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Author

Robbins, J.L.

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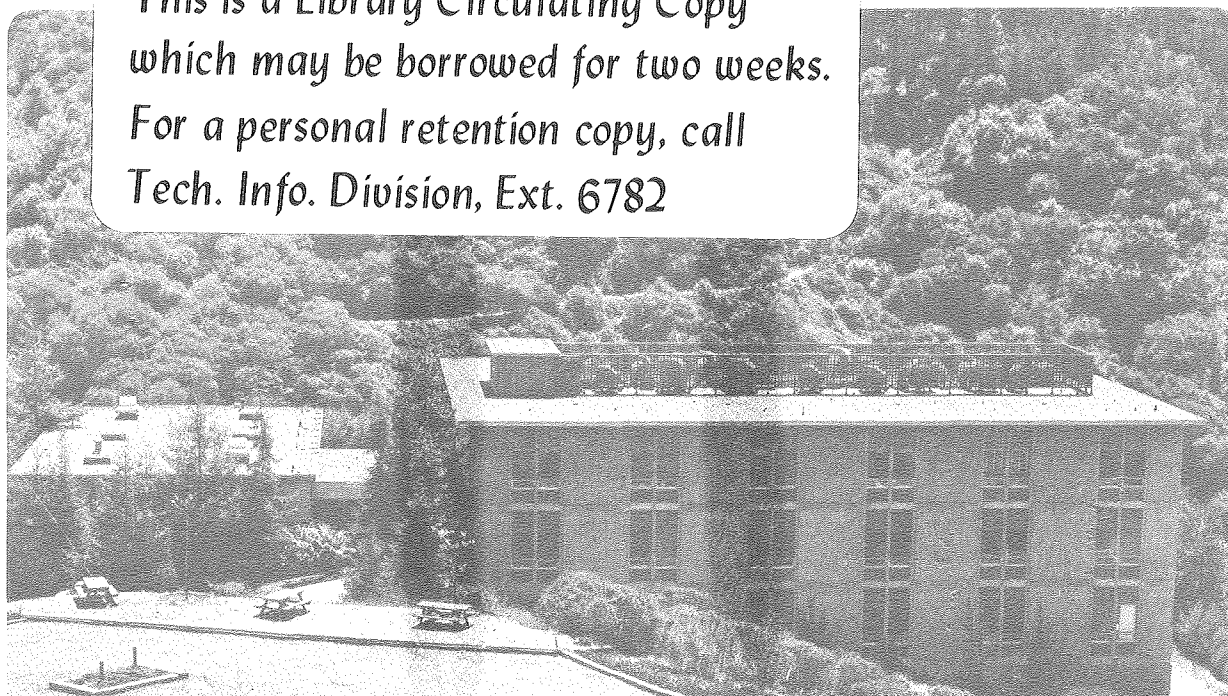
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OF DECAMETHYLMETALLOCENES

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March 1981

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The Syntheses and Electronic Structures
of Decamethylmetallocenes

J.L. Robbins,* N. Edelstein, B. Spencer,** and J.C. Smart***

Materials and Molecular Research Division
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

March 1981

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*Present address: Exxon Research and Engineering Co., P.O. Box 45,
Linden, NJ, 07036.

**Present address: Chemistry Department, Beloit College, Beloit, WI
53511.

***Present address: Solar Energy Research Institute, Golden, CO, 80401.

ABSTRACT

The syntheses of the $(\text{Me}_5\text{Cp})_2\text{M}$ ($\text{M} = \text{Mg}, \text{V}, \text{Cr}, \text{Co}$, and Ni) and $[(\text{Me}_5\text{Cp})_2\text{M}]\text{PF}_6$ ($\text{M} = \text{Cr}, \text{Co}$, and Ni) compounds are described. In addition, a preparative route to a novel, dicationic decamethylmetallocene, $[(\text{Me}_5\text{Cp})_2\text{Ni}](\text{PF}_6)_2$ 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, $[(\text{Me}_5\text{Cp})_2\text{V}(\text{NCCH}_3)]\text{PF}_6$, and a diamagnetic, dicarbonyl derivative, $[(\text{Me}_5\text{Cp})_2\text{V}(\text{CO})_2]\text{PF}_6$, of the cation can be prepared, but pure $[(\text{Me}_5\text{Cp})_2\text{V}]\text{PF}_6$ has not been isolated.

Cyclic voltammetry studies verify the reversibility and the one-electron nature of the $(\text{Me}_5\text{Cp})_2\text{M} \rightleftharpoons [(\text{Me}_5\text{Cp})_2\text{M}]^+$ ($\text{M} = \text{Cr}, \text{Fe}, \text{Co}, \text{Ni}$) and $[(\text{Me}_5\text{Cp})_2\text{Ni}]^+ \rightleftharpoons [(\text{Me}_5\text{Cp})_2\text{Ni}]^{2+}$ 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:

${}^4\text{A}_{2g}[\text{e}_{2g}^2 \text{a}_{1g}^1]$ for the 15-electron compounds $(\text{Me}_5\text{Cp})_2\text{V}$ and $[(\text{Me}_5\text{Cp})_2\text{Cr}]^+$; ${}^3\text{E}_{2g}[\text{e}_{2g}^3 \text{a}_{1g}^1]$ for the 16-electron compounds $(\text{Me}_5\text{Cp})_2\text{Cr}$ and $[(\text{Me}_5\text{Cp})_2\text{Mn}]^+$;

${}^2E_{2g}[e_{2g}^3 a_{1g}^2]$ for the 17-electron compound
 $[(Me_5Cp)_2Fe]^+$; ${}^2E_{1g}[e_{2g}^4 a_{1g}^2 e_{1g}^1]$ for the
19-electron compounds $(Me_5Cp)_2Co$ and $[(Me_5Cp)_2Ni]^+$;
 ${}^3A_{2g}[e_{2g}^4 a_{1g}^2 e_{1g}^2]$ 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.

Introduction

Since the discovery¹ and structural characterization^{2,3} of ferrocene ($\eta^5\text{-(C}_5\text{H}_5)_2\text{Fe}$ or Cp_2Fe) in the early 1950's, at least one cyclopentadienyl derivative of every main group and transition metal, as well as most f-block metals, has been prepared and characterized.^{4,5,6} A large number of monoalkyl- and monoaryl-substituted cyclopentadienyl metal compounds have also been 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 ; $\text{M}=\text{U,Th}$),^{27,28} three Cp^- rings (Cp_3MCl ; $\text{M}=\text{U,Th}$),^{29,30} and one Cp^- ring ($\text{CpUCl}_3(1,2\text{-dimethoxyethane})$)³¹ can be isolated, depending on

reaction conditions and stoichiometry. The missing member of this series, Cp_2UCl_2 , disproportionates to tris- and monocyclopentadienyl derivatives in donor solvents³² 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, ($(\text{Me}_5\text{Cp})\text{ThCl}_3$ ⁶; $(\text{EtMe}_4\text{Cp})\text{UCp}_2\text{Cl}$ ³³) and two peralkylated rings ($(\text{Me}_5\text{Cp})_2\text{MCl}_2$; $\text{M}=\text{Th}, \text{U}$ ¹⁸; $(\text{EtMe}_4\text{Cp})_2\text{UCl}_2$ 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, $^2\text{E}_{2g}$ electronic configuration, in contrast to other manganocenes where high-spin, $^6\text{A}_{1g}$, 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 $(\text{Me}_5\text{Cp})_2\text{Mn}$ are about 0.3 Å shorter than those in high-spin manganocenes. Manganocenes with the low-spin configuration are inert towards 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 analogs exist in other metallocenes.

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 d³, d⁶, and d⁸ 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

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 first transition series 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 to 7000 cm^{-1}) compared to the spin pairing energy, so 15-electron species adopt a high-spin $^4A_{1g}[e_{2g}^2 a_{1g}^1]$ 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 to 20 $\times 10^3 \text{ cm}^{-1}$) 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 $(\text{MeCp})_2\text{Mn}$.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 dessicant (CaH_2 for C_6D_6 and THF- d_8 , P_2O_5 for CD_3CN), then freeze-thaw degassed. All solvents were stored under argon.

1,2,3,4,5-pentamethylcyclopentadiene,⁷ sodium pentamethylcyclopentadienide,¹⁰ $\text{NiBr}_2 \cdot 2\text{DME}$,⁴⁰ and decamethylferrocene⁴¹ were prepared by literature procedures. Chromous acetate, $[\text{Cr}(\text{OAc})_2]_2 \cdot 2\text{H}_2\text{O}$,⁴² and commercially available $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ were dehydrated by heating to 120°C in vacuo. Ferricenium hexafluorophosphate was prepared according to the procedure described by Pinsky.⁴³ Ferricenium tetrafluoroborate was prepared by adding solid NaBF_4 (1 equivalent) to a filtered aqueous solution of $(\text{Cp}_2\text{Fe})\text{FeCl}_4$. Upon cooling (5°C) crystalline $(\text{Cp}_2\text{Fe})\text{BF}_4$ deposited. This was filtered in air, washed with water

1 mL) then THF (2 x 10 mL) and dried under vacuum. All other chemicals were reagent grade and 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 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 $\text{HgCo}(\text{SCN})_4$. 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 ($\sim 0.1M$) or diluted in diamagnetic decamethylmetallocenes at 10-15 K were obtained 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 disc working electrode, a platinum wire auxiliary electrode and an Ag/AgNO₃ (CH₃CN) reference electrode inside an inert atmosphere box. All potentials were referenced to the saturated calomel electrode (SCE) by measuring the ferrocene/ferricenium couple under identical conditions. For controlled potential coulometry, a platinum basket working electrode was employed and the current integrated with the PAR 179 Digital Coulometer.

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 (0.65g; 9.9 mmol) 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 ($60^\circ C$; 10^{-3} torr) for 6 h to remove oily contaminants. The residue was then extracted with pentane (50mL), filtered, and washed with pentane until washings were colorless (3 x 20 mL). Solvent was again removed in vacuo to give a red, microcrystalline solid. Sublimation ($100^\circ C$; 10^{-5} torr), followed by recrystallization from pentane gave $(Me_5Cp)_2V$ as air-sensitive, dark red prisms (2.60g; 65%).

Acetonitrile bis(pentamethylcyclopentadienyl)Vanadium(III)

Hexafluorophosphate

Acetonitrile (40 mL) was added through a cannula to a mixture of $(Me_5Cp)_2V$ (0.20g; 0.62 mmol) and $(Cp_2Fe)PF_6$ (0.20g; 0.60 mmol). The ferricenium 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 x 10 mL) to remove Cp_2Fe , then dried under vacuum to yield the crude product as an air-sensitive, dark green powder (0.22g; 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 $[(\text{Me}_5\text{Cp})_2\text{V}(\text{NCCH}_3)]\text{PF}_6$ (0.40g; 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 x 10 mL) and dried under vacuum (0.38g; 78%).

Bis(pentamethylcyclopentadienyl)Chromium(II)

Solid $\text{Cr}_2(\text{OAc})_4$ (2.15g; 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 (2.6g; 64%) following the procedure described above for $(\text{Me}_5\text{Cp})_2\text{V}$.

Bis(pentamethylcyclopentadienyl)Chromium(III) Hexafluorophosphate

Tetrahydrofuran (40 mL) was added to a mixture of $(\text{Me}_5\text{Cp})_2\text{Cr}$ (0.94g; 2.92 mmol) and $(\text{Cp}_2\text{Fe})\text{PF}_6$ (0.92g; 2.78 mmol). The chromium compound dissolved rapidly with stirring, but the ferricenium salt dissolved only slowly. After stirring for 8 hr at room temperature, the ferricenium salt was no longer visible and the product had deposited as a yellow precipitate. This was collected by filtration, then washed with THF (3 x 10 mL) and dried under vacuum to give a green-yellow solid (1.20g; 90%). Crystallization from a concentrated acetone solution yielded pure $[(\text{Me}_5\text{Cp})_2\text{Cr}]\text{PF}_6$ as orange-yellow prisms.

Bis(pentamethylcyclopentadienyl)Cobalt(III) Hexafluorophosphate

A solution of Me_5CpH (8.00g; 58.7 mmol) in THF (200 mL) was cooled to -78°C (dry-ice/ethanol) and treated with *n*-butyllithium (24.5mL; 2.4M in hexane). Upon warming to room temperature (ca. 1 h) white Me_5CpLi precipitated from a yellow solution. Solid anhydrous CoCl_2 (3.81g; 29.3 mmol) was added against an argon counterstream and the mixture immediately turned brown. After stirring at room temperature for 12 h, the dark brown solution was treated with solid NH_4PF_6 (5.00g; 30.7 mmol) resulting in a mildly exothermic reaction and evolution of gas. After stirring an additional 12 h at room temperature, the mixture was filtered. The resulting brown solid was washed with THF (3 x 20 mL) then H_2O (5 x 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, filtered, and the solution concentrated to ca. 20 mL. Addition of hexane (100 mL) gave a yellow precipitate which was filtered, washed with hexane (2 x 10 mL) and dried in air to yield $[(\text{Me}_5\text{Cp})_2\text{Co}]\text{PF}_6$ as a bright yellow air-stable powder (3.8g; 28%). Crystallization from a concentrated acetone solution gave yellow prisms.

Bis(pentamethylcyclopentadienyl)Cobalt(II)

Tetrahydrofuran (30 mL) was added to a mixture of $[(\text{Me}_5\text{Cp})_2\text{Co}]\text{PF}_6$ (2.75g; 5.80 mmol) and Na/Hg amalgam (17.0g; .83% Na; 6.4 mmol 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) then crystallized from hexane to yield $(\text{Me}_5\text{Cp})_2\text{Co}$ as dark brown, air-sensitive prisms (1.60g; 84%).

Bis(pentamethylcyclopentadienyl)Nickel(II)

Pentamethylcyclopentadiene (8.00g; 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 $[(\text{Me}_5\text{Cp})_2\text{Co}]\text{PF}_6$. Solid $\text{NiBr}_2 \cdot 2\text{DME}$ (9.06g; 29.4 mmol) was added against an argon counterstream to the Me_5CpLi suspension at room temperature and the mixture was stirred for one day at room temperature to yield a

dark brown solution. Following the procedure described in the isolation of $(\text{Me}_5\text{Cp})_2\text{V}$, $(\text{Me}_5\text{Cp})_2\text{Ni}$ was obtained as dark green prisms (5.5g; 57%). Several sublimations were required to separate the product from a yellow, pentane soluble, but involatile impurity.

Bis(pentamethylcyclopentadienyl)Nickel(III) Hexafluorophosphate

Decamethylnickelocene (1.40g; 4.25 mmol) and $(\text{Cp}_2\text{Fe})\text{PF}_6$ (1.30g; 3.93 mmol) were allowed to react in THF in the manner described above in the preparation of $[(\text{Me}_5\text{Cp})_2\text{Cr}]\text{PF}_6$ to give $[(\text{Me}_5\text{Cp})_2\text{Ni}]\text{PF}_6$ as a brown powder (1.67g; 90%).

Crystallization from acetone afforded dark brown prisms. The BF_4^- salt was prepared similarly from $(\text{Cp}_2\text{Fe})\text{BF}_4$ and $(\text{Me}_5\text{Cp})_2\text{Ni}$.

Bis(pentamethylcyclopentadienyl)Nickel(IV) bis(Hexafluorophosphate)

Tetrahydrofuran (30 mL) was added to a mixture of solid $(\text{Me}_5\text{Cp})_2\text{Ni}$ (0.83g; 2.52 mmol) and solid HgCl_2 (0.68g; 2.51 mmol). The solids dissolved rapidly and an orange precipitate separated from a pale green solution. The mixture was stirred for 1 h, then filtered. The orange precipitate was washed with THF (2 x 10 mL) and dried under vacuum. Subsequent reactions were performed in air. The product (1.46g) was dissolved in 0.1 M aqueous HCl (10 mL) to give an orange solution and a metallic precipitate. The solution was filtered, then treated with solid NH_4PF_6 (1.5g). A yellow-brown solid immediately precipitated. This was filtered,

then extracted with warm (40°C) 0.1 M aqueous HCl (1 x 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 disc filter, washed with cold H₂O (2 x 5 mL) and dried in air (0.60g; 38). Recrystallization from warm 0.1 M HCl gave an analytically pure sample.

Solid [(Me₅Cp)₂Ni](PF₆)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 (CH₃)₂CO or CH₃CN solution, but is stable for several days in acidic aqueous solution. The PF₆⁻ salt was not sufficiently soluble in aqueous solution to allow determination of the ring carbon chemical shift in the ¹³C NMR spectrum although the methyl carbon atom resonance was observed at δ 9 ppm after 26,000 pulses. To determine the complete ¹³C NMR spectrum, a sample of the orange precipitate from the HgCl₂/(Me₅Cp)₂Ni reaction (0.3g) was dissolved in a minimum volume of 0.1 M HCl (1 mL), filtered, treated with a deficiency (~ 50) of NH₄PF₆ to precipitate [(Me₅Cp)₂Ni]PF₆ and any paramagnetic impurities, 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 to that of the pure PF₆⁻ salt. The concentrated solution of [(Me₅Cp)₂Ni]Cl₂ was then transferred to a coaxial NMR tube with C₆D₆ in the inner capillary to provide a deuterium lock and reference for the

^{13}C chemical shifts.

Bis(pentamethylcyclopentadienyl)Magnesium(II)

A solution of $i\text{-PrMgCl}$ in THF (66 mL; 1.2 M; 79.2 mmol) was transferred with a syringe into a flask containing Me_5CpH (10.0g; 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, $\text{MgCl}_2 \cdot 1,4\text{-dioxane}$, 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, filtered, and the resulting white solid washed with toluene (2 x 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 $(\text{Me}_5\text{Cp})_2\text{Mg}$ was sublimed (90°C ; 10^{-5} torr) as a white, crystalline, air-sensitive solid (4.45g; 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 $MCl_3 + 3Na^+RCp^- \rightarrow (RCp)_2M + RCp + 3 NaCl$ ($R = H$ or Me) has been used in the preparation of vanadocenes and chromocenes^{35a} where one equivalent of cyclopentadienide serves to reduce the trivalent metal salts. However, the hydrocarbon-soluble products derived from the reaction of three equivalents 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 Prössdorf⁴⁴ have reported the preparation of $(RCp)_2V$ ($R = H$ or Me) from the reaction of $VCl_2 \cdot 2THF$, with two equivalents 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 four equivalents of $(Me_5Cp)Na$ in THF to afford $(Me_5Cp)_2Cr$ in good

yield.

The modest yield obtained in the synthesis of $[(\text{Me}_5\text{Cp})_2\text{Co}]\text{PF}_6$ merits comment. Both Cp_2Co and $(\text{MeCp})_2\text{Co}$ 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 $\text{Co}(\text{OAc})_2$) 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 $(\text{Me}_5\text{Cp})_2\text{Co}$ 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 $[(\text{Me}_5\text{Cp})_2\text{Co}]\text{PF}_6$ as a yellow precipitate in 28% yield. Subsequent reduction of the cation with Na/Hg in THF gives $(\text{Me}_5\text{Cp})_2\text{Co}$ in high yield. Subsequent to the completion of this work, Koelle and Khouzami⁴⁸ reported that the reaction of $\text{CoBr}_2 \cdot 1,2\text{-dimethoxyethane}$ with Me_5CpLi in a refluxing mixture of THF and diethyl ether gives, after oxidation with FeCl_3 and treatment with PF_6^- , $[(\text{Me}_5\text{Cp})_2\text{Co}]\text{PF}_6$ 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 $[(\text{Me}_5\text{Cp})_2\text{Co}]\text{PF}_6$ to $(\text{Me}_5\text{Cp})_2\text{Co}$.

Decamethylnickelocene is obtained in moderate yield from the reaction of $\text{NiBr}_2 \cdot 2\text{DME}$ with Me_5CpLi 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 to 300°C and are volatile, subliming at temperatures greater than 70°C (10^{-5} torr). With the exception of $(\text{Me}_5\text{Cp})_2\text{Fe}$, the neutral compounds are air-sensitive both as solids and in solution.

Like the first transition series metallocenes, the permethylated compounds undergo facile one-electron oxidation to isolable monocationic derivatives. The $[(\text{Me}_5\text{Cp})_2\text{M}]\text{PF}_6$ salts (M = Cr, Mn, Co, Ni) are obtained in nearly quantitative yield via the reaction of $(\text{Me}_5\text{Cp})_2\text{M}$ with one molar equivalent of $(\text{Cp}_2\text{Fe})\text{PF}_6$ 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 $(\text{Cp}_2\text{Fe})\text{PF}_6$ results in extensive decomposition.^{50c}

The $[(\text{Me}_5\text{Cp})_2\text{M}]\text{PF}_6$ 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 $[\text{Cp}_2\text{Cr}]\text{I}$ which is reported to be very air-sensitive.^{50a} The cationic Cr and Ni compounds are air-sensitive in solution.

The cyclic voltammograms of $[(\text{Me}_5\text{Cp})_2]\text{PF}_6$, (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-metallicenium couples. Along similar lines, a UV-PES study of the $(\text{Me}_5\text{Cp})_2\text{M}$ 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 $[(\text{Me}_5\text{Cp})_2\text{Ni}]\text{PF}_6$ in acetonitrile exhibits two reversible, one-electron waves at -0.65 and +0.31 V vs. SCE which correspond to the $[(\text{Me}_5\text{Cp})_2\text{Ni}]^+ / (\text{Me}_5\text{Cp})_2\text{Ni}$ and $[(\text{Me}_5\text{Cp})_2\text{Ni}]^{2+} / [(\text{Me}_5\text{Cp})_2\text{Ni}]^+$ 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 one molar equivalent 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 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 to 700 cm^{-1} is similar to the spectra of the $[(Me_5Cp)_2M]PF_6$ compounds (see below). An Evans' NMR method measurement⁵³ 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 $(\text{Me}_5\text{Cp})_2\text{Ni}^+$ in nonaqueous solvents.

The cyclic voltammogram of $(\text{Me}_5\text{Cp})_2\text{V}$ in acetonitrile solution is complex and exhibits no reversible one-electron waves. Decamethylvanadocene is rapidly oxidized by $(\text{Cp}_2\text{Fe})\text{PF}_6$ in THF, but the blue product polymerizes the solvent. In acetone, acetonitrile, or diethyl ether solution, $(\text{Me}_5\text{Cp})_2\text{V}$ reacts with $(\text{Cp}_2\text{Fe})\text{PF}_6$ to yield paramagnetic, solvated V(III) complexes corresponding to the formulation $[(\text{Me}_5\text{Cp})_2\text{VS}]\text{PF}_6$ (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 $(\text{Cp}_2\text{V})^+$, 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 $(\text{Cp}_2\text{V})^+$, the permethylated derivative reacts with CO (1 atm) to give the diamagnetic 18-electron dicarbonyl complex, $[(\text{Me}_5\text{Cp})_2\text{V}(\text{CO})_2]\text{PF}_6$.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 ($\nu\text{CO} = 1990, 1936 \text{ cm}^{-1}$) than in the unsubstituted

derivative ($\nu_{\text{CO}} = 2050, 2010 \text{ cm}^{-1}$).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 $(\text{Me}_5\text{Cp})_2\text{M}$ ($\text{M} = \text{Mn}, \text{Fe}, \text{Co}$) and $[(\text{Me}_5\text{Cp})_2\text{M}]\text{PF}_6$ ($\text{M} = \text{Cr}, \text{Mn}, \text{Fe}, \text{Co}$).^{35c,36} Infrared spectra of the neutral transition metal compounds are superimposable in the ranges $3000\text{--}2700 \text{ cm}^{-1}$ (4 bands), 1350 and 1500 cm^{-1} (5 bands), and 1000 and 1100 cm^{-1} (2 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" $[(\text{Me}_5\text{Cp})_2\text{V}(\text{CO})_2]^+$ and $[(\text{Me}_5\text{Cp})_2\text{V}(\text{solvent})]^+$ 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. For the planar transition metal compounds, the order of decreasing chemical shift, $\delta(\text{Ni}) > \delta(\text{Co}) > \delta(\text{Fe}) > \delta(\text{Mn})$, follows the expected order of increasing metal to ring electron donation.

Magnetic Susceptibility and EPR

15 and 20-electron systems.

The magnetic properties of the metallocenes have been thoroughly investigated, both from 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 ($2.87 \mu_B$ for $S = 1$; $3.89 \mu_B$ 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 70K, and the susceptibility becomes essentially independent of temperature below 30K.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

${}^3A_{2g} [e_{2g}^4 a_{1g}^2 e_{1g}^2]$ ground state formulation.

This ground state has also been assigned on the basis of UV-visible⁶¹ 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 20K, χ_m^{-1} is proportional to temperature, yielding an effective moment ($2.93 \pm 0.1 \mu_B$) close to the spin-only value for an $S = 1$ molecule. A similar moment is observed in solution at room temperature (Table IV). Below 25K, 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 $g_{||}$ and by fitting the magnetic susceptibility data obtain $g_{\perp} = 1.74$ and $D = 30.5 \pm 1.0 \text{ cm}^{-1}$. 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 ground state. No EPR signal is observed for $(Me_5Cp)_2Ni$ in toluene solution either at 10K or 298K,

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 $(\text{Cp}_2\text{Cr})^+$ indicate that they possess an orbitally nondegenerate $^4\text{A}_{2g}[\text{e}_{2g}^2 \text{a}_{1g}]$ ground state. The magnetic moments of Cp_2V and $(\text{Cp}_2\text{Cr})^+$ 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 $(\text{Cp}_2\text{Cr})^+$ 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 $(\text{Me}_5\text{Cp})_2\text{V}$ and $[(\text{Me}_5\text{Cp})_2\text{Cr}]\text{PF}_6$ show simple Curie behavior in the temperature range 5 to 70K. 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 $^4\text{A}_{2g}$ ground state, an assignment that is confirmed by UV-photoelectron^{34e} and EPR spectroscopy.

The EPR spectra of $(\text{Me}_5\text{Cp})_2\text{V}$ and $[(\text{Me}_5\text{Cp})_2\text{Cr}]^+$ 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 $(\text{Cp}_2\text{Cr})^+$. 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).

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 equation 2 of reference 61). Using these expressions (with a minor modification suggested by Ammeter⁶⁶) we have calculated these parameters for Cp_2V and $(\text{Me}_5\text{Cp})_2\text{V}$. 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 increased delocalization of the metal e_{2g} electrons over the ligand π -orbitals. Since the ligand e_{2g} level is antibonding (with respect

to the rings) and unoccupied in the free ligand, this result implies that Me_5Cp^- can act as a stronger π -acid than Cp^- and the covalency of the metal-ring bond is enhanced by complete alkylation of the ring.

16- and 19-Electron Complexes

Magnetic susceptibility,^{58,59} EPR,³⁸ and UV-photoelectron^{35h} studies have established that the 16-, low-spin 17-, 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. The theoretical expectations for the magnetic parameters of such systems prove to be more complex than the relatively simple treatment applied to metallocenes with non-degenerate 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 towards 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 through F of reference 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. $3.2 \mu_B$; Table IV) substantially larger than the spin-only value for $S=1$ systems ($2.87 \mu_B$) 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 $3.07 \pm 0.1 \mu_B$ ($T = 4$ to $65K$).³⁹ Bulk susceptibility measurements on $(Me_5Cp)_2Cr$ indicate simple Curie behavior with $\mu_{eff} = 3.01 \pm 0.1 \mu_B$ from 6 to $81K$. 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 $[(Me_5Cp)_2Mn]^+$ 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 ($10K$ or $298K$). Samples of $(Me_5Cp)_2Cr$ co-sublimed with

$(\text{Me}_5\text{Cp})_2\text{Mg}$ do give strong EPR signals at liquid helium and room temperature, but these are due to the fortuitous presence of the oxidized derivative, $[(\text{Me}_5\text{Cp})_2\text{Cr}]^+$ (see Table V). Similar negative results were found for Cp_2Cr .

Magnetic susceptibility measurements on the 19-electron metallocenes Cp_2Co and $(\text{Cp}_2\text{Ni})^+$ 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 to 298K, 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 coworkers^{64,67d} have examined the EPR spectra of Cp_2Co and $[\text{Cp}_2\text{Ni}]^+$ 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 nickelicinium 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 $g_{||} = 2(k' + 1)$; $g_{\perp} = 0$ 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 nickelicenium 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 five-fold 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 $(\text{Me}_5\text{Cp})_2\text{Co}$ obeys the Curie Law in the temperature range 6–130K. The solid state and solution magnetic data (Table IV) yield a moment (ca. $1.5 \mu_B$) that is significantly smaller than the spin-only value for an $S = 1/2$ system ($1.73 \mu_B$). The χ_m^{-1} vs. T curve for $[(\text{Me}_5\text{Cp})_2\text{Ni}]\text{PF}_6$ (Figure 2) reveals a pronounced departure from simple Curie-Weiss behavior and is suggestive of antiferromagnetic coupling. Above 30K, the curve is linear, yielding an effective moment of $1.67 \mu_B$. χ_m^{-1} has a minimum at about 18K, then it monotonically increases with decreasing temperature to 4.2K. In contrast, the χ_m^{-1} vs. T plot for the BF_4^- salt of $[(\text{Me}_5\text{Cp})_2\text{Ni}]^+$ (Figure 2) follows the Curie Law and yields a moment ($1.62 \mu_B$) that is strikingly close to that obtained from the linear range of the $[(\text{Me}_5\text{Cp})_2\text{Ni}]\text{PF}_6$ χ_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 $(\text{Me}_5\text{Cp})_2\text{Co}$ and $[(\text{Me}_5\text{Cp})_2\text{Ni}]^+$ are consistent with a ${}^2E_{1g}$ ground state. At 9K, the spectrum of $[(\text{Me}_5\text{Cp})_2\text{Ni}]\text{PF}_6$ diluted in $[(\text{Me}_5\text{Cp})_2\text{Co}]\text{PF}_6$ exhibits three resonances near $g=2$ (Table VII). The g -values are close to those reported for $(\text{Cp}_2\text{Ni})^+$ diluted in $(\text{Cp}_2\text{Co})^+$ matrices and the spectrum is nearly identical to that of $(\text{Cp}_2\text{Ni})\text{PF}_6$ diluted in $(\text{Cp}_2\text{Co})\text{PF}_6$. No EPR signal is observed for $[(\text{Me}_5\text{Cp})_2\text{Ni}]^+$ at room temperature.

The EPR spectrum of $(\text{Me}_5\text{Cp})_2\text{Co}$ was measured in several diamagnetic hosts. In toluene or methylcyclohexane glasses at 6K, the spectrum exhibits a broad resonance centered near $g=2$ and spread over a range of ca. 1200 gauss, with superimposed $^{59}\text{Co}(I=7/2)$ 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 $(\text{Me}_5\text{Cp})_2\text{Co}$ diluted in $(\text{Me}_5\text{Cp})_2\text{Fe}$. 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 $(\text{Me}_5\text{Cp})_2\text{Co}$ in any of these environments at room temperature. EPR data for $(\text{Me}_5\text{Cp})_2\text{Co}$ 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 $(\text{Me}_5\text{Cp})_2\text{Co}$ in matrices of similar composition appear to be comparable.

The observation of an EPR signal for $(\text{Me}_5\text{Cp})_2\text{Co}$ and $[(\text{Me}_5\text{Cp})_2\text{Ni}]^+$ is evidence that the compounds are distorted from pure axial symmetry. The sensitivity of the $(\text{Me}_5\text{Cp})_2\text{Co}$ 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 $(\text{Me}_5\text{Cp})_2\text{Co}$ 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 $(\text{Me}_5\text{Cp})_2\text{Mn}$, involving variation of the ring-carbon to ring carbon distances from 1.412(1) to 1.434(1)Å. In $(\text{Me}_5\text{Cp})_2\text{Fe}$, which has a non-degenerate $^1A_{1g}$ 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 $(\text{Me}_5\text{Cp})_2\text{Co}$) 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 $(\text{Me}_5\text{Cp})_2\text{Mn}$ (viz. a viz. the high-spin complexes Cp_2Mn and $(\text{MeCp})_2\text{Mn}$) 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.

Using 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 \rightarrow 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 reference 68). With the energies of the three relatively weak (singlet) absorption bands observed in the optical spectra of Cp_2Fe , Cp_2Ru , and $[\text{Cp}_2\text{Co}]^+$, 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 Voorst⁶¹ 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,X). As Sohn and co-workers⁶⁸ found for 18-electron metallocenes, only one ligand field assignment scheme $E_{1g}(b) > E_{2g} > E_{1g}(a)$, yielded physically reasonable (non-imaginary) B -values. A re-examination of the Cp_2V and Cp_2Ni absorption spectra by Pavlik, Cerny, and Maxova⁶⁹ revealed additional very weak absorption ($\epsilon < 1$) that were assigned to spin-forbidden d-d transitions.³⁸

Warren and Gordon⁵⁹ 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 kK (1 kK = 10^3 cm^{-1}) in the spectrum of $[(\text{Me}_5\text{Cp})_2\text{Co}]\text{PF}_6$ are assigned to the three spin-allowed ligand field transitions, ${}^1\text{A}_{1g} \rightarrow {}^1\text{E}_{1g}(\text{a})$, ${}^1\text{E}_{2g}$, ${}^1\text{E}_{1g}(\text{b})$. Spectra of concentrated solutions or thick single crystals of $[(\text{Me}_5\text{Cp})_2\text{Co}]\text{PF}_6$ reveal three very weak absorptions at 12.7, 18.5 and 21.3 kK which we assign to the three spin-forbidden ligand field transitions. A weak, but sharp, peak is observed at 8.4 kK. 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 $(\text{Me}_5\text{Cp})_2\text{Fe}$ exhibits only two bands (23.5, 30.5 kK) whose intensity suggests a ligand field assignment. Two shoulders at 34.5 and 36.0 kK 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 kK as a minimum estimate for the energy of the ${}^1\text{A}_{1g} \rightarrow {}^1\text{E}_{2g}(\text{b})$ transition in the calculation of ligand field parameters for $(\text{Me}_5\text{Cp})_2\text{Fe}$.

The spectrum of $[(\text{Me}_5\text{Cp})_2\text{Ni}]^{2+}$ consists of a weak absorption at 22.5 kK, intense peaks at 31.5 and 40.9 kK, and a shoulder at ca. 42.5 kK. The 22.5 kK band is assigned to the ${}^1\text{A}_{1g} \rightarrow {}^1\text{E}_{1g}(\text{a})$ transition. If the shoulder at 42.5 kK 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 31.5 kK absorption.

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 12.7, 18.5, and 21.3 kK bands 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 $B = 680 \text{ cm}^{-1}$ and $\Delta_1 = 13.9$ kK, 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 $(\text{Me}_5\text{Cp})_2\text{Fe}$ and $[(\text{Me}_5\text{Cp})_2\text{Co}]^+$ are comparable to the values found for Cp_2Fe and $[\text{Cp}_2\text{Co}]^+$, but Δ_2 is 4 to 5 kK greater in the peralkylated systems. The parameter B also increases substantially upon permethylation of the Co(III) complex. The B value for $(\text{Me}_5\text{Cp})_2\text{Fe}$ is only slightly larger than that found for Cp_2Fe . However, B is very sensitive to the location of the ${}^1\text{A}_{1g} \rightarrow {}^1\text{E}_{1g}(\text{b})$ transition. We have assumed a minimum energy for this band in the calculation of B for $(\text{Me}_5\text{Cp})_2\text{Fe}$, so the true B value may be somewhat larger than that reported.

The spectrum of $(\text{Me}_5\text{Cp})_2\text{Ni}$ shows a peak at 15.9 kK and shoulder at 18.5 kK (Table IX) which are assigned to the ${}^3\text{E}_{1g}(\text{a})$ and ${}^3\text{E}_{2g}$ ligand field excited states, respectively. The third expected d-d band (${}^3\text{A}_{2g} \rightarrow {}^3\text{E}_{1g}(\text{b})$) is apparently submerged under charge transfer absorptions. Using the intensities of the observed

d-d bands as a guide, we find that 25 kK is a reasonable estimate for the minimum energy of the hidden transition: that is, if it occurred below 25 kK 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 comparable to those found for Cp_2Ni , and a Δ_1 value that is 1.5 kK 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 kK), 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 to 2.0 kK 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 kK that are assigned to the three spin-allowed ligand field transitions, ${}^4A_{2g} \rightarrow {}^4E_{1g}(b)$, ${}^4E_{2g}$, ${}^4E_{1g}(b)$. 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 non-imaginary B value. The B and Δ_2 values calculated from the transition energy expressions⁶¹ 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 kK greater for the $(Me_5Cp)_2V$ than Cp_2V .

The very weak bands observed in the $(Me_5Cp)_2V$ optical spectrum at 10.5 and 14.5 kK 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 14.5 and 10.5 kK absorption bands can be reasonably well accounted for with $B = 0.63$ kK and $C = 2.5$ kK ($C/B = 3.98$) 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 kK and this could account for the broadness of the 10.5 kK band.

Shoulders at 20.4 and 23.1 kK in the $[(Me_5Cp)_2Cr]^+$ spectrum are assigned to the ${}^4A_{1g} \rightarrow {}^4E_{1g}(a)$, ${}^4E_{2g}$ 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 kK) and maximum (32.0 kK) 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 (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 $B[(Me_5Cp)_2Cr^+] > B[(Me_5Cp)_2V]$, as expected. The ligand field splitting parameters are less sensitive to the location of the ${}^4E_{2g}(b)$ state. Both estimates give $\Delta_1 \sim 5$ kK (1.7 kK less than for $(Cp)_2Cr^+$ and $\Delta_2 \sim 20$ kK (3.5 kK greater than for

(Cp₂Cr)⁺). The net ligand field splitting is again 1.4 to 2.1 kK larger in the peralkylated complex.

Very weak absorptions are found in the [(Me₅Cp)₂Cr]⁺ spectrum at 15.4, 13.2, and 8.4 kK. As for [(Me₅Cp)₂Co]⁺, an 8.4 kK band could not be accounted for in terms of a ligand field assignment, so the peak may be a vibrational overtone. If the 15.4 kK band is assigned to the ⁴A_{2g} → ²A_{2g}, ²A_{1g} transitions, the ²E_{2g}(a) state is predicted to lie at 12.6 kK, with B = 0.55 kK and C = 2.9 kK. 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 [(Me₅Cp)₂Cr]⁺ spectrum are much sharper than those found in the (Me₅Cp)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 (Me₅Cp)₂V, the breadth of the 14.5 kK band may be due to its proximity to the far more intense 20.6 kK absorption. As noted before, the broadness of the 10.4 kK band may be due to the coincidence of another spin-forbidden transition, ⁴A_{1g} → ²E_{2g}(a).

Summary and Conclusions

The series of (Me₅Cp)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 [(Me₅Cp)₂M]⁺ derivatives (M = Cr, Fe, Co, Ni) are isolable as

crystalline PF_6^- salts. These cations are also characterized as "sandwich" compounds. Oxidation of $(\text{Me}_5\text{Cp})_2\text{V}$ in donor solvents yields solvated, monocationic derivatives of the form

$[(\text{Me}_5\text{Cp})_2\text{V}(\text{solvent})\text{PF}_6]$. A dicarbonyl derivative, $[(\text{Me}_5\text{Cp})_2\text{V}(\text{CO})_2]\text{PF}_6$, can also be prepared, but the complex, $[(\text{Me}_5\text{Cp})_2\text{V}]\text{PF}_6$ 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, $[(\text{Me}_5\text{Cp})_2\text{Ni}]^{2+}$, can be prepared in aqueous solution and can be isolated as its PF_6^- salt. Nuclear magnetic resonance and UV-visible studies establish that $[(\text{Me}_5\text{Cp})_2\text{Ni}]^{2+}$ is a diamagnetic, 18-electron complex, isoelectronic with $(\text{Me}_5\text{Cp})_2\text{Fe}$, $[(\text{Me}_5\text{Cp})_2\text{Co}]^+$, and $[(\text{Me}_5\text{Cp})_2\text{Mn}]^-$. 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 $(\text{Me}_5\text{Cp})_2\text{M}$ ($\text{M} = \text{V}, \text{Cr}, \text{Co}, \text{Ni}$) and $[(\text{Me}_5\text{Cp})_2\text{M}]^+$ ($\text{M} = \text{Cr}, \text{Fe}, \text{Ni}$) 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 $(\text{Me}_5\text{Cp})_2\text{M}$ 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 to 5000 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 to 3000 cm^{-1} .

All three spin-allowed d-d transitions are located in the electronic spectra of $[(\text{Me}_5\text{Cp})_2\text{Co}]^+$ and $(\text{Me}_5\text{Cp})_2\text{V}$. 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 $(\text{Me}_5\text{Cp})_2\text{Fe}$, $(\text{Me}_5\text{Cp})_2\text{Ni}$, and $[(\text{Me}_5\text{Cp})_2\text{Cr}]^+$, 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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Table I. Physical, analytical, and infrared data for decamethylmetallocenes.

Compound	Melting point	Mass spectrum ^a (p ⁺)	Infrared ^b (cm ⁻¹)	Analysis calcd. (fd.)
(Me ₅ Cp) ₂ V	299-300°C	321(100)	587(w), 463(m), 422(w), 233(w)	C, 74.74(74.90); H, 9.41(9.15)
[(Me ₅ Cp) ₂ V(NCCH ₃)]PF ₆	-	-	459(m), 442(w), ν _{CN} = 2270(s)	C, 52.07(52.24); H, 6.55(6.31) N, 2.76(2.75); P, 6.11(5.93)
[(Me ₅ Cp) ₂ V(CO) ₂]PF ₆	-	-	515(m), 454(w) ν _{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 ₅ Cp) ₂ Cr	296-297°C	322(100)	585(m), 418(m), 235(w)	C, 74.49(74.34); H, 9.09(9.09)
[(Me ₅ Cp) ₂ Cr]PF ₆	-	-	525(m), 440(w), 432(w)	C, 51.39(51.50); H, 6.47(6.39) P, 6.63(6.63)
(Me ₅ Cp) ₂ Co	294-296°C	329(100)	586(m), 429(w), 320(w), 232(w)	C, 72.93(73.06); H, 9.18(9.11)
[(Me ₅ Cp) ₂ Co]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 ₅ Cp) ₂ Ni	296-297°C	328(100)	587(w), 385(m), 320(w)	C, 72.98(73.03); H, 9.19(9.07)
[(Me ₅ Cp) ₂ Ni]PF ₆	-	-	472(w), 225(w)	C, 50.66(50.41); H, 6.38(6.27) P, 6.53(6.68)
[(Me ₅ Cp) ₂ Ni](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 ₅ Cp) ₂ Mg	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), 722(w) cm⁻¹. The PF₆⁻ salts also show bands at 874(s), 845(s), 725(m), 552(s), 530(m) cm⁻¹.

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

Table III. ^1H and ^{13}C NMR data for diamagnetic Me_5Cp^- compounds.^a

Compound	^1H	^{13}C ^b		solvent
		ring C	methyl C	
Me_5CpNa	2.01	105.1	11.8	THF-d_8
$(\text{Me}_5\text{Cp})_2\text{Mg}$	1.93	110.1	9.6	C_6D_6
$[(\text{Me}_5\text{Cp})_2\text{V}(\text{CO})_2]\text{PF}_6$	2.00	107.4	9.3	$(\text{CD}_3)_2\text{CO}$
$\text{Na}[(\text{Me}_5\text{Cp})_2\text{Mn}]^{34\text{b}}$	1.83	72.4	8.5	THF-d_8
$(\text{Me}_5\text{Cp})_2\text{Fe}$	1.70	78.4	9.6	C_6D_6
$[(\text{Me}_5\text{Cp})_2\text{Co}]\text{PF}_6$	1.78	93.4	6.3	$(\text{CD}_3)_2\text{CO}$
$[(\text{Me}_5\text{Cp})_2\text{Ni}]^{2+}$	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.

Table IV. Magnetic susceptibility data for metallocenes and dcamethylmetallocenes, $\chi_m = C/(T-\theta)$

Compound	Solid		Solution		Reference
	μ_{eff}^b	temp. θ range ^c	μ_{eff}^b	temp. ^c	
(Me ₅ Cp) ₂ V	3.69±0.1	0 5-64	3.78±0.1	304	This work
Cp ₂ V	3.78±0.2	6.5 14-430	3.78	298	71,73
[(Me ₅ Cp) ₂ Cr]PF ₆	3.73±0.1	0 4.5-81	3.74±0.1	304	This work
(Cp ₂ Cr)I	3.87	90-296	-	-	50a
(Me ₅ Cp) ₂ Cr	3.01±0.1	0 6-81	2.90±0.1	304	This work
Cp ₂ Cr	3.20±0.16	17 90-295	3.10	298	72,73
(Me ₅ Cp) ₂ Co	1.45±0.1	0 5-130	1.56±0.1	304	This work
Cp ₂ Co	1.75-2.04 ^d	83-298	1.76	298	59,73
[(Me ₅ Cp) ₂ Ni]PF ₆	1.67±0.1 ^f	28 5-75	1.44±0.1	304	This work
[(Me ₅ Cp) ₂ Ni]BF ₄	1.62±0.1	0 6-57	-	-	This work
(Cp ₂ Ni)B(C ₆ H ₅) ₄	1.82±0.15	90-300	-	-	74
(Me ₅ Cp) ₂ Ni	2.93±0.1 ^e	-15 6-100	2.89±0.1	304	This work
Cp ₂ Ni	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 Bohr magnetons.
- c) Temperature in degrees 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 = 18K.

Table V. EPR data for 15-electron metallocenes and decamethylmetallocenes.

Compound	Host	Temp. ^a	$g_{ }$	g_{\perp} ^b	$A_{ }$ ^c	A_{\perp} ^c	Reference
$(Me_5Cp)_2V$	toluene	19	2.001(1)	3.973(1)	24.0(0.2)	16.0(0.2)	This work
	toluene	300	<g> = 1.985		<A> = 23.1(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 degrees 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 $(Me_5Cp)_2Mg$.

Table VI. Metal orbital mixing coefficients for vanadocene and decamethylvanadocene.

	c_o^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 reference 61.

b) Calculated from $(Me_5Cp)_2V$ in toluene

(19K) EPR spectrum.

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
	methyl-cyclohexane	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-methyl THF	4	$g_{\perp}=1.81$		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 degrees K.

b) In units of 10^{-4} cm^{-1} .

c) Calculated from Figure 3. Includes second order shift. Signs for A-values uncertain.

Table VIII. Ligand field absorption data and parameters for 18-electron metallocenes and decamethylmetallocenes.^a

Transition	Cp ₂ Fe ^b	(Me ₅ Cp) ₂ Fe	(Cp ₂ Co) ⁺ ^b	[(Me ₅ Cp) ₂ Co] ⁺	[(Me ₅ Cp) ₂ Ni] ²⁺
¹ A _{1g} → ¹ E _{1g} (a)	21.8(36)	23.5(121)	24.3(140)	23.8(330)	22.5(455)
→ ¹ E _{2g}	24.0(72)	30.5(180)	26.4(120)	29.5(1430)	31.5(60,000) ^c
→ ¹ E _{1g} (b)	30.8(49)	34.5(2970) ^c	33.3(1200)	40.0(1170)	42.5(7800) ^d
→ ³ E _{1g} (a)	18.9(7)	--	21.8(7)	12.7(0.2)	--
→ ³ E _{2g}	--	--	--	18.5(0.8)	--
→ ³ E _{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 kK (10^3 cm^{-1}). Extinction coefficients are enclosed in parentheses. Δ₂ values calculated assuming C/B = 4.0.
- b) Data and parameters from reference 68. Ferrocene spectrum measured in 2-methylbutane solution; (Cp₂Co)ClO₄ spectrum measured in aqueous solution.
- c) Estimated energy of transition.
- d) Assignment uncertain.
- e) Δ₁, Δ₂ and B values calculated from singlet absorption spectrum. Analysis of spin-forbidden transitions yields B = 0.68 kK and Δ₁ = 13.9 kK.

Table IX. Ligand field spectral data and parameters for 20-electron metallocenes and decamethylmetallocenes.^a

Transition	Cp ₂ Ni ^b	(Me ₅ Cp) ₂ Ni	
		I	II
³ A _{2g} → ³ E _{1g} (a)	14.38(62)	15.9(99)	
→ ³ E _{2g}	16.90(23)	18.5(58)	
→ ³ E _{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 kK (10³ cm⁻¹). Extinction coefficients enclosed in parentheses.

b) Data from reference 69a (measured in n-heptane solution). Parameters from reference 38.

c) Estimated values.

Table X Ligand field absorption data and parameters for 15-electron metallocenes and decamethylmetallocenes.^a

Transition	Cp ₂ V ^b	(Me ₅ Cp) ₂ V	(Cp ₂ Cr) ⁺ ^c	[(Me ₅ Cp) ₂ Cr] ⁺	
⁴ A _{2g} → ⁴ E _{1g} (a)	17.33(58)	18.7(23)	17.86(270)	20.4(1386)	
→ ⁴ E _{2g}	20.24(46)	20.6(25)	21.98(210)	23.1(2450)	
→ ⁴ E _{1g} (b)	24.50(66)	28.2(1037)	27.03(630)	I 29.0(2400) ^d	II 32.0(16,000) ^d
→ ² E _{1g}	8.96(.09)	10.5(1.8)	--	--	
→ ² A _{1g} , ² A _{2g}	13.00(.06)	14.5(5.7)	--	15.4(0.50)	
→ ² E _{2g} (a)	--	--	25.0(480)	13.2(0.4)	
→ ² E _{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 kK (10³ cm⁻¹). Extinction coefficients enclosed in parentheses.

b) Data from reference 69b (measured in diethylether and n-pentane solutions). Parameters from reference 38.

c) Data from reference 50a (measured as I⁻ salt in aqueous solution). Parameters from reference 38.

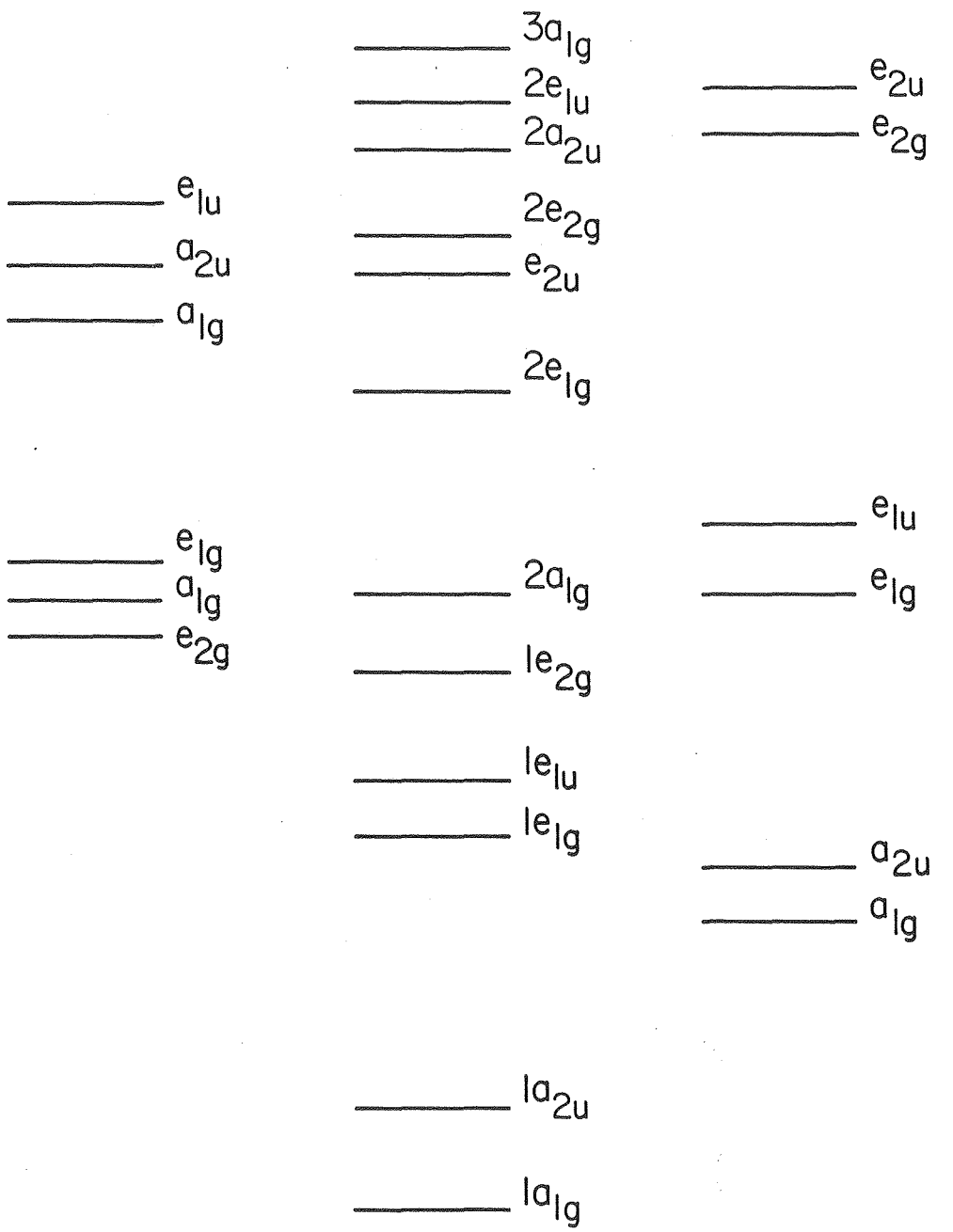
d) Estimated value.

Figure Captions

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

Figure 2. $1/\chi_m$ (mole/emu) vs. T plot for solid
 $[(\text{Me}_5\text{Cp})_2\text{Ni}]\text{PF}_6$ and $[(\text{Me}_5\text{Cp})_2\text{Ni}]\text{BF}_4$.

Figure 3. X-band EPR spectrum of $(\text{Me}_5\text{Cp})_2\text{Co}$ diluted in
 $(\text{Me}_5\text{Cp})_2\text{Fe}$ at 9K with g- and A-tensors indicated.

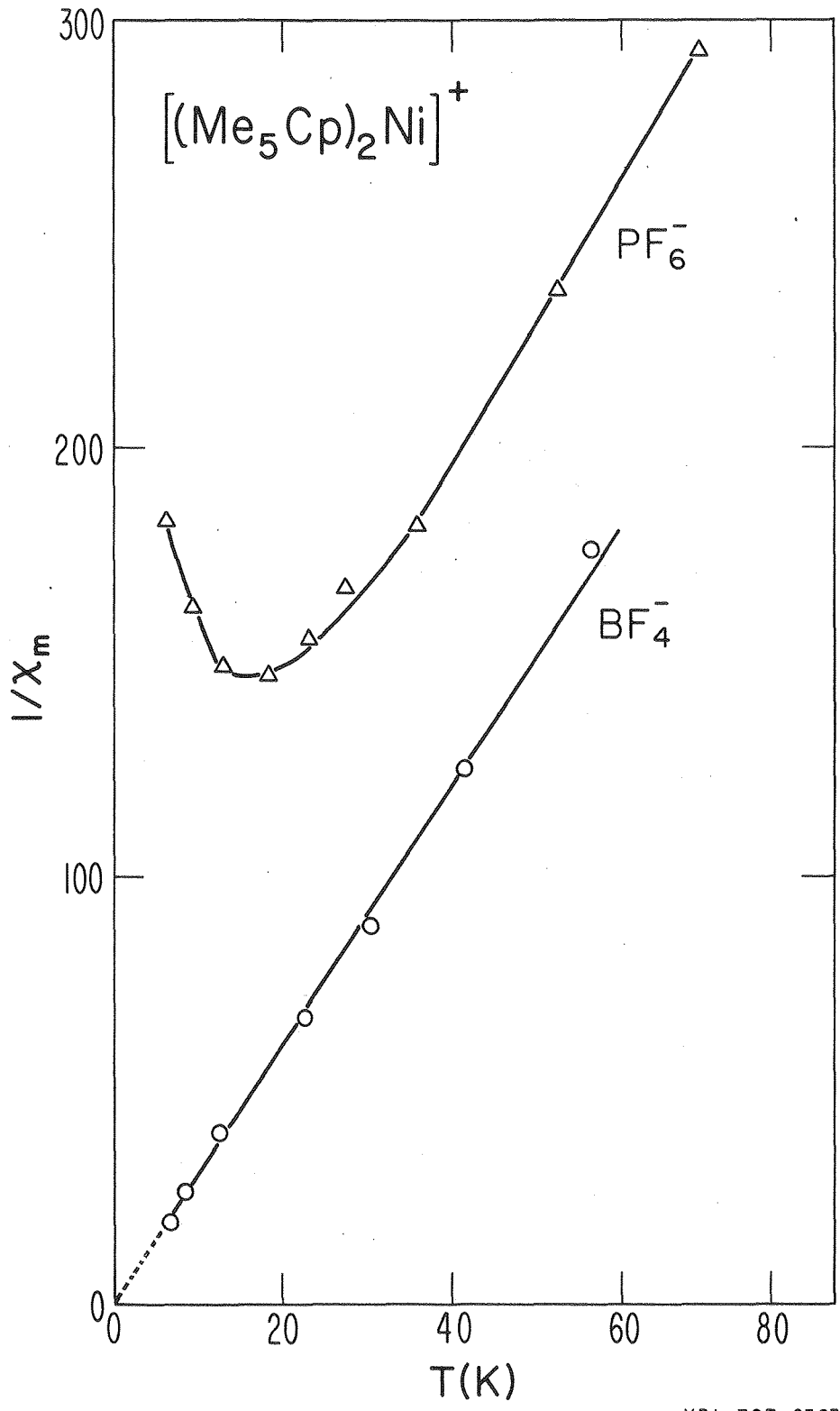


Metal orbitals

Ligand π -orbitals

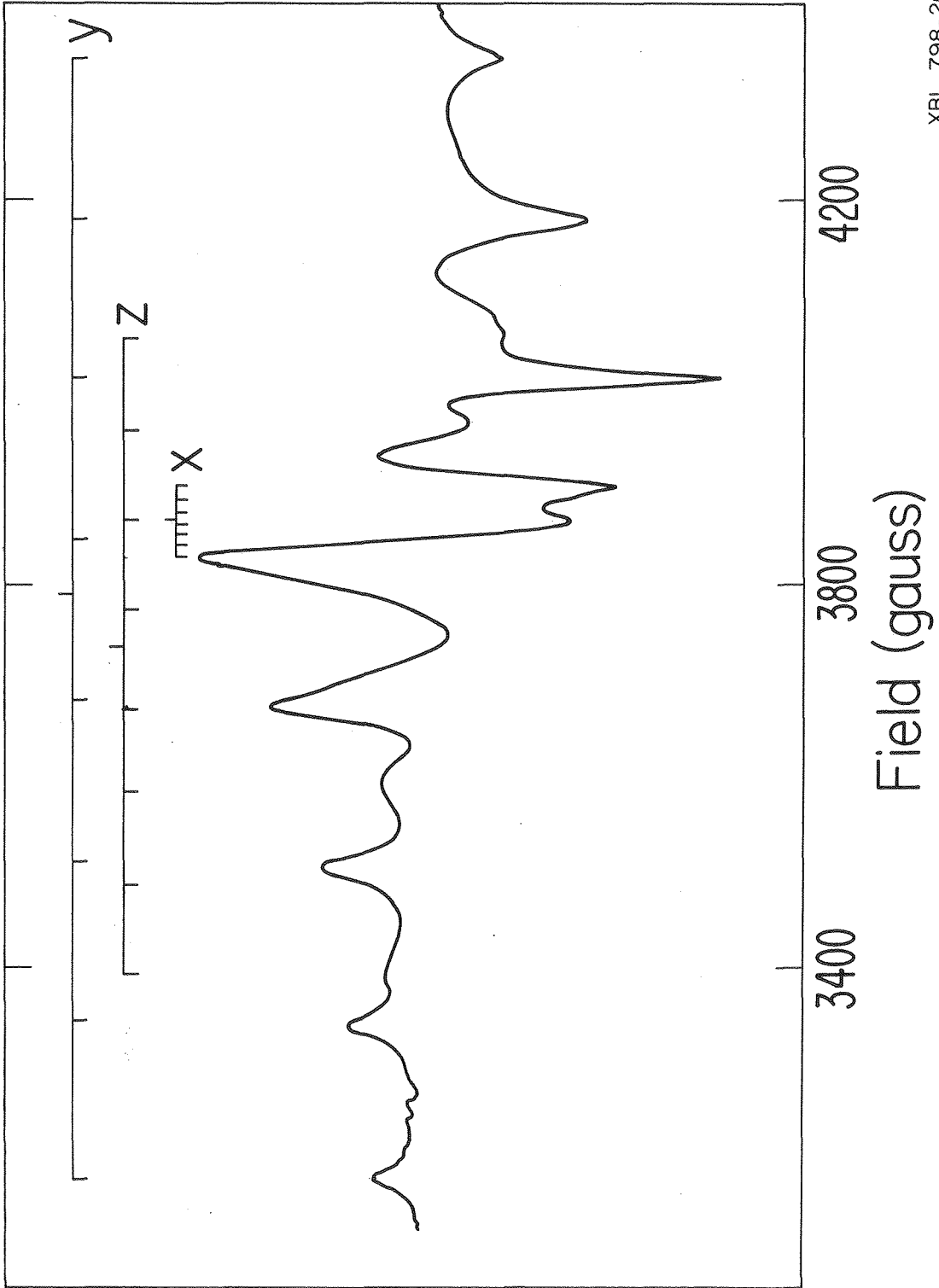
XBL 798-2693

Figure 1



XBL 797-2323

Figure 2



XBL 798-2696

Figure 3