Organometallics 1987, *6*, 1703–1712

Syntheses, Reactivities, Molecular Structures, and Physical Properties of Paramagnetic Bis(tetraphenylcyclopentadienyl) Complexes of Vanadium, Chromium, Cobalt, and Nickel

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Received December 10, 1986

The reactions between I, K(C_5HPh_4)·0.5THF, and metal halides of the first transition series yield complexes of the type $(C_5HPh_4)_2M$ (M = V, Cr, Co, and Ni, compounds II, III, V, and VII, respectively). Crystals of all four complexes belong to the space group $P\bar{1}$, $Z = 1$, and possess rigorous molecular inversion symmetry. The unit-cell parameters for II are $a = 8.431$ (2) Å, $b = 10.893$ (3) Å, $c = 13.012$ (3) Å, $\alpha = 66.30$ (2)°, $\beta = 75.56$ (2)°, $\gamma = 85.54$ (2)°, and $V = 1059.4$ (5) Å^3 with final values of R_F and 5.56% and R_{wF} = 6.09%. Complex III crystallizes with $a = 8.300$ (4) Å, $b = 10.900$ (3) Å, $c = 12.930$ (5) Å, $\alpha = 66.53$ (3)°, $\beta = 75.02$ (3)°, $\gamma = 85.18$ (3), and $V = 1036.2$ (7) Å^3 with final values of R_F = 5.71% and R_{wF} = 6.36%. The unit-cell parameters for V are $a = 8.297$ (2) Å, $b = 10.938$ (4) Å, $c = 12.936$ (4) Å, $\alpha = 66.74$ (2)°, $\beta = 74.78$ (4)°, $\gamma = 84.99$ (2)°, and $V = 1040.5$ (6) Å^3 with final values of R_F = 5.67% and R_{wF} = 5.66%. Complex VII crystallizes with $a = 8.237$ (6) Å, $b = 10.874$ (8) Å, $c = 12.946$ (11) Å, $\alpha = 66.91$ (6)°, $\beta = 75.78$ (6)°, $\gamma = 86.02$ (6)°, and $V = 1033$ (1) Å^3 with final values of R_F = 9.86% and R_{wF} = 10.6%. The difference in metal–carbon bond lengths between $(C_5H_5)_2M$ and $(C_5HPh_4)_2M$ complexes decreases on going from Fe (0.05 Å) to V (0.02 Å), which suggests decreasing interaction between phenyl groups on opposing C_5 rings. Redox potentials of $(C_5HPh_4)_2M$ complexes resemble those of $(C_5H_5)_2M$ and $[(C_5HPh_4)_2Cr]PF_6$, $[(C_5HPh_4)_2Co]PF_6$, and $[(C_5HPh_4)_2Ni]PF_6$ were prepared by oxidation of the neutral metallocenes with $AgPF_6$. EPR and solid-state magnetic moment measurements show that $(C_5HPh_4)_2M$ complexes occupy the same ground-state electronic configurations as corresponding $(C_5H_5)_2M$ and $(C_5Me_5)_2M$ derivatives. The EPR measurements on $[(C_5HPh_4)_2Cr]PF_6$ and $(C_5HPh_4)_2Co$ suggest that the low molecular symmetry (C_i) of these complexes perturbs the metallocene energy levels more than Jahn–Teller distortions in the unsubstituted complexes (D_{5d}). The $(C_5HPh_4)_2M$ complexes show much reduced reactivity when compared with $(C_5H_5)_2M$ complexes.

Introduction

Many substituted bis(cyclopentadienyl)iron,[2] cobalt,[3] and nickel,[4] complexes have been prepared; however, few such complexes of other first-row transition metals are known.[5] Except for ferrocene,[2,6] few metallocene derivatives exclusively incorporate phenyl substituents.[7-9] While physical properties have been measured for many substituted neutral metallocenes of the first-row transition metals,[2-5,11] studies of phenyl-substituted metallocenes have been limited primarily to ^{1}H NMR[9] and ^{13}C NMR[10] spectral characterization.

Crystal structures have been reported for one substituted vanadocene[12] and nickelocene.[13] No structural data is available for substituted chromocenes or cobaltocenes.[14] Structural studies of bis(pentamethylcyclopentadienyl)metal complexes have been limited to $(C_5Me_5)_2M$ (M = V,[12] Mn,[15] Fe[15]), and the vanadium structure suffers from disorder. This lack of structural information for substituted metallocenes, and our interest[16] in the physical properties of phenyl-substituted metallocenes, led us to prepare complexes of the type $(C_5HPh_4)_2M$ (M = V, Cr, Mn, Co, Ni). Given the $\bar{1}$ symmetry (anti rotamer) observed[16] for $(C_5HPh_4)_2Fe$ in the solid state, we wondered whether a similar rotamer would be observed for other octaphenylmetallocenes. Structural studies of these sterically congested complexes lay the foundation for a conformational analysis of sterically crowded organometallic complexes, a topic of current interest in organic[17] and organometallic[18] chemistry. Complexes incorporating the pentamethylcyclopentadienyl ligand exhibit significant

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0276-7333/87/2306-1703$01.50/0

changes in reactivity from the corresponding cyclopentadienyl complexes because of steric and electronic differences.[19] The tetraphenylcyclopentadienyl ligand may be prepared easily and yields complexes that often crystallize. A delineation of tetraphenylcyclopentadienyl metallocene chemistry is needed before it finds general use as a ligand. This work examines how the steric bulk of the phenyl rings affects the reactivities, molecular structures, EPR spectra, and magnetic and redox properties of $(C_5HPh_4)_2M$ (M = V, Cr, Co, Ni).

Experimental Section

Except where noted, reactions of materials used standard Schlenk techniques. Solids were manipulated under nitrogen in a Vacuum Atmospheres glovebox equipped with a HE-493 dri-train. Benzene, tetrahydrofuran (THF), toluene, diethyl ether, and pentane were refluxed over sodium–benzophenone ketyl and distilled under nitrogen. Dichloromethane was refluxed over CaH_2 and distilled under nitrogen. Lithium tetraphenylcyclopentadienide was prepared as described previously,[16] except that tetraphenylcyclopentadienone was prepared by a literature synthesis.[20] The $[Ni(NH_3)_6]Cl_2$[21] and $Cr_2(O_2CCH_3)_4$[22] reagents were prepared by literature methods. The $Mn(CF_3SO_3)_2$ reagent was prepared by the reaction between $MnCO_3$ and CF_3SO_3H in water, followed by dehydration under vacuum at 135 °C for 2 h. Anhydrous $CrCl_2$ (Aesar), VCl_3, $CoBr_2$ (Strem), $NiCl_2{\cdot}6H_2O$ (Mallinkrodt), $AgPF_6$, and CF_3CO_2H (Aldrich) were purchased and used without purification. The KH reagent (Aldrich) was separated from the accompanying mineral oil by Soxhlet extraction with pentane under a nitrogen atmosphere.

Magnetic susceptibilities were measured with a BTi Model VTS-905 SQUID (Super Quantum Interference Device) Susceptometer on samples (ca. 50 mg) wrapped in Parafilm (ca. 0.1 g) and suspended from a cotton thread. The samples were transferred rapidly from a nitrogen-filled Schlenk tube into the instrument and placed under a helium atmosphere. Samples were corrected for wax diamagnetism and for ligand diamagnetism with a bis(tetraphenylcyclopentadienyl)iron(II)[16] blank. Measurements were made at 20–22 temperatures on each sample in the temperature range 7–300 K at a constant field strength of 10.00 kG.

Cyclic voltammograms were recorded with a BAS-100 Electrochemical Analyzer and a Houston Instruments DMP-40 digital plotter. A conventional three-electrode cell [Pt button working electrode, Pt wire auxiliary electrode, and a Ag/Ag^+ (0.1 M $AgNO_3$ in CH_3CN) reference electrode] contained 2 mM solutions of the complexes in electrolyte (0.25 M) solution. The supporting electrolyte (tetra-*n*-butylammonium perchlorate, Baker Polarographic Grade) was recrystallized twice from a mixture of ethyl acetate and isooctane. EPR spectra were recorded with a Varian E-3 spectrometer with the use of diphenylpicrylhydrazyl as the field marker. Samples were cooled to 77 K by immersion in an N_2 filled Dewar or by placing them in a stream of N_2 gas cooled to 78–80 K. Proton NMR spectra were recorded on a GE QE-300 NMR spectrometer at 300.152 MHz. Elemental analyses were performed by Schwartzkopf Microanalytical Laboratories.

Synthesis of Potassium Tetraphenylcyclopentadienide–0.5-Tetrahydrofuran, I. Addition of dry THF (100 mL) to a solid mixture of tetraphenylcyclopentadiene (9.55 g, 25.8 mmol) and potassium hydride (1.47 g, 36.6 mmol) produced an orange-red solution with concurrent H_2 gas evolution. After gas evolution ceased (3 h), the reaction mixture was filtered through a frit. The filtrate was evaporated to dryness under vacuum, and the resulting solid was vacuum dried overnight. The solid was ground in a mortar and pestle and heated to 50 °C for 2 h under vacuum to remove residual THF. The beige powder was obtained in 96% yield (11.0 g, 24.7 mmol). Anal. Calcd for $C_{62}H_{50}K_2O$: C, 83.74; H, 5.67. Found: C, 83.91; H, 5.90.

Synthesis of Bis(tetraphenylcyclopentadienyl)vanadium(II), II. A THF solution (20 mL) of VCl_3 (0.47 g, 2.8 mmol) and 2–3 mg of NaH was refluxed overnight, followed by addition of Zn dust (105 mg, 1.6 mmol) and a continued 12 h reflux of the solution. The mixture was cooled to room temperature and transferred via cannula (without filtering) into a solution of $K(C_5HPh_4)$ (2.23 g, 5.9 mmol) in THF (30 mL). The solution was refluxed overnight followed by solvent removal in vacuo. The green solid was purified by extraction with boiling benzene. The benzene extract was evaporated to dryness under vacuum, and the resulting solid was dissolved in a minimum of boiling toluene (ca. 50 mL). The hot solution was filtered rapidly followed by cooling the solution to −15 °C. After several days green, microcrystalline II precipitated in 50% yield (1.17 g, 1.5 mmol). Anal. Calcd for $C_{58}H_{42}V$: C, 88.19; H, 5.36. Found: C, 87.82; H, 5.36.

Synthesis of Bis(tetraphenylcyclopentadienyl)chromium(II), III. Dry THF (30 mL) was added to a solid mixture of $CrCl_2$ (0.20 g, 1.6 mmol) and $K(C_5HPh_4)$ (1.52 g, 3.4 mmol) and refluxed overnight. Removal of solvent in vacuo yielded a magenta residue, which was extracted with boiling benzene. The extract was dried under vacuum, and the resulting solid was dissolved in a minimum (40 mL) of boiling toluene, filtered, and cooled to −15 °C overnight. Microcrystals of III were obtained in 47% yield (0.61 g, 0.77 mmol). Anal. Calcd for $C_{58}H_{42}Cr$: C, 88.07, H, 5.35. Found: C, 87.50; H, 5.47.

Synthesis of Bis(tetraphenylcyclopentadienyl)chromium(III) Hexafluorophosphate–0.5-Dichloromethane, IV. Dry CH_2Cl_2 (15 mL) was added to a solid mixture of III (0.20 g, 0.25 mmol) and $AgPF_6$ (0.071 g, 0.28 mmol). After being stirred for several hours, the red-brown solution was filtered into a Schlenk tube. The volume was reduced under vacuum to saturation before layering an equal volume of pentane on top. After several days, filtering the solution yielded IV (0.18 g, 0.18 mmol) as black crystals in 72% yield. Anal. Calcd for $C_{117}H_{86}Cl_2Cr_2F_{12}P_2$: C, 71.82; H, 4.43. Found: C, 72.29; H, 4.45.

Synthesis of Bis(tetraphenylcyclopentadienyl)cobalt(II), V. A mixture of anhydrous $CoBr_2$ (0.50 g, 2.3 mmol) and $K(C_5HPh_4)$ (2.13 g, 4.8 mmol) reacted in THF (25 mL) to form a purple solution. After the solution was stirred for 1 day, the THF was removed in vacuo and the resulting solid was purified by extraction with boiling benzene. The volume of the benzene extract was reduced in vacuo, and the resulting solution was heated to reflux. The solution volume was then adjusted until all solid dissolved (110 mL) before it was cooled slowly to room temperature. After several days, dark purple, crystalline V was isolated in 76% yield (1.39 g, 1.7 mmol). Anal. Calcd for $C_{58}H_{42}Co$: C, 87.31; H, 5.30. Found: C, 88.15; H, 5.67.

Synthesis of Bis(tetraphenylcyclopentadienyl)cobalt(III) Hexafluorophosphate, VI. To a mixture of V (0.60 g, 0.75 mmol) and $AgPF_6$ (0.19 g, 0.75 mmol) was added 15 mL of THF. After the solution was stirred overnight, the THF was removed in vacuo and the residue was extracted with a minimum of CH_2Cl_2 (in air) to yield a red solution. Hexanes were layered on this solution to yield red crystals of air-stable VI (0.58 g, 0.62 mmol) in 82% yield after it was left standing for several days. Anal. Calcd for $C_{58}H_{42}CoF_6P$: C, 73.88; H, 4.49. Found: C, 74.72; H, 4.57.

Synthesis of Bis(tetraphenylcyclopentadienyl)nickel(II), VII. A mixture of $[Ni(NH_3)_6]Cl_2$ (0.52 g, 2.2 mmol) and $K(C_5HPh_4)$ (2.09 g, 4.7 mmol) in THF (50 mL) was refluxed for 70 h and then cooled to room temperature. After solvent removal in vacuo, the residue was extracted with boiling benzene. The extract was evaporated to dryness under vacuum, and the residue was dissolved in a minimum of boiling toluene and filtered. Cooling the filtrate to −15 °C for several days produced brown, microcystalline VII (1.24 g, 1.6 mmol) in 69% yield. Anal. Calcd for $C_{58}H_{42}Ni$: C, 87.33; H, 5.31. Found: C, 87.52; H, 5.52.

Synthesis of Bis(tetraphenylcyclopentadienyl)nickel(III) Hexafluorophosphate–0.5-Dichloromethane, VIII. Dry CH_2Cl_2 (20 mL) was added to a solid mixture of VII (0.63 g, 0.79 mmol) and $AgPF_6$ (0.20 g, 0.79 mmol). After being stirred ov-

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Table I. Crystal and Refinement Data for Octaphenylmetallocenes

	$C_{58}H_{42}V$	$C_{58}H_{42}Cr$	$C_{58}H_{42}Fe^b$	$C_{58}H_{42}Co$	$C_{58}H_{42}Ni$
cryst system	triclinic	triclinic	triclinic	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a, Å	8.431 (2)	8.300 (4)	8.339 (4)	8.297 (2)	8.237 (6)
b, Å	10.893 (3)	10.900 (3)	10.867 (5)	10.938 (4)	10.874 (8)
c, Å	13.012 (3)	12.930 (5)	12.830 (7)	12.936 (4)	12.946 (11)
α, deg	66.30 (2)	66.53 (3)	66.40 (4)	66.74 (2)	66.91 (6)
β, deg	75.56 (2)	75.02 (3)	73.47 (4)	74.78 (2)	75.78 (6)
γ, deg	85.45 (2)	85.18 (3)	83.72 (4)	84.99 (2)	86.02 (6)
V, Å^3	1059.4 (5)	1036.2 (7)	1021.3 (9)	1040.5 (6)	1033 (1)
Z	1	1	1	1	1
cryst dimens, mm	0.23 × 0.24 × 0.36	0.23 × 0.28 × 0.30	0.31 × 0.31 × 0.31	0.20 × 0.20 × 0.40	0.18 × 0.23 × 0.42
abs coeff, cm^{-1}	2.9	3.1	4.2	4.5	5.1
2θ scan range, deg	4–45	4–45	4–52	4–48	4–42
scan technique	$\theta/2\theta$	$\theta/2\theta$	omega	$\theta/2\theta$	$\theta/2\theta$
weighting factor, g^a	0.0008	0.0025	0.0008	0.0010	0.0075
unique data	2777 (2924 read)	2725 (2870 read)	4019 (4209 read)	3287 (3614 read)	2204 (2924 read)
unique data obsd	2145 (> $5\sigma(F_o)$)	1943 (> $5\sigma(F_o)$)	3498 (> $3\sigma(F_o)$)	2363 (> $4\sigma(F_o)$)	1722 (> $5\sigma(F_o)$)
data/parameter	9.58	8.67	15.62	10.55	7.69
std rflns	3 stds/197 rflns				
GOF^a	1.866	1.223	1.432	1.274	1.541
$R_F{}^a$	5.56	5.71	4.52	5.67	9.86
$R_{wF}{}^a$	6.09	6.36	5.09	5.66	10.60

[a] GOF = $[\sum w(|F_o| - |F_c|)^2/(N_{obsd} - N_p)]^{1/2}$; $R_F = \sum|F_o| - |F_c|/\sum|F_o|$; $R_{wF} = \sum(|F_o| - |F_c|w^{1/2})/\sum(|F_o|w^{1/2})$; $w^{-1} = \sigma^2|F_o| + g|F_o|^2$. [b] Reference 16.

ernight, the solution was cannula filtered into a Schlenk tube and the solid residue was extracted with CH_2Cl_2 to remove all the green-brown product. An equal volume of pentane was layered on this solution. After several days green-brown crystals of VIII (0.47 g, 64%) were collected by filtration, washed with benzene (to remove residual VII), and dried in vacuo. Anal. Calcd for $C_{117}H_{86}Cl_2F_{12}Ni_2P_2$: C, 71.33; H, 4.40. Found: C, 71.21; H, 4.56.

X-ray Structural Determination. Crystal data and parameters used during the collection of intensity data for $C_{58}H_{42}V$, $C_{58}H_{42}Cr$, $C_{58}H_{42}Co$, and $C_{58}H_{42}Ni$ are given in Table I. Crystals of V, Cr, and Ni were grown by layer diffusion of pentane into saturated dichloromethane solutions of the particular compound. The Co compound was crystallized similarly from THF solution. Crystals of V (green), Cr (magenta), Co (purple), and Ni (orange–brown) were attached to fine glass fibers with epoxy cement. All four crystallized in the triclinic space group $P\bar{1}$ and are isomorphous with the previously reported structure of octaphenylferrocene.[16] Unit-cell dimensions were derived from the least-squares fit of the angular settings of 25 reflections with 14 < 2θ < 26° for each crystal. A profile fitting procedure was applied to all intensity data to improve the precision of the measurement of weak reflections. Reflections for the Ni complex were corrected for absorption effects by using the program XABS (H. Hope), which is based on deviations in F_o and F_c values. An absorption correction was not needed for V, Cr, and Co because of uniform crystal dimensions and low absorption coefficients (V, 2.9 cm^{-1}; Cr, 3.1 cm^{-1}; Co, 4.5 cm^{-1}; Ni, 5.1 cm^{-1}). Including an absorption correction for Co had no significant effect on the refinement. A hemisphere ($\pm h$, $\pm k$, $+l$) of data were collected on a Nicolet R3m/μ automated diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71053 Å) at ambient temperatures (22–24 °C) and a variable scan speed (5–20 deg/min). Three standard reflections were monitored for each 197-reflection block. For all complexes decay of the standard reflections was <2%.

Structures of V, Cr, Co, and Ni were solved by using the metal and Cp atom coordinates of the $C_{58}H_{42}Fe$ isomorph. The remaining non-hydrogen atoms were located from difference Fourier syntheses. All non-hydrogen atoms were refined anisotropically (except for C(2) in $C_{58}H_{42}Ni$), and hydrogen atoms were treated as idealized, isotropic contributions (d(C–H) = 0.96 Å, $U = 1.2U_{iso}$ of attached C) for all hydrogen atoms except H(1), which was located and refined in all cases. Phenyl rings were treated as rigid hexagons, d(C–C) = 1.395 Å. Final difference Fourier syntheses showed only diffuse backgrounds (maximum contours: V, 0.48 e Å^{-3}; Cr, 0.39 e Å^{-3}; Co, 0.48 e Å^{-3}; Ni, 1.28 e Å^{-3} (near Ni)). An inspection of F_o vs. F_c values and trends based on sin θ, Miller index, or parity group did not show any systematic errors in the data for any crystal. All computer programs used in the data collections and refinements are contained in the Nicolet program packages P3 and SHELXTL (version 5.1).

Table II. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3) for $C_{58}H_{42}V$

	x	y	z	U^a
V	0	0	0	36 (1)
C(1)	2390 (5)	1069 (4)	−314 (4)	40 (2)
C(2)	2466 (5)	788 (4)	−1305 (3)	39 (2)
C(3)	2435 (5)	−644 (4)	−917 (3)	39 (2)
C(4)	2356 (5)	−1216 (4)	293 (3)	41 (2)
C(5)	2326 (5)	−143 (4)	675 (3)	39 (2)
C(21)	3299 (3)	3059 (3)	−2810 (2)	49 (2)
C(22)	3338	4079	−3909	64 (2)
C(23)	2613	3871	−4681	75 (3)
C(24)	1850	2644	−4354	63 (2)
C(25)	1811	1624	−3256	48 (2)
C(26)	2536	1832	−2484	40 (2)
C(31)	1627 (4)	−2587 (3)	−1264 (3)	58 (2)
C(32)	1893	−3323	−1973	89 (4)
C(33)	3144	−2931	−3034	101 (4)
C(34)	4128	−1802	−3385	88 (3)
C(35)	3861	−1067	−2676	61 (2)
C(36)	2611	−1459	−1615	46 (2)
C(41)	1210 (3)	−3482 (3)	1878 (3)	56 (2)
C(42)	1451	−4851	2465	71 (3)
C(43)	2989	−5433	2145	73 (3)
C(44)	4286	−4645	1236	69 (3)
C(45)	4045	−3276	649	54 (2)
C(46)	2507	−2694	969	42 (2)
C(51)	1665 (4)	840 (2)	2174 (2)	52 (2)
C(52)	1535	761	3308	61 (2)
C(53)	2053	−395	4124	67 (3)
C(54)	2700	−1471	3806	68 (3)
C(55)	2831	−1392	2673	56 (2)
C(56)	2313	−236	1856	43 (2)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

The metal atom of each octaphenylmetallocene resides at a crystallographic center of symmetry. Atomic coordinates, selected bond distances, and angles are provided in Tables II–VII.

Results and Discussion

Synthesis and Reactivity. Reaction of tetraphenylcyclopentadiene and potassium hydride yielded potassium tetraphenylcyclopentadienide, I, as a beige powder in near quantitative yield according to eq 1. Recrystallization

$$C_5H_2Ph_4 + KH \xrightarrow{THF} K(C_5HPh_4)\cdot{}^1/_2THF + H_2 \quad (1)$$

Table III. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters (Å^2 × 10^3) for $C_{58}H_{42}Cr$

	x	*y*	*z*	U^a
Cr	0	0	0	34 (1)
C(1)	2231 (6)	1089 (4)	−323 (4)	40 (2)
C(2)	2310 (5)	781 (5)	−1313 (4)	37 (2)
C(3)	2335 (6)	−638 (4)	−930 (4)	37 (2)
C(4)	2288 (6)	−1196 (5)	267 (4)	39 (2)
C(5)	2250 (6)	−129 (4)	663 (4)	37 (2)
C(21)	3227 (4)	3044 (3)	−2811 (3)	49 (2)
C(22)	3322	4061	−3906	63 (3)
C(23)	2618	3863	−4699	72 (3)
C(24)	1821	2648	−4398	62 (3)
C(25)	1726	1631	−3303	47 (2)
C(26)	2430	1829	−2510	40 (2)
C(31)	1634 (4)	−2604 (3)	−1300 (3)	56 (3)
C(32)	1910	−3352	−1986	81 (4)
C(33)	3129	−2937	−3035	95 (5)
C(34)	4074	−1774	−3397	89 (4)
C(35)	3798	−1025	−2710	59 (3)
C(36)	2579	−1440	−1662	46 (2)
C(41)	1274 (4)	−3493 (3)	1811 (3)	55 (3)
C(42)	1578	−4846	2377	74 (3)
C(43)	3138	−5358	2055	79 (4)
C(44)	4393	−4519	1167	70 (3)
C(45)	4088	−3167	601	55 (3)
C(46)	2529	−2654	922	44 (2)
C(51)	1684 (4)	878 (3)	2141 (3)	50 (3)
C(52)	1594	809	3255	62 (3)
C(53)	2078	−346	4076	68 (3)
C(54)	2653	−1434	3783	67 (3)
C(55)	2744	−1366	2669	54 (3)
C(56)	2260	−210	1848	43 (2)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table IV. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters (Å^2 × 10^3) for $C_{58}H_{42}Co$

	x	*y*	*z*	U^a
Co	0	0	0	36 (1)
C(1)	2137 (5)	1104 (4)	−317 (3)	39 (2)
C(2)	2263 (5)	807 (4)	−1315 (3)	41 (2)
C(3)	2253 (5)	−601 (4)	−949 (3)	41 (2)
C(4)	2212 (5)	−1168 (4)	292 (3)	40 (2)
C(5)	2188 (5)	−113 (4)	676 (3)	42 (2)
C(21)	3214 (4)	3050 (3)	−2819 (2)	52 (2)
C(22)	3315	4061	−3912	67 (2)
C(23)	2599	3872	−4701	72 (3)
C(24)	1783	2671	−4399	63 (2)
C(25)	1682	1660	−3307	47 (2)
C(26)	2398	1850	−2517	41 (2)
C(31)	1605 (4)	−2588 (3)	−1290 (3)	58 (2)
C(32)	1899	−3348	−1967	82 (3)
C(33)	3114	−2937	−3019	95 (4)
C(34)	4035	−1766	−3394	84 (3)
C(35)	3741	−1006	−2717	59 (2)
C(36)	2526	−1417	−1665	46 (2)
C(41)	1281 (3)	−3495 (3)	1789 (3)	58 (2)
C(42)	1642	−4832	2331	72 (3)
C(43)	3233	−5298	1996	77 (3)
C(44)	4462	−4426	1118	70 (3)
C(45)	4101	−3089	576	56 (2)
C(46)	2511	−2623	912	44 (2)
C(51)	1699 (4)	924 (2)	2137 (2)	53 (2)
C(52)	1626	859	3248	63 (3)
C(53)	2098	−297	4065	69 (3)
C(54)	2643	−1389	3773	66 (3)
C(55)	2716	−1324	2663	57 (2)
C(56)	2244	−168	1845	43 (2)

[a] Equivalent isotropic *U* defined as one third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table V. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters (Å^2 × 10^3) for $C_{58}H_{42}Ni$

	x	*y*	*z*	U^a
Ni	0	0	0	32 (1)
C(1)	2297 (13)	1015 (12)	−269 (8)	38 (5)
C(2)	2416 (11)	686 (10)	−1232 (8)	34 (2)
C(3)	2351 (12)	−684 (10)	−886 (8)	38 (4)
C(4)	2312 (13)	−1256 (9)	347 (8)	35 (4)
C(5)	2256 (12)	−171 (11)	702 (8)	41 (5)
C(21)	3321 (9)	2977 (6)	−2756 (5)	45 (5)
C(22)	3412	3985	−3847	59 (6)
C(23)	2694	3771	−4635	69 (6)
C(24)	1886	2550	−4333	52 (5)
C(25)	1794	1543	−3242	46 (5)
C(26)	2512	1757	−2453	42 (5)
C(31)	1535 (9)	−2656 (7)	−1201 (6)	59 (6)
C(32)	1713	−3417	−1871	84 (9)
C(33)	2920	−3047	−2915	96 (10)
C(34)	3950	−1914	−3289	76 (7)
C(35)	3772	−1152	−2618	63 (6)
C(36)	2564	−1523	−1574	42 (5)
C(41)	1241 (7)	−3480 (7)	1921 (6)	52 (5)
C(42)	1488	−4834	2513	70 (6)
C(43)	2990	−5405	2178	75 (7)
C(44)	4246	−4622	1251	69 (7)
C(45)	4000	−3268	659	49 (5)
C(46)	2497	−2697	994	43 (5)
C(51)	1670 (10)	841 (6)	2186 (5)	50 (5)
C(52)	1586	789	3292	58 (6)
C(53)	2115	−341	4105	58 (6)
C(54)	2727	−1420	3814	61 (6)
C(55)	2811	−1369	2708	43 (5)
C(56)	2282	−239	1894	47 (5)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table VI. Selected Bond Distances (Å) for Octaphenylmetallocenes

	M				
	V	Cr	Fe[a]	Co	Ni
M–CNT[b]	1.922 (4)	1.832 (5)	1.695 (2)	1.771 (4)	1.87 (1)
M–C(1)	2.272 (5)	2.141 (5)	2.054 (3)	2.091 (4)	2.14 (1)
M–C(2)	2.246 (3)	2.173 (4)	2.093 (2)	2.151 (3)	2.17 (1)
M–C(3)	2.234 (4)	2.218 (5)	2.097 (2)	2.156 (4)	2.24 (1)
M–C(4)	2.282 (4)	2.234 (5)	2.088 (3)	2.172 (4)	2.30 (1)
M–C(5)	2.306 (4)	2.220 (5)	2.099 (3)	2.188 (5)	2.23 (1)
C(1)–C(2)	1.405 (7)	1.432 (9)	1.423 (5)	1.427 (7)	1.41 (2)
C(2)–C(3)	1.432 (6)	1.424 (7)	1.438 (4)	1.421 (6)	1.38 (1)
C(3)–C(4)	1.407 (6)	1.410 (7)	1.429 (4)	1.467 (6)	1.46 (1)
C(4)–C(5)	1.429 (7)	1.441 (8)	1.435 (5)	1.423 (7)	1.42 (1)
C(5)–C(1)	1.409 (5)	1.331 (6)	1.421 (3)	1.447 (5)	1.40 (1)
C(1)–H(1)	0.90 (4)	0.97 (5)	1.00 (3)	1.04 (4)	0.82 (9)
C(2)–C(26)	1.473 (4)	1.497 (5)	1.483 (3)	1.504 (4)	1.54 (1)
C(3)–C(36)	1.463 (6)	1.494 (8)	1.481 (4)	1.488 (6)	1.48 (1)
C(4)–C(46)	1.500 (4)	1.498 (5)	1.496 (3)	1.504 (5)	1.48 (1)
C(5)–C(56)	1.476 (5)	1.501 (7)	1.500 (4)	1.502 (6)	1.52 (1)

[a] Reference 16. [b] CNT = centroid of cyclopentadienyl ring.

from THF/pentane affords I as light yellow flakes. Presence of THF in the crystals was confirmed by ^1H NMR spectroscopy. Complex I dissolves in THF and decomposes in dichloromethane. It decomposes rapidly in air, even as a solid, but has the advantage of being significantly easier to purify than lithium tetraphenylcyclopentadienide.[16] A reduced solvent volume may be used for reactions. The higher solubility of I, as compared to $C_5H_2Ph_4$, and the H_2 evolution on reaction provide a convenient indication for complete reaction. Use of I increases the yields of reactions as compared to the use of lithium tetraphenylcyclopentadienide (vida infra).

Octaphenylvanadocene, II, is obtained as olive green crystals in a preparation analogous of that of Köhler and Prössdorf[23] (eq 2 and 3). Crystalline octaphenyl-

$$4[VCl_3{\cdot}3THF] + 2Zn \xrightarrow[\Delta]{THF} [V_2Cl_3(THF)_6]_2[Zn_2Cl_6] \quad (2)$$

$$[V_2Cl_3(THF)_6]_2[Zn_2Cl_6] + 8K(C_5HPh_4) \xrightarrow[\Delta]{THF} 4(C_5HPh_4)_2V \quad (3)$$

Table VII. Selected Bond Angles (deg) for Octaphenylmetallocenes

	M				
	V	Cr	Fe[a]	Co	Ni
C(1)-M-C(2)	36.2 (2)	38.7 (2)	40.1 (1)	39.3 (2)	37.9 (5)
C(1)-M-C(3)	60.7 (2)	63.6 (2)	67.3 (1)	65.5 (2)	62.7 (5)
C(2)-M-C(3)	37.3 (1)	37.8 (2)	40.1 (1)	38.5 (2)	36.3 (4)
C(1)-M-C(4)	60.3 (1)	63.3 (2)	67.1 (1)	65.0 (2)	61.7 (4)
C(2)-M-C(4)	61.2 (1)	63.0 (2)	67.2 (1)	65.1 (1)	61.1 (3)
C(3)-M-C(4)	36.3 (1)	36.9 (2)	39.9 (1)	39.6 (2)	37.6 (3)
C(1)-M-C(5)	35.8 (1)	38.2 (2)	40.0 (1)	39.4 (1)	37.3 (3)
C(2)-M-C(5)	60.6 (1)	64.1 (2)	67.5 (1)	65.6 (2)	62.1 (4)
C(3)-M-C(5)	60.6 (2)	63.0 (2)	67.4 (1)	65.5 (2)	62.5 (4)
C(4)-M-C(5)	36.3 (2)	37.8 (2)	40.1 (1)	38.1 (2)	36.5 (4)
M-C(1)-H(1)	121 (2)	123 (3)	124 (2)	122 (2)	130 (5)
M-C(1)-C(2)	70.9 (3)	71.8 (3)	71.4 (2)	72.6 (3)	72.7 (7)
M-C(1)-C(5)	73.4 (2)	73.9 (3)	71.7 (2)	73.9 (2)	74.7 (7)
C(2)-C(1)-C(5)	109.5 (4)	109.2 (5)	110.0 (3)	109.8 (4)	108.4 (11)
M-C(2)-C(1)	72.9 (2)	69.4 (2)	68.4 (1)	68.1 (2)	69.4 (5)
M-C(2)-C(3)	70.9 (2)	72.8 (2)	70.1 (1)	71.0 (2)	73.8 (5)
C(1)-C(2)-C(3)	106.8 (3)	107.1 (4)	107.0 (2)	107.6 (3)	109.7 (9)
M-C(2)-C(26)	120.7 (2)	125.2 (3)	130.3 (2)	126.7 (3)	120.7 (6)
C(1)-C(2)-C(26)	123.6 (4)	123.2 (4)	124.3 (2)	123.8 (4)	122.4 (9)
C(3)-C(2)-C(26)	129.6 (4)	129.6 (5)	128.5 (3)	128.6 (4)	127.9 (10)
M-C(3)-C(2)	71.8 (2)	69.4 (3)	69.8 (1)	70.5 (2)	69.9 (6)
M-C(3)-C(4)	73.7 (2)	72.1 (3)	69.7 (1)	70.8 (2)	73.5 (6)
C(2)-C(3)-C(4)	108.6 (4)	108.6 (5)	107.7 (3)	107.4 (4)	106.8 (10)
M-C(3)-C(36)	124.8 (3)	129.9 (3)	134.1 (2)	131.7 (3)	129.5 (7)
C(2)-C(3)-C(36)	128.9 (3)	127.4 (4)	127.6 (2)	129.0 (3)	130.5 (8)
C(4)-C(3)-C(36)	122.3 (3)	123.6 (4)	123.9 (2)	122.9 (3)	121.9 (8)
M-C(4)-C(3)	70.0 (2)	70.9 (3)	70.4 (1)	69.6 (2)	68.9 (5)
M-C(4)-C(5)	72.8 (2)	70.6 (3)	70.3 (1)	71.6 (2)	69.1 (6)
C(3)-C(4)-C(5)	107.7 (3)	108.9 (4)	108.8 (2)	108.9 (3)	107.0 (8)
M-C(4)-C(46)	128.5 (2)	132.1 (3)	135.7 (2)	134.2 (2)	132.0 (6)
C(3)-C(4)-C(46)	123.5 (4)	123.0 (5)	121.5 (3)	121.4 (4)	122.8 (10)
C(5)-C(4)-C(46)	128.3 (4)	127.3 (5)	128.3 (3)	128.6 (4)	129.8 (9)
M-C(5)-C(1)	70.7 (3)	67.9 (3)	68.3 (2)	66.7 (2)	68.0 (7)
M-C(5)-C(4)	70.9 (3)	71.6 (3)	69.6 (2)	70.4 (3)	74.4 (7)
C(1)-C(5)-C(4)	107.4 (4)	106.2 (5)	106.5 (3)	106.1 (4)	107.9 (10)
M-C(5)-C(56)	125.8 (2)	125.9 (3)	129.8 (2)	128.4 (2)	126.5 (6)
C(1)-C(5)-C(56)	124.6 (4)	124.8 (5)	124.8 (3)	124.4 (4)	124.6 (11)
C(4)-C(5)-C(56)	128.0 (3)	129.1 (4)	128.6 (2)	129.6 (3)	127.3 (8)
C(2)-C(26)-C(21)	118.9 (2)	118.2 (3)	118.1 (2)	118.2 (2)	118.1 (5)
C(2)-C(26)-C(25)	121.1 (2)	121.7 (3)	121.8 (2)	121.8 (2)	121.9 (5)
C(3)-C(36)-C(31)	123.6 (2)	121.1 (2)	121.5 (1)	121.0 (2)	120.4 (4)
C(3)-C(36)-C(35)	116.4 (2)	118.9 (2)	118.4 (1)	119.0 (2)	119.6 (4)
C(4)-C(46)-C(41)	123.5 (2)	123.0 (2)	123.4 (1)	122.9 (2)	122.3 (4)
C(4)-C(46)-C(45)	116.5 (2)	117.0 (2)	116.6 (1)	117.1 (2)	117.7 (4)
C(5)-C(56)-C(51)	118.1 (2)	118.5 (2)	118.4 (1)	119.0 (2)	118.1 (5)
C(5)-C(56)-C(55)	121.8 (2)	121.5 (2)	121.4 (1)	120.9 (2)	121.8 (5)

[a] Reference 16.

vanadocene decomposes only after several minutes of air exposure. This contrasts with the behavior of vanadocene, which reacts instantly with air (often with deflagration). Solutions of II in THF, dichloromethane, and benzene turn brown rapidly on exposure to dry O_2 or when stirred over 1 equiv of PhIO, to yield a black insoluble powder. The reduced reactivity of II with oxygen led us to compare the relative reactivities of II and vanadocene.

Vanadocene and decamethylvanadocene bind several neutral donor molecules under mild conditions.[12,24–28] In contrast, II does not add CO (5.5 atm),[12,24] 2,2′-bipyridine,[25] or dimethyl acetylenedicarboxylate[26] even under forcing conditions. Several reagents that oxidize vanadocene and decamethylvanadocene, such as $V(CO)_6$,[29] AgCl,[30] PCl_3,[31] HCl,[32] and PhN_3[33] fail to oxidize II. Unlike vanadocene,[25] Na/Hg amalgam (or potassium–benzophenone ketyl) fails to reduce II. These results are surprising in light of the oxidation and reduction potentials of these complexes (vida infra). The steric bulk of the phenyl groups in II may prevent coordination or close approach of the oxidants and reductants necessary for electron transfer.

Metathesis of $CrCl_2$ with I in refluxing THF gives octaphenylchromocene, III, in 47% yield (eq 4).[23a,34,35] The

$$CrCl_2 + 2K(C_5HPh_4) \xrightarrow[\Delta]{THF} (C_5HPh_4)_2Cr + 2KCl \qquad (4)$$

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analogous reaction between $Cr_2(O_2CCH_3)_4$ and $Li[C_5HPh_4]$[11] gave the same product in yields reduced by 10–25%. Complex III has solubilities similar to II. Solutions of III react rapidly with the air, while the solid reacts more slowly. Like II, it is less reactive than its unsubstituted counterpart. Complex III does not bind CO (1 atm) in THF solution. Bis(cyclopentadienyl)chromium binds CO reversibly[36] at 22 °C with $K = 6.53$ atm^{-1}. While the ring exchange reaction between Cp_2Cr and $FeCl_2$ is rapid at room temperature,[34] no reaction occurs between III and $FeCl_2$ even after a 12 h reflux in THF. Octaphenylchromocene reacts cleanly with $AgPF_6$ to yield $[(C_5HPh_4)_2Cr]PF_6{\cdot}0.5CH_2Cl_2$ (IV), (75%) in dichloromethane solution.

The substituted manganocenes reported in the literature are generally prepared by the reaction between $MnCl_2$ and an alkali-metal salt of the appropriate cyclopentadienyl derivative.[34,37] Our attempts to prepare octaphenylmanganocene were unsuccessful (eq 5–8). A polymeric material was produced in all these reactions.

$$MnCl_2 + 2K(C_5HPh_4) \xrightarrow[\Delta]{THF} NR \tag{5}$$

$$Mn(O_3SCF_3)_2 + 2K(C_5HPh_4) \xrightarrow[\Delta]{THF} NR \tag{6}$$

$$MnCl_2 + 2MeLi \xrightarrow[2.\ 2C_5H_2Ph_4]{1.\ -78\ ^\circ C} NR \tag{7}$$

$$Mn(acac)_3 + 3Li(C_5HPh_4) \xrightarrow[\Delta]{THF} NR \tag{8}$$

Reaction of cobalt dibromide and I produces octaphenylcobaltocene, V, as dark purple crystals in 76% yield according to eq 9. Complex V exhibits solubilities lower than those of II or III. The analogous reaction with $Li(C_5HPh_4)$ proceeds in about 10% lower yield. Dichloromethane solutions of I decompose slowly, even at −15 °C, over several days. Reactions between V and other halomethanes (CH_2I_2 and $CHBr_3$) occur slower than corresponding reactions of cobaltocene.[38] While cobaltocene reacts immediately with O_2 at −78 °C,[39] dilute room-temperature solutions of V exhibit little decomposition after 30 min under an O_2 purge, and after 12 h, decomposition is only partially complete. Like cobaltocene, V reacts slowly with water.[34]

$$CoBr_2 + 2K(C_5HPh_4) \xrightarrow{THF} (C_5HPh_4)_2Co + 2KBr \tag{9}$$

Silver hexafluorophosphate readily oxidizes octaphenylcobaltocene to yield red, crystalline $[(C_5HPh_4)_2Co]PF_6$ (VI) in 82% yield. A ^1H NMR spectrum in CD_2Cl_2 displays resonances only in the aromatic region (6.8–7.5 ppm), which suggests the cyclopentadienyl proton overlaps the phenyl protons. Preparation of a deuteriated analogue with $K(C_5DPh_4)$ yields a species with a singlet at 6.9 ppm in the ^2H NMR spectrum, which supports this conclusion. This agrees with the observation that proton resonances in cobaltocinium cations tend to be shifted 1.5–2.0 ppm downfield from the corresponding ferrocene.[40]

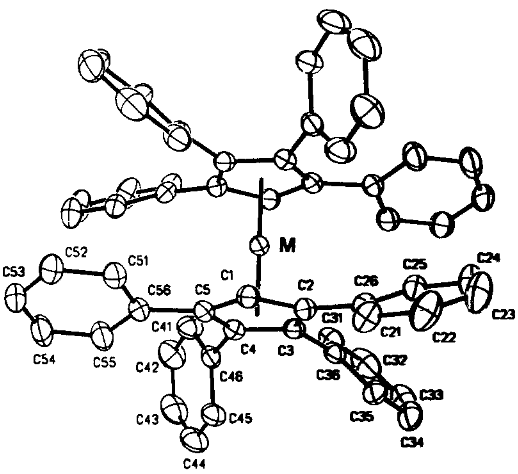

Figure 1. Thermal ellipsoid diagram and labeling scheme for the octaphenylmetallocenes (M = V, Cr, Co, Ni). The metal atom occupies a crystallographic center of symmetry.

Table VIII. Average M–C and C–C Bond Distances[a] in Metallocenes and Octaphenylmetallocenes

compd	⟨M–C⟩	⟨C–C⟩	ref
Cp_2V	2.245 (6)	1.377 (9)	41
$(C_5HPh_4)_2V$	2.268 (4)	1.416 (6)	this work
Cp_2Cr^b	2.169 (4)	1.431 (2)	42
$(C_5HPh_4)_2Cr$	2.197 (5)	1.408 (8)	this work
Cp_2Fe	2.033	1.389	43
$(C_5HPh_4)_2Fe$	2.094 (3)	1.429 (2)	16
Cp_2Co	2.096 (8)	1.41 (1)	44
$(C_5HPh_4)_2Co$	2.152 (4)	1.437 (6)	this work
Cp_2Ni	2.164 (7)	1.381 (10)	45
$(C_5HPh_4)_2Ni$	2.22 (1)	1.41 (1)	this work

[a] In Å. [b] Electron-diffraction data. Metallocene bond distances obtained from electron diffraction are generally slightly longer than those determined by X-ray diffraction.[46]

In a procedure analogous to that of Cordes,[21] hexaamminenickel(II) chloride and I react (eq 10) to form octaphenylnickelocene, VII, in 69% yield. Unlike nickelocene, long reaction times (70 h) are required to obtain VII in good yields. Attempts to prepare VII from $NiCl_2$ or $NiCl_2{\cdot}DME$ resulted in lower yields as did reactions using $Li(C_5HPh_4)$. Benzene, THF, and dichloromethane dissolve VII, and its solubility in these solvents appears higher than that of V or of octaphenylferrocene. Like nickelocene, it is moderately air-stable as a solid. Treatment of VII with 1 equiv of $AgPF_6$ in dichloromethane solvent yields $[Ni(C_5HPh_4)_2]PF_6{\cdot}0.5CH_2Cl_2$, in analytically pure form. The presence of dichloromethane in crystals of VII was confirmed by ^1H NMR spectroscopy of solutions of the crystals.

$$[Ni(NH_3)_6]Cl_2 + 2K(C_5HPh_4) \xrightarrow[\Delta]{THF} (C_5HPh_4)_2Ni + 2KCl \tag{10}$$

Molecular Structures. Crystal structures of the neutral octaphenylmetallocenes (compounds II, III, V, and VII) all are isomorphous to that of $(C_5HPh_4)_2Fe$ (Figure 1).[16] Each crystallizes as discrete, well-separated molecules with a staggered C_5 ring configuration on a crystallographic center of symmetry. Bond distances and angles for the octaphenylmetallocenes are reported in Tables VI and VII, respectively. The M–C bond distances show the expected trends, increasing (as compared to $(C_5HPh_4)_2Fe$) both on

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Table IX. Phenyl Ring Torsion Angles (deg)

Cp carbon	V	Cr	Fe[a]	Co	Ni	$C_5H_2Ph_4$[b]
2	30.7 (4)	31.9 (4)	33.0 (2)	32.6 (4)	31.8 (9)	32.5
3	46.6 (3)	46.9 (4)	47.5 (3)	46.0 (4)	46.2 (9)	69.0
4	69.2 (4)	69.9 (4)	77.1 (2)	71.1 (3)	64.8 (9)	−69.2
5	23.7 (4)	19.7 (4)	15.3 (2)	18.8 (4)	22.7 (9)	−22.8

[a] Reference 16. [b] Reference 47.

Table X. Deviations (in Å) of Phenyl Ipso Carbons from the Cyclopentadienyl Plane

ipso carbon	V	Cr	Fe	Co	Ni
C26	−0.006	0.086	0.133	0.110	0.038
C36	0.099	0.145	0.204	0.156	0.101
C46	0.160	0.172	0.248	0.219	0.188
C56	0.057	0.062	0.123	0.115	0.090

Table XI. Electrochemical Data[a] for First-Row Metallocene Complexes

complex	solv	1− → 0	0 → 1+	1+ → 2+	ref
Cp_2V	THF	2.95	−0.76	0.38[b,c]	48
$(C_5Me_5)_2V$	CH_3CN		*d*		11
$(C_5HPh_4)_2V$	THF		0.18[b]		this work
Cp_2Cr	CH_3CN	−2.51	−0.88		48
$(C_5Me_5)_2Cr$	CH_3CN		−1.35		11
$(C_5HPh_4)_2Cr$	THF	−2.13[e]	−0.77		this work
Cp_2Fe	THF		0.10		this work
$(C_5Me_5)_2Fe$	CH_2Cl_2		−0.45		16
$(C_5HPh_4)_2Fe$	CH_2Cl_2		0.13		16
Cp_2Co	CH_3CN	−2.09	−1.15		48, 49
$(C_5Me_5)_2Co$	CH_3CN		−1.78		11
$(C_5HPh_4)_2Co$	THF	−1.80	−0.90		this work
Cp_2Ni	CH_3CN	−1.87[b]	−0.30	0.53[c]	48
$(C_5Me_5)_2Ni$	CH_3CN		−0.96	0.00	11
$(C_5HPh_4)_2Ni$	THF	−1.67	−0.21	0.40	this work

[a] In V, vs. Ag|Ag$^+$ in 0.1 M $AgNO_3$. Ferrocene potentials reported in the literature references were used to place reported potentials on a common scale. [b] Irreversible. [c] Anodic peak potential. [d] No reversible one-electron waves observed. [e] Partly reversible.

removal of bonding electrons (M = V, Cr) and on addition of electrons to antibonding orbitals (M = Co, Ni). As the cyclopentadienyl rings move further from the metal, the steric effects of the phenyl groups on the M–C bond lengths decrease. Differences in the M–C bond lengths between the unsubstituted metallocenes and octaphenylmetallocenes decrease from 0.05 Å in M = Fe to 0.02 Å in M = V. Larger errors in the bond lengths of M = Co and Ni prevent a comparison for these compounds. The C–C bond distances are also longer in the octaphenylmetallocenes than in corresponding cyclopentadienylmetallocenes (Table VIII),[41–46] but these distances do not vary significantly within either system. Steric crowding of the phenyl groups and partial π-delocalization between the C_5 and C_6 rings should lead to expansion of cyclopentadienyl rings containing multiple phenyl substituents.

Variation of the M–C bond lengths also effects the torsion angles of the phenyl rings with the C_5 ring. The torsion angles (Table IX) of phenyl rings 2 and 3 do not change significantly between any of the complexes, whereas a large variation occurs for phenyl rings 4 and 5 (ca. 13° and 8°, respectively). As the M–C bond distance increases, crowding from phenyl groups attached to opposing C_5 rings should be reduced and the phenyl rings should relax toward an unperturbed arrangement (i.e., free $C_5HPh_4^-$). The crowding between phenyl rings on opposing cyclopentadienyls can be seen in the deviations of the phenyl ring ipso carbons from the least-squares plane of the cyclopentadienyl ring (Table X). The trends follow the variation in M–C distances in Table VIII. As the C_5 rings get closer, the phenyl groups bend away from one another to a greater extent. In $(C_5HPh_4)_2Fe$, with the shortest M–C bond distances, phenyl ring 4 is almost perpendicular (77°) to the C_5 ring and ring 5 is the most nearly coplanar (15°). In contrast, $(C_5HPh_4)_2V$ (with the longest M–C distances) has rings 4 and 5 at 69° and 23° angles about the C_5 ring, respectively. The torsion angles for phenyl rings 2, 4, and 5 of $(C_5HPh_4)_2V$ are the same as the absolute values of those for $C_5H_2Ph_4$[47] (Table IX). Phenyl rings 4 and 5 differ in the direction of twist in the two molecules because interactions between the two metal bound cyclopentadienyl rings cause the rings to mesh in a gear-like fashion.

Electrochemistry. Cyclic voltammograms of II, III, V, VII, and Cp_2Fe were obtained in THF solution with 0.25 M tetra-*n*-butylammonium perchlorate as supporting electrolyte. Oxidations and reductions for Cp_2M,[48,49] $(C_5Me_5)_2M$,[11] and $(C_5HPh_4)_2M$ complexes (M = V, Cr, Fe,[16] Co, and Ni) are listed in Table XI. In general, octaphenylmetallocenes have their redox couples shifted anodically by only 50–200 mV from the corresponding cyclopentadienylmetallocene couple. This is much reduced from the separation of corresponding decamethylmetallocene and metallocene couples (500–600 mV).[11] This observation may be explained by the similar Hammet coefficients of phenyl groups and protons.[16]

Unlike vanadocene, which exhibits a reversible one-electron oxidation,[48] complex II (like $(C_5Me_5)_2V$[11]) undergoes irreversible oxidations in both THF and CH_2Cl_2. No reduction was observed out to the solvent limit (ca. 2.4 V). The electrochemistry of complexes III and V resembles that of Cp_2Cr and Cp_2Co, respectively. Each exhibits a chemically reversible, one-electron oxidation and a one-electron reduction, although the reduction of III is only partly reversible. Unlike cobaltocene, which forms a stable anion,[49] attempts to reduce V with Mg or K led only to decomposition. Octaphenylnickelocene possesses a partly reversible reduction, a chemically reversible one-electron oxidation, and a second partly reversible oxidation. An attempt to isolate the dication by the oxidation of VII with 2 equiv of $AgPF_6$ in THF solvent was unsuccessful; the purple product decomposes within seconds of formation.

Magnetic Susceptibilities and EPR Spectra. As a 15-electron system vanadocene possesses an orbitally nondegenerate ground state ($^4A_{2g}$), which precludes first-order orbital contributions to the moment.[50] Thus va-

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Table XII. Magnetic Susceptibility Data for First-Row Metallocene Complexes[a]

complex	μ_{eff}, μ_B	Θ,[c] K	temp range, K	ref
Cp_2V	3.78 ± 0.19	−6.5	14–400	51, 52
$(C_5Me_5)_2V$	3.69 ± 0.1	0	5–64	11
$(C_5HPh_4)_2V$	3.74 ± 0.01	0	7–301	this work
Cp_2Cr	2.97 ± 0.03	0	13–300	57
	3.20	17	77–298	56, 61
$(C_5Me_5)_2Cr$	3.01 ± 0.1	0	6–81	11
$(C_5HPh_4)_2Cr$[d]	2.90 ± 0.04	−1	15–180	this work
Cp_2Co[e]	1.75 - 2.04		83–298	56
	1.44 - 1.73		7–298	57
$(C_5Me_5)_2Co$	1.45 ± 0.1	0	5–130	11
$(C_5HPh_4)_2Co$[d]	1.71 ± 0.02	0	7–160	this work
Cp_2Ni	2.89 ± 0.15	6.5	70–300	51, 60, 61
$(C_5Me_5)_2Ni$	2.93 ± 0.1	−15	6–100	11
$(C_5HPh_4)_2Ni$[d]	2.83 ± 0.03	3	50–300	this work

[a] Solid state. Due to the low solubilities of the complexes studied in this work, Evan's NMR method magnetic moment determinations were not possible. [b] $\mu_{\text{eff}} = 2.828\,(\chi_M T)^{1/2}$. [c] y intercept of the Curie–Weiss plot (χ_M^{-1} vs. T). [d] Measured on the linear part of the Curie–Weiss plot. [e] Substantial curvature is observed in the Curie–Weiss plot in this temperature region.

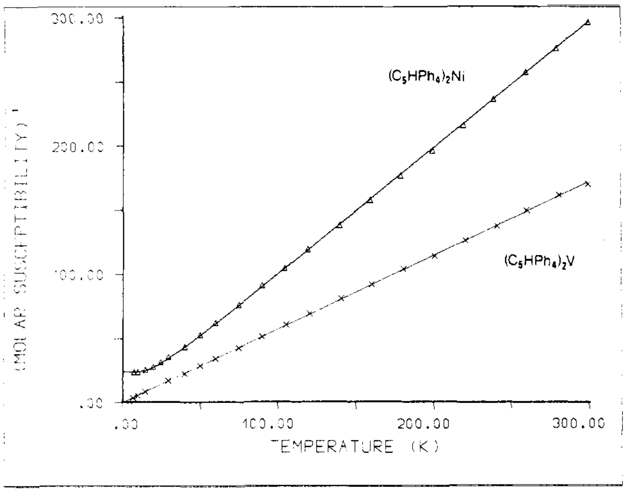

Figure 2. The Curie–Weiss plots for octaphenylvanadocene and octaphenylnickelocene. The line through the experimentally determined octaphenylnickelocene points was calculated from eq 12.

nadocenes are expected to obey the Curie law ($\chi_m^{-1} \propto T$) with magnetic moments close to the spin-only value (3.87 μ_B). Indeed, Cp_2V (3.78 μ_B)[51,52] and $(C_5Me_5)_2V$ (3.69 μ_B)[11] follow Curie–Weiss behavior with moments close to the spin-only value and Θ near or equal to zero. Octaphenylvanadocene (Table XII) also follows the Curie law over a wide temperature range (7–300 K, Figure 2) with a moment, 3.74 μ_B, close to the spin-only value and Θ = 0 K. This suggests that $(C_5HPh_4)_2V$ also occupies a $^4A_{2g}$ ground state.

Ligand field theory treatments of metallocenes assume axial symmetry to simplify the calculations,[50,53] and this assumption holds for cyclopentadienyl- and decamethylmetallocenes. Octaphenylmetallocenes possess low symmetry (C_i), and the assumption of axial symmetry should break down. In the EPR spectrum of $(C_5HPh_4)_2V$ in frozen THF at 77 K $g_\perp$ appears asymmetric; however, individual x and y components cannot be resolved. The g values ($g_\parallel$ = 1.996; $g_\perp^{\text{eff}}$ = 4.000) resemble those of Cp_2V[54,55] and $(C_5Me_5)_2V$ (Table XIII).[11] Note that $g_\perp^{\text{eff}}$ corresponds to a $\Delta m_s = 2$ transition and $g_\perp = g_\perp^{\text{eff}}/2$. The ^{51}V hyperfine couplings ($A_\parallel$, $A_\perp$) were well-resolved and similar to the values for Cp_2V and $(C_5Me_5)_2V$ (Table XIII).[56-61] Octaphenylvanadocene exhibited no EPR signals at room temperature in toluene solutions, consistent with a similar observation for Cp_2V.[54] The similar EPR data of these complexes supports the assignment of a $^4A_{2g}$ ground state to $(C_5HPh_4)_2V$.

Chromocene, a 16-electron system, should have an orbitally degenerate ground state. This leads to temperature-dependent magnetic moments, which ligand field theory predicts to be greater than the spin-only value. Orbital angular momentum is partly quenched by the static Jahn–Teller effect in orbitally degenerate molecules with D_{5d} pseudosymmetry.[56,61] Imposing a C_{2v} distortion on a D_{5d} molecule increases the distortion parameter, Δ, which breaks the orbital degeneracy. A second quenching effect arises from a smaller than expected orbital reduction parameter, k'. This parameter reflects electron delocalization from the metal d orbitals onto the ligand.[53] Measurements of the magnetic moment of Cp_2Cr as a function of temperature yielded two different values (2.97[57] and 3.20 μ_B[56,61]). While there is disagreement over the value of the moment, each follows Curie–Weiss behavior over wide temperature ranges. Both Gordon and Warren[56] and König et al.[57] conclude the ground state for chromocene is $^3E_{2g}$, and both claim to treat their data satisfactorily with ligand field theory. This assignment, which agrees with UV-photoelectron spectroscopic studies,[58] arises from the observed moment being much greater than the spin-only value (2.83 μ_B).

Octaphenylchromocene possesses low symmetry (C_i) that precludes orbital degeneracy. If the energy difference between the levels were much smaller than the Jahn–Teller splittings in the higher symmetry analogues, a second-order Jahn–Teller distortion could occur in $(C_5HPh_4)_2Cr$. If site splitting of the ground-state degeneracy is sufficiently large, the susceptibility will obey the Curie law. We find that $(C_5HPh_4)_2Cr$ follows Curie–Weiss behavior between 7 and 180 K with μ_{eff} = 2.90 μ_B and Θ = −1 K (Table XII). Above 180 K, the moment increases at a faster rate and the points curve below the Curie–Weiss line as predicted above. The degree of curvature, which is small, suggests that the C_i site symmetry in $(C_5HPh_4)_2Cr$ mimics the effect of the Jahn–Teller distortion in Cp_2Cr. As our measured moment is not much larger than the spin-only value, a conclusive assignment of the ground state ($^3E_{2g}$ or $^3A_{2g}$) cannot be made; however, in light of the results for Cp_2Cr[56,57] and $(C_5Me_5)_2Cr$[11] a $^3E_{2g}$ derived state seems more probable. No EPR spectrum was observed for $(C_5HPh_4)_2Cr$ in toluene at 77 K or 300 K, which resembles the behavior of Cp_2Cr[11] and $(C_5Me_5)_2Cr$.[11]

As discussed earlier for Cp_2V and $(C_5HPh_4)_2V$, $[(C_5HPh_4)_2Cr]PF_6$, another 15-electron complex, should

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Table XIII. EPR Data for First-Row Metallocenes

complex	host	temp, K	g_x or $g_\perp$	g_y	g_z	10^4A_x, cm^{-1}	10^4A_y, cm^{-1}	10^4A_z, cm^{-1}	ref
Cp_2V	methylcyclohexane	77	3.980/2		2.002	21.5 ($A_\perp$)		36.7	54
	Cp_2Mg	4	3.9764/2		2.0014	20.9		36.3	55
$(C_5Me_5)_2V$	toluene	19	3.973/2		2.001	16.0		24.0	11
$(C_5HPh_4)_2V$	THF	77	4.000/2		1.996	17.1		31.8	this work
Cp_2Cr^+	Cp_2Mg	4	3.954/2		2.002	*b*		*b*	55
$[(C_5Me_5)_2Cr]PF_6$	$(C_5Me_5)_2Mg$	17	4.01/2		1.99	*b*		*b*	11
$[(C_5HPh_4)_2Cr]PF_6$[a]	toluene/CH_2Cl_2 (1:2)	77	3.968/2	4.050/2	2.005	*b*	*b*	*b*	this work
Cp_2Co	2-MeTHF	4	1.81		1.69				55
$(C_5Me_5)_2Co$	toluene	14	2.0 (g_{iso})						11
	$(C_5Me_5)_2Fe$	9	1.693	1.733	1.754	<6[c]	111[c]	65[c]	11
$(C_5HPh_4)_2Co$[a]	toluene	77	1.999	2.095	1.884	33[c]	133[c]	82[c]	this work
Cp_2Ni^+	$[Cp_2Co]PF_6$	4	1.972	2.016	1.801				55
$[(C_5Me_5)_2Ni]PF_6$	$[(C_5Me_5)_2Co]PF_6$	8	1.973	2.014	1.831				11
$[(C_5HPh_4)_2Ni]PF_6$[a]	toluene/CH_2Cl_2 (1:2)	77	2.018	2.072	1.884				this work

[a] Solutions were prepared ca. 2 mM in complex. [b] Hyperfine couplings are not resolved. [c] Signs for these values uncertain.

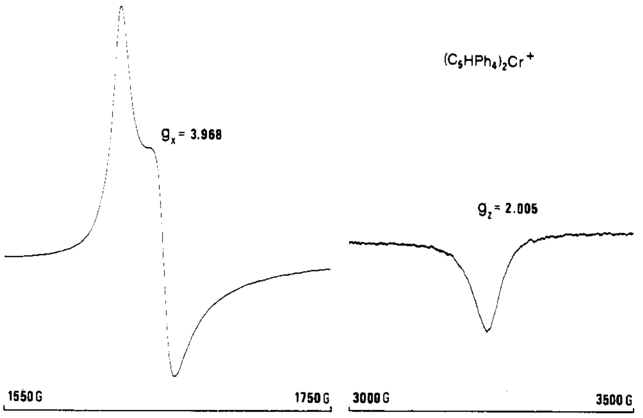

Figure 3. The EPR spectrum of octaphenylchromocinium hexafluorophosphate in a toluene/dichloromethane (1:2) glass at 77 K. The *y* scale for the *z* component is ca. 1/50 that of the *x* and *y* components.

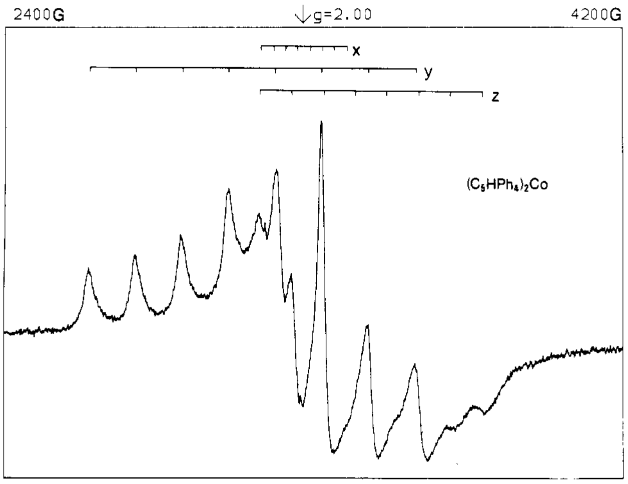

Figure 4. The EPR spectrum of octaphenylcobaltocene in a toluene glass at 77 K with the *g* and *A* positions shown.

exhibit an EPR spectrum similar to that of Cp_2Cr^+, except that $g_\perp$ should be split into g_x and g_y. The EPR spectrum of $[(C_5HPh_4)_2Cr]PF_6$ taken at 77 K in a toluene/dichloromethane glass (1:2) is displayed in Figure 3. In it the *x*, *y*, and *z* components appear clearly resolved. The values of $^1/_2(g_x^{\text{eff}} + g_y^{\text{eff}})$ (4.009) and $g_\parallel$ (2.005) resemble those of Cp_2Cr^+ and $(C_5Me_5)_2Cr^+$ (Table XIII). The *x* and *y* components are assigned by a comparison with the EPR spectrum[55] of Cp_2Ni^+. Again $g_{x,y} = g_{x,y}^{\text{eff}}/2$ for the $\Delta m_s = 2$ transitions. No ^{53}Cr hyperfine coupling is observed in the EPR spectra of $(C_5HPh_4)_2Cr^+$ or Cp_2Cr^+.[55] No room-temperature spectrum is observed for $[(C_5HPh_4)_2Cr]PF_6$.

Cobaltocene, a 19-electron system, possesses an orbitally degenerate ground state ($^2E_{1g}$). As such, it behaves like other orbitally degenerate systems such as Cp_2Cr (vida supra). As with Cp_2Cr, Gordon and Warren[56] and König et al.[57] report different magnetic moments for Cp_2Co, with the latter group reporting the lower moment in each case. Both groups observe marked curvature of their χ_m^{-1} vs. *T* plots. In contrast $(C_5Me_5)_2Co$[11] and $(C_5HPh_4)_2Co$ follow Curie–Weiss behavior over wide temperature ranges (Table XII), but display small deviations from linearity at higher temperatures. Octaphenylcobaltocene exhibits a magnetic moment (1.71 μ_B) equal to the spin-only value (1.73 μ_B). This suggests that the low symmetry of $(C_5HPh_4)_2M$ removes the degeneracy of the highest occupied orbital in these compounds, and the energy gap between the levels exceeds that induced by a Jahn–Teller distortion in Cp_2Co or Cp_2Cr.

In orbitally degenerate metallocene systems ligand field calculations show $g_\parallel$ and $g_\perp$ differ substantially from 2. The calculations predict $g_\perp = 0$, in which case no EPR spectrum should be obtained[50] (as observed for the chromocenes). Jahn–Teller distortions in Cp_2Co and $(C_5Me_5)_2Co$ partially quench orbital contributions to the magnetic moment and permit EPR signals to be observed with anisotropic *g* values that differ appreciably from 2 (Table XIII). The *g* values of $(C_5HPh_4)_2Co$ are closer to 2 than those of Cp_2Co and $(C_5Me_5)_2Co$. Since the distortion parameter increases as the *g* values approach 2, the distortion observed in $(C_5HPh_4)_2Co$ must be greater than the Jahn–Teller distortion arising in Cp_2Co or in $(C_5Me_5)_2Co$. The EPR spectrum of $(C_5HPh_4)_2Co$ in a frozen toluene solution at 77 K appears in Figure 4. Slow cooling of a second toluene solution of $(C_5HPh_4)_2Co$ to 78–80 K allowed the solution to achieve higher order than in a fast cooled glass. This produced an enhancement of the *x* components over the *y* and *z* components, which permitted the determination of g_x and A_x. The consistent ordering of the hyperfine coupling constants within each cobaltocene system[11,55] ($A_y > A_z > A_x$) permitted assignment of the *x*, *y*, and *z* components for $(C_5HPh_4)_2Co$.

Octaphenylnickelocene, a nondegenerate 20-electron system, should behave like Cp_2Ni and $(C_5Me_5)_2Ni$. Magnetic measurements show that Cp_2Ni follows Curie–Weiss behavior above 77 K but deviates from it at lower temperatures.[51b] Prins, van Voorst, and Schinkel proposed that a large zero-field splitting of the ground state accounts for this behavior and successfully fit their data to eq 11, where *D* is the zero-field splitting parameter and $g_\parallel$ is assumed to be 2.0023.[60] From their data, $g_\perp$ was determined to be 2.06 ± 0.10 and *D* was calculated to be 25.6 ± 3.0 cm^{-1}. Because of the large zero-field splitting the

$$\chi_m = \tfrac{2}{3}N\beta^2\left[\left(\frac{g_{\parallel}^2}{kT}\,\frac{\exp(-D/kT)}{1+2\exp(-D/kT)}\right)+\left(\frac{2g_{\perp}}{D}\,\frac{1-\exp(-D/kT)}{1+2\exp(-D/kT)}\right)\right] \quad (11)$$

ground state was assigned as $^3A_{2g}$. For $(C_5Me_5)_2Ni$[11] $g_{\perp} = 1.74$ and $D = 30.5 \pm 1.0$ cm^{-1}. When the value of $g_{\perp}$ (2.015) is employed, D is found to be 34.2 cm^{-1} for $(C_5HPh_4)_2Ni$, which is close to the values found for the other Ni compounds. Figure 2 contains a graph of the line calculated from eq 11, plotted with the data. Above 50 K $(C_5HPh_4)_2Ni$ follows Curie–Weiss behavior with $\mu_{eff} = 2.83$ μ_B; below 10 K χ_m becomes nearly independent of temperature. In accord with its large zero-field splitting, $(C_5HPh_4)_2Ni$ does not exhibit an EPR signal in toluene at either 300 or 77 K. This is also found for Cp_2Ni[59] and $(C_5Me_5)_2Ni$.[11]

The nickelocinium cation is isoelectronic with cobaltocene ($^2E_{1g}$ ground state). Therefore the EPR spectrum should be anisotropic, and the proximity of the g value to 2 depends on the amount of Jahn–Teller distortion. The EPR spectra of Cp_2Ni^+, $(C_5Me_5)_2Ni^+$, and $(C_5HPh_4)_2Ni^+$ all exhibit rhombic $\mathbf{g}$ tensors with components close to 2. This suggests a greater degree of Jahn–Teller distortion in nickelocinium cations than in cobaltocenes.[55] No room-temperature EPR spectra are observed for any of the nickelocinium cations.

Conclusions. Octaphenylmetallocenes of most first-row transition metals are prepared in high yield by metathical procedures with use of $K(C_5HPh_4)$. All are crystalline solids, and this allows a systematic comparison of molecular structures as the d-electron count varies. Octaphenylferrocene possesses the shortest metal–carbon bonds, where ring–ring interactions seem important. For electron-rich (Co, Ni) or electron-deficient (V, Cr) analogues the metal–carbon bonds lengthen, consistent with molecular orbital schemes proposed for the parent metallocenes.[50,62] These bonds appear longer than in the parent cyclopentadienyl metallocenes for all metals studied. This suggests that even in $(C_5HPh_4)_2V$ the phenyl groups on one C_5 ring exert a steric influence on those of the other C_5 ring. As the metal–ring distance increases, the conformation adopted by the C_5HPh_4 ring increasingly resembles that found for the neutral free ligand and the deviation of the ipso carbon atoms of the phenyl rings from the cyclopentadienyl plane decreases.

Steric bulk of the phenyl substituents profoundly alters reactivity of octaphenylmetallocenes as compared to their cyclopentadienyl or pentamethylcyclopentadienyl analogues. Octaphenylmetallocenes exhibit great resistance toward ligand addition and formation of a bent metallocene derivative. The hindered environment of the metal center even slows redox processes. Redox potential and magnetic measurements for a series of bis(tetraphenylcyclopentadienyl) complexes of first-row transition metals show the ligand tetraphenylcyclopentadienide to be electronically similar to cyclopentadienide. This suggests that tetraphenylcyclopentadiene may be used as a bulky substitute for cyclopentadiene as a ligand without altering the electronic properties of the metal complex. In addition, the products formed with this ligand crystallize well because of the phenyl substituents.

Acknowledgment. This material is based on work supported by the National Science Foundation (CHE-8504088 to W.C.T.). Funds supporting the purchase of the University of Delaware diffractometer were provided by NSF, and W.C.T. thanks the Alfred P. Sloan Foundation for a research fellowship. We thank Dr. J. Manrique and the Revlon, Materials Research Center, San Diego, CA, for providing some variable-temperature equipment used in the EPR studies.

Registry No. I, 58081-04-2; II, 109086-40-0; III, 109086-41-1; IV, 109086-43-3; V, 109086-44-4; VI, 109086-46-6; VII, 109086-47-7; VIII, 109086-49-9; $C_5H_2Ph_4$, 15570-45-3; VCl_3, 7718-98-1; $CrCl_2$, 10049-05-5; $CoBr_2$, 7789-43-7; $[Ni(NH_3)_6]Cl_2$, 10534-88-0; $(C_5H_5)_2Fe$, 102-54-5.

Supplementary Material Available: For $V(C_5HPh_4)_2$, $Cr(C_5HPh_4)_2$, $Co(C_5HPh_4)_2$, and $Ni(C_5HPh_4)_2$, respectively, as follows: thermal ellipsoid plots 1S–4S, Tables 5S–8S, anisotropic thermal parameters, Tables 9S–12S, hydrogen atom coordinates, and Tables 17S–20S, least-squares planes (16 pages); Tables 13S–16S, observed and calculated structure factors (50 pages). Ordering information is given on any current masthead page.

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