

Halogen Oxidation Reactions of $(C_5Ph_5)Cr(CO)_3$ and Lewis Base Addition to $[(C_5Ph_5)Cr(\mu-X)X]_2$: Electrochemical, Magnetic, and Raman Spectroscopic Characterization of $[(C_5Ph_5)CrX_2]_2$ and $(C_5Ph_5)CrX_2(THF)$ ($X = Cl, Br, I$) and X-ray Crystal Structure of $[(C_5Ph_5)Cr(\mu-Cl)Cl]_2$

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The 17-electron complex $(C_5Ph_5)Cr(CO)_3$ reacts with halogens ($C_6H_5I \cdot Cl_2$, Br_2 , and I_2) in C_6H_6 to yield the dimeric oxidation products $[(C_5Ph_5)Cr(\mu-X)X]_2$ as thermally stable solids. Reactions with other chlorinating agents similarly yield $[(C_5Ph_5)CrCl_2]_2$. An X-ray crystal structure of $[(C_5Ph_5)Cr(\mu-Cl)Cl]_2$ was obtained. The magnetic properties of the Cl_2 -bridged dimer have been determined and modeled using the usual isotropic Hamiltonian $H = -2J\hat{S}_1 \cdot \hat{S}_2$, which yields $J/k = -30$ K. Low-temperature (77 K) Raman spectra of solid $[(C_5Ph_5)CrX_2]_2$ ($X = Cl, I$) allow assignments to be made for the metal-ring and metal halogen stretching modes in the low-frequency region (<600 cm^{-1}). Tetrahydrofuran (THF) cleaves these dimers to yield complexes of the form $(C_5Ph_5)CrX_2(THF)$.

Introduction

Over the past two decades, the study of paramagnetic organometallic complexes has greatly expanded.¹ These complexes are generally highly reactive, and many have been postulated as reaction intermediates. In particular, the $(\eta^5-C_5R_5)Cr(CO)_3$ ($R = H, Me, Ph$) family of complexes recently has received much attention. The $R = H$ and Me complexes both exist in equilibria between 17e monomers and 18e dimers in solution and as dimers in the solid state,² while for $R = Ph$ the complex exists solely as a 17e monomer both in solution and in the solid state.³

The isolation of $(C_5Ph_5)Cr(CO)_3$ allowed comparison of predicted and actual structural parameters, as well

as a comparison of the physical properties of the three radical species $(C_5R_5)Cr(CO)_3$ ($R = H, Me, Ph$). In many ways the physical properties of these species are similar; however in some notable ways (e.g., reduction potentials) they differ significantly. A question that naturally follows such an examination is how the large size and electron-withdrawing capabilities of the pentaphenyl-

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cyclopentadienyl ligand affect the reactivity of complexes incorporating it.

Previous work has shown that reaction of the $[(C_5R_5)Cr(CO)_3]_2$ ($R = H$ (Cp),⁴ Me (Cp*)⁵) dimers with halogens yields complexes of the form $(C_5R_5)Cr(CO)_3X$ ($X = Cl, Br, I$). Likewise, Baird^{5–8} and co-workers have shown that alkyl and allyl halides also produce $(C_5R_5)Cr(CO)_3X$ complexes. Herrmann and co-workers found that reacting excess chlorine or bromine with $[(C_5H_5)Cr(CO)_3]_2$ in acetonitrile yielded the complexes $CpCrX_2(CH_3CN)$ ($X = Cl, Br$).⁹ Theopold and co-workers have prepared $[Cp^*Cr(\mu-X)X]_2$ by direct reaction of $LiCp^*$ with $CrCl_3 \cdot 3THF$,¹⁰ while several other methods have been reported by other groups.^{11–15}

Interestingly, Fischer reports that allyl bromides convert $[CpCr(CO)_3]_2$ to $[CpCrBr_2]_2$ at elevated temperatures,¹⁴ while Baird reports that alkyl and benzyl bromides react with $[CpCr(CO)_3]_2$ to yield $CpCr(CO)_3Br$ at or below ambient temperatures.⁷ The two most reasonable pathways for $[CpCrX_2]_2$ formation are $CpCr(CO)_3X$ compounds decomposing or further reaction with RX . Although all known $(C_5R_5)Cr(CO)_3X$ complexes decompose slowly both in solution and in the solid state, to our knowledge no determination of the decomposition products has been reported. Herein, we report the synthesis and characterization of $(C_5Ph_5)Cr(CO)_3X$ and $[(C_5Ph_5)Cr(\mu-X)X]_2$ ($X = Cl, Br, I$) compounds by a variety of pathways and show the halide-bridged dimer results from the decomposition of the tricarbonyl halide in both solution and the solid state.

Experimental Section

General Data. All reactions of air- and moisture-sensitive materials were performed under a nitrogen atmosphere employing standard Schlenk techniques unless otherwise stated. Solids were manipulated under argon in a Vacuum Atmospheres glovebox equipped with a HE-493 dri-train. Solvents (Fisher) were distilled from the appropriate drying agent under nitrogen: toluene, hexane (sodium/benzophenone), benzene, tetrahydrofuran (THF) (potassium/benzophenone), carbon tetrachloride, chloroform, and dichloromethane (CaH_2). $(C_5Ph_5)Cr(CO)_3 \cdot C_6H_6$ ³ and $CrCl_3 \cdot 3THF$ ¹⁶ were prepared according to literature procedures. NMR solvents were vacuum distilled from CaH_2 and placed under a nitrogen atmosphere. $C_6H_5I \cdot Cl_2$ was prepared following a literature procedure,¹⁷ and I_2 was sublimed prior to use. Br_2 (Fisher), $SOCl_2$ (Acros), PCl_3

(Mallinckrodt), and all other materials (Fisher) were used as received without further purification. Elemental analyses were performed by Mikroanalytisches Labor Pascher, Remagen, Germany.¹⁸

Electrochemistry. Cyclic voltammetry was performed with EG&G equipment (175 programmer and 173 potentiostat) as previously described¹⁹ at a Pt electrode on 10^{-3} M substrate solutions in dichloromethane and THF using tetrabutylammonium hexafluorophosphate as the supporting electrolyte. Scan rates were generally $0.1 V s^{-1}$. Data were stored on a Nicolet 3091 digital oscilloscope and transferred to a PC. Simulations were done with a Windows adaptation of the Gosser program.²⁰ The potential scale is versus aqueous SCE, which is converted to the ferrocene scale by subtracting 0.40 V from the figures given.

Raman Spectroscopy. Raman spectra were obtained using a Coherent Innova 90-6 Ar^+ ion laser by collecting backscattered photons directly from the surface of a KCl-supported pellet held under vacuum in a liquid- N_2 dewar.²¹ The radiation used was 514.5 nm. Laser power was varied from 150 to 400 mW. Under these conditions, no decomposition of the samples was observed. A Spex 1403 double monochromator equipped with a pair of 1800 grooves/mm holographic gratings and a Hamamatsu 928 photomultiplier detector was used to record the spectra under the control of a Spex DM3000 microcomputer system, as described in detail elsewhere.²² Multiple scans (15–20) were averaged to improve the signal-to-noise ratio. Each scan was obtained with 6–8 cm^{-1} slit widths at $1 cm^{-1}/s$ intervals. Manipulation of Raman data was performed using LabCalc software (Galactic Industries, Inc.).

Magnetic Susceptibility. Magnetization versus temperature data were obtained on a Quantum Design MPMS 5T or 7T SQUID magnetometer in 1000 G applied field. Samples were loaded between two cotton plugs in gelatin capsules or in glass holders as previously described.²³ Diamagnetic corrections for the samples were calculated from Pascal's constants. The corrections for the holders were calculated from the measured average gram susceptibility of several nominally identical holders.

X-ray Structural Determination. Crystallographic data for $[(C_5Ph_5)Cr(\mu-Cl)Cl]_2 \cdot 2CH_2Cl_2$ are collected in Table 1. Dark green block crystals were photographically characterized and determined to belong to the triclinic crystal system. The centrosymmetric space group alternative was initially chosen by its frequency of occurrence and the distribution of E values; the choice was confirmed by subsequent refinement behavior. An empirical correction for absorption was applied to the data. The structure was solved by direct methods, completed from difference Fourier maps, and refined with anisotropic thermal parameters for all nonhydrogen atoms. Hydrogen atoms were placed in idealized positions, except for the disordered (two positions, 70/30 distribution) solvent molecule (CH_2Cl_2). All computations used SHELXTL (4.2) software (G. Sheldrick, Siemens XRD, Madison, WI).

$[(C_5Ph_5)Cr(\mu-Cl)Cl]_2$ (1). Method 1. $(C_5Ph_5)Cr(CO)_3$ (1.00 g, 1.72 mmol) was dissolved in benzene (50 mL) and then transferred via cannula to a separate flask containing $C_6H_5I \cdot$

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Table 1. Crystal and Refinement Data for [(C₅Ph₅)Cr(μ-Cl)Cl]₂·2CH₂Cl₂

a. Crystal Data	
formula	C ₇₂ H ₅₄ Cl ₈ Cr ₂
fw	1306.8
cryst syst	triclinic
space group	P1
a, Å	12.072(6)
b, Å	12.290(6)
c, Å	12.638(6)
α, deg	67.23(4)
β, deg	65.28(4)
γ, deg	75.99(2)
V, Å ³	1565(5)
Z	1
color	dark green
cryst size, mm	0.42 × 0.44 × 0.48
D(calcd), g/cm ³	1.362
abs coeff, mm ⁻¹	0.732
b. Data Collection	
diffractometer	Siemens P3m/V
radiation	Mo Kα (λ = 0.710 73 Å)
temp, K	296
2θ scan range, deg	4.0–48.0
scan type	Wycoff
no. of reflns colld	5191
no. of obsd rflns	2868 (F > 5.0σ(F))
c. Solution and Refinement	
solution	direct methods
refinement method	full-matrix least-squares
quantity minimized	Σ w(F _o - F _c) ²
weighting scheme	w ⁻¹ = σ ² (F) + 0.0010F ²
no. of params refined	311
final R indices (obsd data), %	R = 6.73, wR = 8.25
R indices (all data), %	R = 11.19, wR = 9.32
GOF	1.58
data-to-param ratio	9.2:1
largest diff peak, e Å ⁻³	0.75
largest diff hole, e Å ⁻³	-0.61

Cl₂ (0.53 g, 2.02 mmol). The stirred solution immediately turned yellowish brown, then quickly to olive green with gas evolution. After stirring overnight, a green solid precipitated. The mixture was filtered via cannula and the solid dried in vacuo to yield 0.86 g (0.75 mmol, 88%) of **1** as an olive green powder. Crystals were grown by dissolving (C₅Ph₅)CrCl₂(THF) (vide infra) in CH₂Cl₂ and layering with a 1:1 mixture of Me₃-SiCl/hexane. Mp: 335 °C (dec). Anal. Calcd for C₇₀H₅₀Cl₄Cr₂: C, 73.95; H, 4.43. Found: C, 73.55; H, 4.38.

Method 2. Na[C₅Ph₅] (2.50 g, 5.34 mmol) and CrCl₃·3THF (2.00 g, 5.34 mmol) were combined in dry benzene (80 mL) to give a dark olive green colored solution. The mixture was refluxed overnight, cooled to room temperature, and filtered via cannula. The resulting solid was dried in vacuo to yield 2.13 g (1.87 mmol, 70%) of **1** as an olive green powder. The identity of the product in this reaction (and that in method 3) was confirmed by comparison of its IR spectrum (KBr pellet) with that of a sample generated by method 1.

Method 3. (C₅Ph₅)Cr(CO)₃ was dissolved in chloroform to give a blue solution. This reaction mixture was stirred overnight. Stirring was stopped, and the suspended **1** was allowed to settle out.

[(C₅Ph₅)Cr(μ-Br)Br]₂ (2). Bromine (0.082 mL, 3.18 mmol) was added to a stirred solution of (C₅Ph₅)Cr(CO)₃ (1.00 g, 1.72 mmol) in benzene (30 mL). The resulting reddish-brown solution changed to a dark olive green in ca. 10 min. Stirring was stopped and a dark olive green solid precipitated. The mixture was filtered via cannula, and the resulting solid was dried in vacuo to yield **2** (0.99 g, 87%) as an olive green powder. Visible (CH₂Cl₂): λ_{max} 410 (sh), 480 (sh), 655. Mp: 330–333 °C (dec). Anal. Calcd for C₇₀H₅₀Br₄Cr₂: C, 63.95; H, 3.83. Found: C, 64.00; H, 3.82.

[(C₅Ph₅)Cr(μ-I)I]₂ (3). I₂ (0.38 g, 3.0 mmol) was dissolved in benzene (50 mL) and transferred via cannula to a flask

containing (C₅Ph₅)Cr(CO)₃ (1.00 g, 1.72 mmol). The mixture was refluxed overnight, cooled to room temperature, and filtered via cannula. The solid was then dried in vacuo to yield **3** as a dark green powder (0.75 g, 58%). Mp: 335 °C (dec).¹⁸

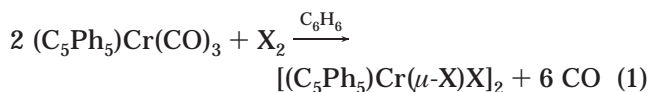
(C₅Ph₅)CrCl₂(THF) (4). [(C₅Ph₅)Cr(μ-Cl)Cl]₂ (0.25 g, 0.22 mmol) was dissolved in THF (25 mL). After filtering via cannula, the solvent was removed in vacuo to yield the product as an olive green powder in near quantitative yield. Microcrystalline samples may be obtained by layering a THF solution of **4** with hexane. Anal. Calcd for C₃₉H₃₃Cl₂CrO: C, 73.12; H, 5.19. Found: C, 72.56; H, 6.32.

(C₅Ph₅)CrBr₂(THF) (5) and (C₅Ph₅)CrI₂(THF) (6). These compounds are prepared in an analogous fashion to **4**. Anal. Calcd for C₃₉H₃₃Br₂CrO: C, 64.21; H, 4.56. Found: C, 64.27; H, 4.98.¹⁸

(C₅Ph₅)Cr(CO)₃Br (7). (C₅Ph₅)Cr(CO)₃ (0.50 g, 0.86 mmol) was dissolved in CH₂Cl₂ (30 mL) and cooled to -90 °C using a liquid nitrogen/acetone bath. Adding bromine (0.041 mL, 1.59 mmol) immediately caused the solution to change from dark blue to dark reddish-brown. This solution was filtered into a second flask and mixed with cold hexane (40 mL). This solution was transferred to a -50 °C freezer overnight to yield **7** (0.31 g, 55%) as a thermally sensitive, reddish-brown powder.

Results and Discussion

Syntheses. Reaction of the (C₅Ph₅)Cr(CO)₃ radical with C₆H₅I·Cl₂, Br₂, or I₂ yielded olive green complexes of the form [(C₅Ph₅)Cr(μ-X)X]₂ (X = Cl (**1**), Br (**2**), I (**3**)) in high yields (eq 1).



Complex **1** can also be prepared from the reaction of CrCl₃·3THF and Na(C₅Ph₅) in refluxing benzene or from the reaction of CHCl₃, CCl₄, SOCl₂, or PCl₃ with (C₅Ph₅)Cr(CO)₃. All three complexes are poorly soluble in noncoordinating solvents, although solubility increases in the order **1** < **2** < **3**. Crystalline materials are produced by layering a solution of the appropriate Me₃-SiX in hexane above a solution of a dichloromethane solution of the THF adduct (vide infra).²⁴

Dissolving these complexes in THF results in their cleavage to monomeric species, (C₅Ph₅)CrX₂(THF) (eq 2). All solids of these monomers are very similar in color



to their parent dimers, but form blue-green solutions. They are much more soluble than their parent dimers.

Initial reaction of (C₅Ph₅)Cr(CO)₃ and each halogen results in formation of the expected 18-electron (C₅Ph₅)Cr(CO)₃X, which then further reacts with additional halogen to yield [(C₅Ph₅)CrX₂]₂. At ambient temperature, solutions of (C₅Ph₅)Cr(CO)₃I decompose over a period of days to **3**, those of (C₅Ph₅)Cr(CO)₃Br, **7**, decompose to **2** in less than 10 min, and those of (C₅Ph₅)Cr(CO)₃Cl decompose in seconds to **1**. CO stretching frequencies for (C₅Ph₅)Cr(CO)₃X (X = Br, I) are collected in Table 4. Attempts to isolate (C₅Ph₅)Cr(CO)₃I at room temperature always resulted in substantial conversion to [(C₅Ph₅)CrI₂]₂. Solutions of (C₅Ph₅)Cr(CO)₃Br pre-

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Table 2. Selected Bond Distances (Å) in $[(C_5Ph_5)Cr(\mu-Cl)Cl]_2 \cdot 2CH_2Cl_2$

	$[(C_5Ph_5)Cr(\mu-Cl)Cl]_2^a$	$[(C_5H_5)Cr(\mu-Cl)Cl]_2^b$	$[(C_5Me_5)Cr(\mu-Cl)Cl]_2^c$
Cr–C(1)	2.270(5)		
Cr–C(2)	2.285(5)		
Cr–C(3)	2.266(6)		
Cr–C(4)	2.240(7)		
Cr–C(5)	2.242(7)		
Cr–CNT ^d	1.911	1.867	1.88
Cr–Cl(1)	2.247(3)	2.274(2)	2.291(2)
Cr–Cl(2)	2.380(3)	2.377(1)	2.393(1)
Cr–Cl(2A)	2.360(3)	2.374(1)	2.383(1)
Cr(A)–Cl(2)	2.360(3)		
Cr–Cr	3.375	3.362(1)	

^a This work. ^b Ref 11. ^c Ref 12. There were two conformers in the unit cell. Averaged values are presented. ^d CNT = centroid of the cyclopentadienyl ring.

Table 3. Selected Bond Angles (deg) in $[(C_5Ph_5)Cr(\mu-Cl)Cl]_2 \cdot 2CH_2Cl_2$

	$[(C_5Ph_5)Cr(\mu-Cl)Cl]_2^a$	$[(C_5H_5)Cr(\mu-Cl)Cl]_2^b$	$[(C_5Me_5)Cr(\mu-Cl)Cl]_2^c$
Cl(1)–Cr–Cl(2)	92.2 (1)	96.12 (6)	97.0 (1)
Cl(1)–Cr–Cr(2A)	92.2 (1)		96.5 (1)
Cl(2)–Cr–Cl(2A)	89.2 (1)	89.89 (5)	87.7 (1)
Cr–Cl(2)–Cr(A)	92.2 (1)		92.3 (1)
CNT–Cr–Cl(1)	124.4	123.6	123.2
CNT–Cr–Cl(2) ^d	124.6	121.8	122.0
CNT–Cr–Cl(2A) ^d	124.2	120.5	122.4

^a This work. ^b Ref 11. ^c Ref 12. There were two conformers in the unit cell. Averaged values are presented. ^d CNT = centroid of the cyclopentadienyl ring.

Table 4. Infrared Spectral Data for $(C_5Ph_5)Cr(CO)_3X$ Complexes

complex	solvent	$\nu(C\equiv O)$, cm^{-1}	reference
$(C_5H_5)Cr(CO)_3Br$	CS ₂	2041, 1986, 1954	15
$(C_5Me_5)Cr(CO)_3Br$	hexane	2032, 1979, 1935	5
$(C_5Ph_5)Cr(CO)_3Br^a$	THF	2031, 1980, 1939	this work
$(C_5H_5)Cr(CO)_3I$	CS ₂	2029, 1975, 1953	15
$(C_5Me_5)Cr(CO)_3I$	hexane	2018, 1967, 1934	5
$(C_5Ph_5)Cr(CO)_3I$	THF	2016, 1965, 1937	this work

^a A cold solution of $(C_5Ph_5)Cr(CO)_3Br$ was rapidly transferred to an IR cell at ambient temperature, and the spectrum was immediately taken.

pared and stored below -30 °C are sufficiently stable that **7** may be isolated as a thermally sensitive, red-brown solid. On standing for several weeks at ambient temperature, this solid converts to $(C_5Ph_5)Cr(CO)_3$ and **2**, presumably via a solid-state disproportionation reaction.

The other known $(C_5R_5)Cr(CO)_3X$ ($R = H, Me$) compounds also exhibit poor stability. King²⁵ and Baird²⁶ report that $CpCr(CO)_3Cl$ is quite unstable. Likewise, although $Cp^*Cr(CO)_3X$ ($X = Br, I$) can be isolated, they decompose slowly in the solid state.⁵ Despite being sufficiently stable to isolate, Manning found $CpCr(CO)_3Br$ and $CpCr(CO)_3I$ decompose on gentle heating (76 and 91 °C, respectively),¹⁵ while King found them too unstable to isolate pure.²⁵ No decomposition product was identified for any of these compounds. In all cases, the $(C_5Ph_5)Cr(CO)_3X$ compounds are less stable than either their Cp or Cp* analogues. Finally, cyclic voltammetric studies of $[CpCr(CO)_3]_2$ suggest that under appropriate conditions the very unstable $CpCr(CO)_3L^+$ ($L = THF, CH_2Cl_2$) ion forms, although it was not directly observed.²⁷

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The C_5Ph_5 ligand probably decreases the stability of the $(C_5Ph_5)Cr(CO)_3X$ complexes relative to their Cp and Cp* analogues because its large size increases crowding and because it releases far less electron density to the metal than either Cp or Cp*.^{3,28} Furthermore seven-coordinate first-row transition metal complexes are uncommon because of the small size of the metal atoms/ions.²⁹

The aforementioned reports on $(C_5R_5)Cr(CO)_3X$ ($X = halide$), coupled to reports on the thermal stabilities of $X = H$ ³⁰ and the $[(C_5R_5)Cr(CO)_3]_2$ dimers,^{2b,e} suggest that the crowding associated with the seven-coordinate geometry significantly reduces the stabilities of these molecules to a point of marginal viability. However, if only steric factors affected complex stability, the order of stability would be $Cl > Br > I$. The actual ordering is $I > Br > Cl$ for both $R = H$ and Ph, consistent with electronic factors also playing an important role. A reasonable explanation for this observation posits that as the halogens become more electronegative, the complexes more readily decompose because of decreased electron density available for π -back-bonding to the CO ligands.

Molecular Structure of $[(C_5Ph_5)Cr(\mu-Cl)Cl]_2 \cdot 2CH_2Cl_2$. The X-ray crystal structure of $[(C_5Ph_5)Cr(\mu-Cl)Cl]_2 \cdot 2CH_2Cl_2$ is displayed in Figure 1. Bond distances and angles are listed in Tables 2 and 3, respectively. The geometry is that of an edge-shared biotetrahedron with C_5Ph_5 ligands capping opposite faces and bridging

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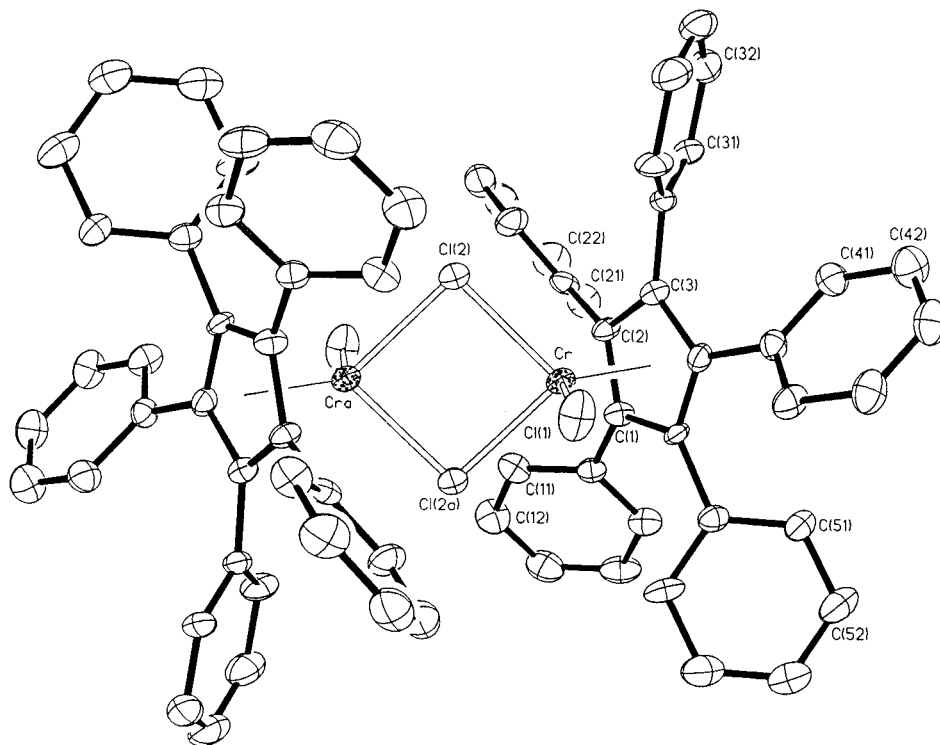


Figure 1. Molecular structure and labeling scheme for $[(C_5Ph_5)Cr(\mu-Cl)Cl]_2 \cdot 2CH_2Cl_2$ (**1**) (30% thermal ellipsoid probability).

chloride ligands occupying the shared edge. As in $[(C_5H_5)CrCl_2]_2$ ¹¹ and $[(C_5Me_5)CrCl_2]_2$,¹² the chromium atoms and bridging chlorines in **1** form a square in the center of the complex. The chromium atoms lie too far apart to bond, and their separation is nearly identical in the C_5H_5 and C_5Ph_5 complexes. Bond distances differ only slightly from those in the C_5H_5 and C_5Me_5 complexes. Most bond angles differ between these complexes by 0–3°; however, the Cl(bridging)–Cr–Cl(terminal) angles on **1** are 4–5° smaller than those on the other complexes. Inspection of a space-filling model of **1** generated from the crystal structure shows close contacts between the terminal chlorine atoms and phenyl rings bound to the Cp on the same chromium atom. These contacts may cause the contraction of the Cr–Cr–Cl bond angle.

Electrochemistry. The electrochemistry of complexes **2–6** was investigated by cyclic voltammetry in THF and dichloromethane. $[(C_5Ph_5)CrCl_2]_2$ did not give informative electrochemistry in any solvent. Reduction occurs outside the solvent/electrolyte window, and the observed rather positive, irreversible oxidation probably arises from bound chloride.

$[(C_5Ph_5)CrBr_2]_2$ exhibits a quasi-reversible reduction at -0.45 V in dichloromethane. Incomplete electrochemical reversibility does not allow the number of transferred electrons to be determined from the peak separation. The THF complex, $(C_5Ph_5)CrBr_2(THF)$, displays two successive reductions in the same solvent: the first one reversible and the second irreversible at about -0.5 and -1.4 V, respectively. This pattern more clearly develops after the solution has been kept at ambient temperature for about 30 min prior to data collection. Since the first reduction is very close to the one found for the dimeric complex and much different from the reduction pattern of the mononuclear complex in THF (vide infra), we suggest complex **5** reverts to dimeric

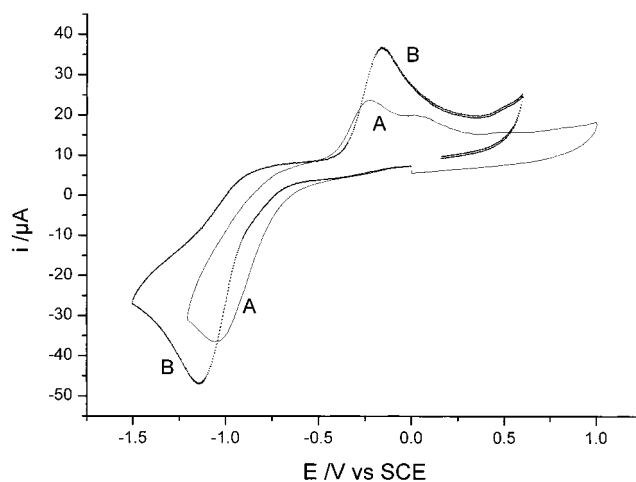


Figure 2. Cyclic voltammograms of $(C_5Ph_5)CrBr_2(THF)$: (A) in THF at $v = 100$ mV/s, (B) same after addition of $[PPh_3Me]Br$.

complex **2** in dichloromethane. The observation of two successive reduction peaks then argues for stepwise reduction of each Cr(III) to Cr(II) with concomitant loss of bromide, slower for the first reduction and faster for the second. A large peak at 1.1 V on the successive anodic scan is assigned to the liberation of Br^- .

The mononuclear THF complex, $(C_5Ph_5)CrBr_2(THF)$, in THF instead gave one chemically irreversible reduction, $E_{pc} = -1.04$ V, with close lying follow-up peaks at -0.23 and 0.03 V, respectively (Figure 2). Simulation clearly shows these to be direct electrode products of the reduction. Loss of bromide in the course of the reduction is a plausible assumption in this case too, where the follow-up peaks are assigned to the reoxidation of the dehalogenated reduction product with and without incorporation of bromide. This conclusion is drawn from the observation that only one single reoxi-

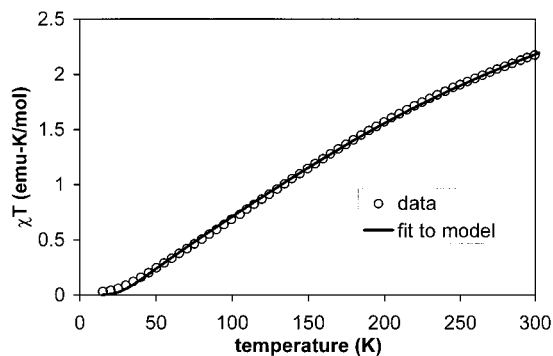


Figure 3. Plot of χT vs T for $[(C_5Ph_5)CrCl_2]_2$ and fit to Heisenberg Hamiltonian model.

dation (at -0.166 V) follows the -1.04 V reduction on addition of excess Br^- (as $[PPh_3Me]Br$).

Reduction of $(C_5Ph_5)CrI_2(THF)$ in dichloromethane gave very similar electrochemistry to the bromide complex with potentials of -0.75 and -0.33 V for reduction and reoxidation, respectively. In addition, there are two oxidation peaks at 0.31 and 0.57 V that occur on the initial anodic scan. The potential range and the fact that the final oxidation is partly reversible argue in favor of a bound iodide, which is liberated at two successive potentials.

Magnetic Susceptibility. The values of χT for all of the mononuclear species, $(C_5Ph_5)CrX_2(THF)$, $X = Cl$ (1.94), Br (1.72), I (1.83), are essentially consistent with the expected spin only value of 1.875 emu-G/mol for d^3 $Cr(III)$ in a pseudo-octahedral field.³¹ The data are temperature independent from 25 to 250 K with a slight downturn below 25 K and warrant no further comment.

The magnetic properties of $[(C_5Ph_5)CrCl_2]_2$ are illustrated in the plot of χT versus T (Figure 3). At room temperature, the value of χT is less than that expected for two uncoupled $S = 3/2$ centers (3.75 emu-G/mol), indicating the presence of antiferromagnetic coupling. This fact has previously been noted by Köhler and co-workers for the corresponding Cp and Cp* analogues, but was apparently never quantified.¹² The data were fit (eq 3) to the analytical solution of the Heisenberg Hamiltonian³² $H = -2J\hat{S}_1 \cdot \hat{S}_2$.

$$\chi T = \frac{2Ng^2\mu_B^2}{k} \left\{ \frac{\exp[x] + 5 \exp[3x] + 14 \exp[6x]}{1 + 3 \exp[x] + 5 \exp[3x] + 7 \exp[6x]} \right\} \quad (3)$$

$$\text{where } x = \frac{2J}{kT}$$

The two-parameter fit gives $g = 2.1$ and $J/k = -30$ K. The g value is slightly high compared to the expected value of 2, but the coupling is in the range of other doubly hydroxy-bridged chromium dimers.³³

Raman Spectroscopy. Due to the sensitivity of the $[(C_5Ph_5)CrX_2]_2$ samples to air and prolonged exposure to high temperature, Raman spectra could only be obtained under low-temperature conditions. Solid sam-

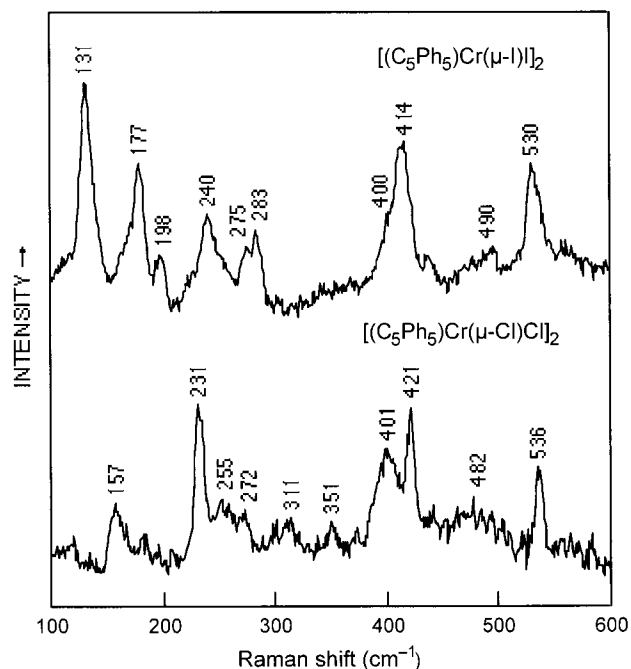


Figure 4. Low-temperature (77 K) Raman spectra (100 – 600 cm^{-1}) of **1** (bottom) and **3** (top) excited at 514.5 nm. Both spectra obtained via backscattering on KCl pellets in a liquid- N_2 dewar: (**1**) 400 mW laser power, 6 cm^{-1} slit widths, average of 16 scans; (**3**) 150 mW laser power, 8 cm^{-1} slit widths, average of 15 scans.

Table 5. Raman Low Frequencies (cm^{-1}) and Assignments for $[(C_5Ph_5)Cr(\mu-X)X]_2$ Complexes ($X = Cl^-, I^-$)

$[(C_5Ph_5)CrCl_2]_2$	$[(C_5Ph_5)CrI_2]_2$	assignment
157	131	$\delta(X-Cr-X)$
231	177	$\nu_b(Cr-X)$
255	198	$\nu_b(Cr-X)$
272, 311	240	$\nu_b(Cr-X)$
351	283, 275	$\nu_t(Cr-X)$
421	414	$\nu(Cr-Cp)$, A
401	400 sh	$\nu(Cr-Cp)$, B
482 br	490 br	Cp ring tilt
536	530	Cp ring tilt

ples were used because the solid precipitates from solution in liquid samples upon laser exposure. The strongest peaks obtained for each sample are observed in the region containing chromium–halogen and Cp–ring tilting vibrations as seen in Figure 4. All band identifications and assignments are given in Table 5. Samples of $[(C_5Ph_5)Cr(\mu-Br)Br]_2$ (**2**) gave very high scattering backgrounds and did not provide Raman spectra.

The skeletal vibrational modes are designated by the symbol ν and represent stretching motions. The metal–halogen stretching modes were assigned after those of *trans*-planar $M_2X_4L_2$ and tetrahedral Cp_2MX_2 and $Cp-MX_3$ compounds ($M =$ a transition metal).^{34–37} The ν_b stretches represent stretching of the $Cr-X$ bonds in the $Cr_2(\mu-X)_2$ bridge and occur in the 175 – 240 and 230 – 315 cm^{-1} regions in **3** ($X = I$) and **1** ($X = Cl$), respectively. These are lower in frequency compared to the terminal $Cr-X$ stretching modes³⁴ represented by ν_t ,

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which occur at $\sim 283\text{ cm}^{-1}$ in **3** and $\sim 350\text{ cm}^{-1}$ in **1**. Other halogen-sensitive bands in this region at 131 cm^{-1} (**3**) and 157 cm^{-1} (**1**) appear to be X–Cr–X bending (δ) vibrations.³⁵

The second Raman region of interest is that containing metal–cyclopentadienyl (Cp) ring stretching and tilting vibrations ($400\text{--}550\text{ cm}^{-1}$). Due to the fact that the $[(\text{C}_5\text{Ph}_5)\text{CrX}_2]_2$ compounds are classified in the C_2 point group, the $\nu(\text{Cr}\text{--}\text{Cp})$ stretches can be easily identified as the A- and B-symmetry modes.^{35,36} These two $\nu(\text{Cr}\text{--}\text{Cp})$ modes occur in the narrow range of $400\text{--}425\text{ cm}^{-1}$ and are distinguishable in the chloride dimer **1** as seen in Figure 4 and Table 5. However, the B mode ($\sim 400\text{ cm}^{-1}$) for the iodide dimer **3** cannot be clearly identified due to close overlap with the A mode at 414 cm^{-1} . The Cp ring tilting motions³⁶ are found in the $450\text{--}550\text{ cm}^{-1}$ region. As expected, these Raman bands are almost independent of X and quite similar for both compounds (Figure 4). Finally, the Raman spectra of **1** and **3** taken above 600 cm^{-1} (not shown) also contain internal C_5Ph_5 ligand vibrational modes associated with the Cp and Ph rings at the frequencies typical of centrally π -bonded complexes³⁴ and monosubstituted benzenes.³⁸

Summary. $(\text{C}_5\text{Ph}_5)\text{Cr}(\text{CO})_3$ rapidly reacts with halogens to initially yield $(\text{C}_5\text{Ph}_5)\text{Cr}(\text{CO})_3\text{X}$ complexes (X = Cl, Br, I), which then decompose to $[(\text{C}_5\text{Ph}_5)\text{CrX}(\mu\text{-X})]_2$ dimers in solution. The larger size of C_5Ph_5 (as compared to Cp or Cp*) combined with its reduced tendency

to release electron density to metals to which it binds makes the seven-coordinate $(\text{C}_5\text{Ph}_5)\text{Cr}(\text{CO})_3\text{X}$ compounds much less stable than their Cp or Cp* analogues. A crystal structure of $[(\text{C}_5\text{Ph}_5)\text{CrCl}_2]_2$ shows the molecule to exhibit only limited intramolecular crowding consistent with the reduced strain in a six-coordinate environment. Magnetic susceptibility measurements show the chromium centers to couple antiferromagnetically. All complexes exhibit complex electrochemical behavior, and Raman spectra for the X = Cl and I dimers are assigned. The dimers react with Lewis bases (e.g., THF) to yield monomeric species: $(\text{C}_5\text{Ph}_5)\text{CrX}_2\text{(THF)}$.

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Supporting Information Available: For $[(\text{C}_5\text{Ph}_5)\text{Cr}(\mu\text{-Cl})\text{Cl}]_2\cdot 2\text{CH}_2\text{Cl}_2$ as follows: Table 1S (bond distances), Table 2S (bond angles), Table 3S (atomic coordinates and equivalent isotropic displacement coefficients), Table 4S (anisotropic displacement coefficients), and Table 5S (hydrogen atom coordinates). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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