar analysis, the energy expressions for the spin-forbidden d–d transitions yield $B = 680$ cm^{-1} and $\Delta_1 = 13.9 \times 10^3$ cm^{-1}, in good agreement with the values determined from the spin-allowed transitions (Table VIII). Calculation of Δ_2 again requires knowledge of the parameter C. A reasonable agreement of the Δ_2 parameters is obtained from analysis of the spin-allowed and spin-forbidden transitions with $C = 4.0$ ($C/B = 5.8$–6.3).

Ligand-field spectral data and the derived parameters for 18-electron metallocenes and decamethylmetallocenes are compared in Table VIII. The Δ_2 parameter is approximately constant in the series of decamethylmetallocenes, but the Δ_1 and B values follow the expected order Ni(IV) > Co(III) > Fe(II). The Δ_2 values determined for $(Me_5Cp)_2Fe$ and $[(Me_5Cp)_2Co]^+$ are comparable to the values found for Cp_2Fe and $[Cp_2Co]^+$, but Δ_1 is 4–7 × 10^3 cm^{-1} greater in the peralkylated systems. The parameter B also increases substantially upon permethylation of the Co(III) complex. The B value for $(Me_5Cp)_2Fe$ is only slightly larger than that found for Cp_2Fe. However, B is very sensitive to the location of the $^1A_{1g} \rightarrow {}^1E_{1g}(b)$ transition. We have assumed a *minimum* energy for this band in the calculation of B for $(Me_5Cp)_2Fe$, so the true B value may be somewhat larger than that reported.

The spectrum of $(Me_5Cp)_2Ni$ shows a peak at 15.9 × 10^3 cm^{-1} and a shoulder at 18.5 × 10^3 cm^{-1} (Table IX), which are assigned to the $^3E_{1g}(a)$ and $^3E_{2g}$ ligand-field excited states, respectively. The third expected d–d band ($^3A_{2g} \rightarrow {}^3E_{1g}(b)$) is apparently submerged under charge-transfer absorptions. Using the intensities of the observed d–d bands as a guide, we find that 25 × 10^3 cm^{-1} is a reasonable estimate for the minimum energy of the hidden transition; that is, if it occurred below 25 × 10^3 cm^{-1} it should be resolved at least as a shoulder. With this estimate, the transition energy expressions for $^3A_{2g}$ metallocenes yield B and Δ_1 values

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Table X. Ligand-Field Absorption Data and Parameters for 15-Electron Metallocenes and Decamethylmetallocenes[a]

transition	Cp_2V[b]	$(Me_5Cp)_2V$	(Cp_2Cr)[c]	$[(Me_5Cp)_2Cr]^+$	
				I	II
$^4A_{2g} \rightarrow {}^4E_{1g}(a)$	17.33 (58)	18.7 (23)	17.86 (270)	20.4 (1386)	
$\rightarrow {}^4E_{2g}$	20.24 (46)	20.6 (25)	21.98 (210)	23.1 (2450)	
$\rightarrow {}^4E_{1g}(b)$	24.50 (66)	28.2 (1037)	27.03 (630)	29.0 (2400)[d]	32.0 (16 000)[d]
$\rightarrow {}^2E_{1g}$	8.96 (.09)	10.5 (1.8)			
$\rightarrow {}^2A_{1g}, {}^2A_{2g}$	13.00 (.06)	14.5 (5.7)		15.4 (0.50)	
$\rightarrow {}^2E_{2g}(a)$			25.0 (480)	13.2 (0.4)	
$\rightarrow {}^2E_{2g}(b)$					
Δ_1	4.93	3.8	6.76	4.9	5.2
Δ_2	16.42	18.7	16.57	19.8	20.2
B	0.42	0.63	0.51	0.54	0.76

[a] Energies in $cm^{-1} \times 10^3$. Extinction coefficients enclosed in parentheses. [b] Data from ref 69b (measured in diethyl ether and *n*-pentane solutions). Parameters from ref 38. [c] Data from ref 50a (measured as I^- salt in aqueous solution). Parameters from ref 38. [d] Estimated value.

comparable to those found for Cp_2Ni and a Δ_2 value that is 1.5 $\times 10^3$ cm^{-1} greater in the peralkylated derivative (scheme I, Table IX). If the $^3A_{2g} \rightarrow {}^3E_{1g}(b)$ transition is located at a somewhat higher energy (26.5×10^3 cm^{-1}), the Δ_2 and B parameters are increased relative to those of Cp_2Ni and Δ_1 is comparable for the two complexes (scheme II, Table IX). The net ligand-field splitting ($\Delta_T = \Delta_1 + \Delta_2$) is 1.5–2.0 $\times 10^3$ cm^{-1} greater in $(Me_5Cp)_2Ni$ than in Cp_2Ni.

The absorption spectrum of $(Me_5Cp)_2V$ exhibits three relatively weak features at 18.7, 20.6, and 28.2 $\times 10^3$ cm^{-1} that are assigned to the three spin-allowed ligand-field transitions, $^4A_{2g} \rightarrow {}^4E_{1g}(a)$, $^4E_{2g}$, and $^4E_{1g}(b)$. A ligand-field analysis of these bands again shows that the energetic ordering $^4E_{1g}(b) > {}^4E_{2g} > {}^4E_{1g}(a)$ is the only one that gives a nonimginary B value. The B and Δ_2 values calculated from the transition energy expressions[61] are appreciably larger for $(Me_5Cp)_2V$ than for Cp_2V, but Δ_1 is somewhat smaller in the peralkylated compound (Table X). The net ligand-field splitting ($\Delta_T = \Delta_1 + \Delta_2$) is about 1.1 $\times 10^3$ cm^{-1} greater for $(Me_5Cp)_2V$ than for Cp_2V.

The very weak bands observed in the $(Me_5Cp)_2V$ optical spectrum at 10.5 and 14.5 $\times 10^3$ cm^{-1} are due to spin-forbidden ligand-field transitions. For $^4A_{2g}$ ground-state systems, five such transitions are expected to occur in the visible–near-infrared region. The orbital occupations, symmetry labels, and transition energy expressions (including configuration interaction between the two $^2E_{2g}$ levels) for these excited states have been given.[34e] The absorption bands at 14.5 and 10.5 $\times 10^3$ cm^{-1} can be reasonably well accounted for with $B = 0.63 \times 10^3$ cm^{-1} and $C = 2.5 \times 10^3$ cm^{-1} ($C/B = 3.98$), if the former is assigned to the $^2A_{1g}$, $^2A_{2g}$ excited states (these are degenerate if $C/B = 4$) and the latter is assigned to the $^2E_{1g}$ excited state. The $^4A_{2g} \rightarrow {}^2E_{2g}(a)$ transition is predicted to occur at 9.4 $\times 10^3$ cm^{-1} and this could account for the broadness of the band at 10.5 $\times 10^3$ cm^{-1}.

Shoulders at 20.4 and 23.1 $\times 10^3$ cm^{-1} in the $[(Me_5Cp)_2Cr]^+$ spectrum are assigned to the $^4A_{1g} \rightarrow {}^4E_{1g}(a)$ and $^4E_{2g}$ transitions (Table X). The $^4A_{1g} \rightarrow {}^4E_{1g}(b)$ transition is masked by charge-transfer bands, so we follow the procedure used for $(Me_5Cp)_2Ni$, estimating a minimum (29.0×10^3 cm^{-1}) and maximum (32.0×10^3 cm^{-1}) energy for the absorption to evaluate the ligand-field parameters. If the $^4E_{2g}(b)$ excited state lies within this region, the transition energy expressions yield B values ranging from 0.55 to 0.76 $\times 10^3$ cm^{-1} (Table X). While the smaller B value is more consistent with our analysis of the spin-forbidden transitions (vide infra), the larger value results in B-$[(Me_5Cp)_2]Cr^+] > B[(Me_5Cp)_2V]$, as expected. The ligand-field splitting parameters are less sensitive to the location of the $^4E_{2g}(b)$ state. Both estimates give $\Delta_1 \sim 5 \times 10^3$ cm^{-1} (1.7×10^3 cm^{-1} less than for $(Cp_2Cr)^+$) and $\Delta_2 \sim 20 \times 10^3$ cm^{-1} (3.5×10^3 cm^{-1} greater than for $(Cp_2Cr)^+$). The net ligand-field splitting is again 1.4–2.1 $\times 10^3$ cm^{-1} larger in the peralkylated complex.

Very weak absorptions are found in the $[(Me_5Cp)_2Cr]^+$ spectrum at 15.4, 13.2, and 8.4 $\times 10^3$ cm^{-1}. As for $[(Me_5Cp)_2Co]^+$, a band at 8.4 $\times 10^3$ cm^{-1} could not be accounted for in terms of a ligand-field assignment, so the peak may be a vibrational overtone. If the band at 15.4 $\times 10^3$ cm^{-1} is assigned to the $^4A_{2g} \rightarrow {}^2A_{2g}$ and $^2A_{1g}$ transitions, the $^2E_{2g}(a)$ state is predicted to lie at 12.6 $\times 10^3$ cm^{-1}, with $B = 0.55$ and $C = 2.9 \times 10^3$ cm^{-1}. No other assignments for these two bands yield reasonable values for B and C.

We note that the absorption bands ascribed to spin-forbidden transitions in the $[(Me_5Cp)_2Cr]^+$ spectrum are much sharper than those found in the $(Me_5Cp)_2V$ spectra. These spin-forbidden transitions should be rather sharp, as the ground-state and excited-state geometries are expected to be quite similar. For $(Me_5Cp)_2V$, the breadth of the band at 14.5 $\times 10^3$ cm^{-1} may be due to its proximity to the far more intense absorption at 20.6 $\times 10^3$ cm^{-1}. As noted before, the broadness of the band at 10.4 $\times 10^3$ cm^{-1} may be due to the coincidence of another spin-forbidden transition, $^4A_{1g} \rightarrow {}^2E_{2g}(a)$.

Summary and Conclusions

The series of $(Me_5Cp)_2M$ compounds (M = Mg, V, Cr, Fe, Co, Ni) has been prepared and characterized as decamethylmetallocenes. The transition-metal derivatives are resistant to hydrolysis and ring exchange reactions but do undergo facile one-electron oxidation. The $[(Me_5Cp)_2M]^+$ derivatives (M = Cr, Mn, Fe, Co, Ni) are isolable as crystalline PF_6^- salts. These cations are also characterized as "sandwich" compounds. Oxidation of $(Me_5Cp)_2V$ in donor solvents yields solvated, monocationic derivatives of the form $[(Me_5Cp)_2V(solvent)]PF_6$. A dicarbonyl derivative, $[(Me_5Cp)_2V(CO)_2]PF_6$, can also be prepared, but the complex $[(Me_5Cp)_2V]PF_6$ has not yet proven isolable.

The decamethylmetallocenes and their cationic derivatives are, for the most part, closely related to their well-known metallocene and metallocene cation counterparts. However, some notable exceptions to this generalization exist. The decamethylnickelocene dication, $[(Me_5Cp)_2Ni]^{2+}$, can be prepared in aqueous solution and can be isolated as its PF_6^- salt. Nuclear magnetic resonance and UV–visible studies establish that $[(Me_5Cp)_2Ni]^{2+}$ is a diamagnetic, 18-electron complex, isoelectronic with $(Me_5Cp)_2Fe$, $[(Me_5Cp)_2Co]^+$, and $[(Me_5Cp)_2Mn]^-$. Electrochemical studies have indicated that a dicationic derivative of Cp_2Ni has a fleeting existence, but to date it has not been isolated or characterized in solution.[52]

Electrochemical measurements show that the transition-metal decamethylmetallocenes are much more easily oxidized than their corresponding metallocenes. This result reflects the enhanced electron-donor properties of the Me_5Cp^- ligand and indicates that the peralkylmetallocenes are much more electron rich than the metallocenes.

Magnetic susceptibility and EPR studies of the $(Me_5Cp)_2M$ (M = V, Cr, Co, Ni) and $[(Me_5Cp)_2M]^+$ (M = Cr, Fe, Ni) compounds indicate that they are isoelectronic with their metallocene counterparts. The 16-, 17-, and 19-electron decamethylmetallocenes possess orbitally degenerate ground states. Consequently, the magnetic parameters of these systems are subject to the effects of orbital contributions, covalency, and distortions from axial symmetry.

For d^3, d^6, and d^8 systems, the ligand-field absorption bands occur at higher energy in the $(Me_5Cp)_2M$ compounds than in the Cp_2M derivatives. A ligand-field analysis of the spectra shows that the net ligand-field splitting is larger in the peralkylated complexes than in the unsubstituted compounds. The effect is quite substantial in the d^6 Fe(II) and Co(III) systems where Δ_1 increases by 4000–7000 cm^{-1} upon peralkylation. For the 15- and 20-electron compounds, Δ_1 is only modestly affected by peralkylation, but Δ_2 increases by 1500–3000 cm^{-1}.

All three spin-allowed d–d transitions are located in the electronic spectra of $[(Me_5Cp)_2Co]^+$ and $(Me_5Cp)_2V$. The *B* values obtained from a ligand-field analysis of the spectra are about 200 cm^{-1} greater than those determined for the unsubstituted compounds. In the case of $(Me_5Cp)_2Fe$, $(Me_5Cp)_2Ni$, and $[(Me_5Cp)_2Cr]^+$, the highest energy ligand-field band cannot be located with certainty, but the proposed range of probable energies for the transitions also yields *B* values that are moderately to significantly increased relative to the unsubstituted compounds. Electrochemical and UV–photoelectron spectral data[34e] show that the decamethylmetallocenes, as a class, are more electron rich than the corresponding metallocenes. We conclude that the increased *B* values are a result of increased electron density at the metal center in the decamethylmetallocenes.

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Registry No. $(Me_5Cp)_2V$, 74507-60-1; $[(Me_5Cp)_2V(NCCH_3)]PF_6$, 80679-48-7; $[(Me_5Cp)_2V(CO)_2]PF_6$, 80679-49-8; $(Me_5Cp)_2Cr$, 74507-61-2; $[(Me_5Cp)_2Cr]PF_6$, 80084-14-6; $(Me_5Cp)_2Co$, 74507-62-3; $[(Me_5Cp)_2Co]PF_6$, 79973-42-5; $(Me_5Cp)_2Ni$, 74507-63-4; $[(Me_5Cp)_2Ni]PF_6$, 80084-15-7; $[(Me_5Cp)_2Ni](PF_6)_2$, 80084-17-9; $(Me_5Cp)_2Mg$, 74507-64-5; $[(Me_5Cp)_2Fe]PF_6$, 54182-44-4; $(Me_5Cp)_2Fe$, 12126-50-0; $[(Me_5Cp)_2Ni]Cl_2$, 80679-50-1; Me_5CpNa, 40585-51-1; $[(Me_5Cp)_2Ni]BF_4$, 80679-51-2; $(Cp_2Fe)PF_6$, 11077-24-0; $VCl_3{\cdot}2THF$, 80679-52-3; $Cr_2(OAc)_4$, 15020-15-2; $NiBr_2{\cdot}2DME$, 18346-62-8; *i*-prMgCl, 1068-55-9.

Synthesis and Conformational Properties of 3,8-Phosphonanedione 1-Oxides [1]

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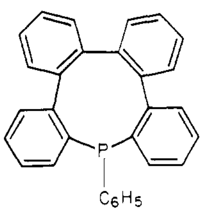
Abstract: Ozonolysis at −78 °C of 3-phospholene derivatives with cyclohexane or substituted cyclohexanes fused at the double bond provides a useful route to derivatives of the 3,8-phosphonanedione 1-oxide system. Synthesized were the 1-methyl, 1-phenyl, 1-hydroxy, 1-phenyl-*cis*-5,6-dimethyl, 1-phenyl-*trans*-5,6-dibromo, and 1-phenyl-5,6-epoxy derivatives. Opening of the 9,10 bond of a phenanthrene fused to a 3-phospholene provided a dibenzo[*d,f*]phosphonanedione derivative. 1-Methyl-3,8-phosphonanedione 1-oxide, shown by X-ray analysis to exist in a twist chair–chair form in the solid state, undergoes rapid interconversion of conformers at room temperature, giving an averaged ^{13}C NMR spectrum. The interconversion is halted at −97 °C, where signals for two conformers are obtained (T_c = −84 °C, approximate $\Delta G^\ddagger$ = 9.6 kcal/mol). 1-Phenyl-5,6-dibromo-3,8-phosphonanedione 1-oxide, which X-ray analysis also showed to be in a twist chair–chair form in the solid state, however, showed nonequivalence of comparable ring carbons, implying the existence of a strongly biased equilibrium or a high barrier to ring inversion. The dibenzo[*d,f*]phosphonanedione derivative has marked rigidity, and the ^{13}C NMR spectrum reveals that comparable ring carbons are non-equivalent at room-temperature. The other phosphonanedione derivatives gave ^{13}C NMR spectra showing equivalence of comparable ring carbons, through either conformational interconversion or adoption of a symmetrical conformation.

The 9-membered phosphonin ring system is known in the literature only in specialized forms such as tetrabenzo derivatives[2] (e.g., **1**), the tetracarboxylate **2**,[3] and possibly **3**;[4] no partially or fully saturated (phosphonane) structures are known. We have devised a scheme which has led to the synthesis of a considerable number of derivatives of this ring, some of which are potential precursors of the phosphonin system in greater simplicity than is represented by structures **1**–**3**. Simpler structures are highly desirable for the initiation of the first studies directed to exploring the possiblity of the ten π-electron system of the phosphonins endowing these structures with "aromatic" character. This point has never before been addressed, and even in the closely related sulfur analogue (thionin) the matter is open for study. In the sulfur system, the parent monocycle remains unknown, and only dibenzo derivatives, devoid of any special properties related to the ten



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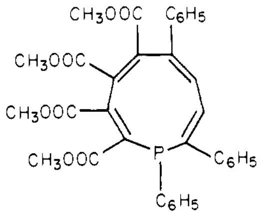

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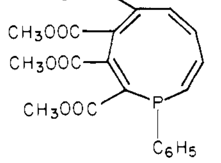

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[1] Supported in part by NSF Grant CHE-7717876.

[2] (a) Wittig, G.; Maercker, H. *Chem. Ber.* **1964**, *97*, 747. (b) Hellwinkel, D. *Ibid.* **1965**, *98*, 576.

[3] Waite, N. E.; Tebby, J. C. *J. Chem. Soc. C* **1970**, 386.

[4] A substance assigned this structure was obtained in only 2.7% yield, in an experiment that could not be duplicated: Holah, D. G.; Hughes, A. N.; Kleemola, D. *J. Heterocycl. Chem.* **1978**, *15*, 1319.

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