1934 *Organometallics* **1994,** *13,* 1934–1939

Tricarbonyl(η^6-hexachlorobenzene)chromium(0)

Paul G. Gassman*,[†] and Paul A. Deck[1]

Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455

Received December 28, 1993[⊛]

Lithiation of (η^6-C_6H_5Cl)(Cr(CO)$_3$ (**1**) with *n*-butyllithium in tetrahydrofuran at −78 °C followed by chlorination of the intermediate lithioarene complex with hexachloroethane afforded primarily (η^6-1,2-$C_6H_4Cl_2$)Cr(CO)$_3$ (**2**) and significant amounts of four new substances: (η^6-1,2,3-$C_6H_3Cl_3$)Cr(CO)$_3$ (**3**), (η^6-1,2,3,4-$C_6H_2Cl_4$)Cr(CO)$_3$ (**4**), (η^6-C_6HCl_5)Cr(CO)$_3$ (**5**), and (η^6-C_6Cl_6)Cr(CO)$_3$ (**6**). Regioisomers of **2**–**4** were not observed. The wavenumber of the symmetric CO stretch ($\tilde{\nu}^{A}_{CO}$, determined by infrared spectroscopy) and the oxidation potential ($E^{\circ\prime}$, determined by cyclic voltammetry) increased regularly with the increasing number of chloro substituents. Crystalline **6** was structurally characterized by X-ray diffractometry: triclinic, $P\bar{1}$, $a = 7.538(2)$ Å, $b = 7.734(3)$ Å, $c = 13.511(3)$ Å, $\alpha = 75.26(2)°$, $\beta = 74.48(2)°$, $\gamma = 60.94°$, $V = 656.1(8)$ Å^3, $Z = 2$, $R = 0.053$, $R_w = 0.069$. Noteworthy in **6** is the short chromium to C_6 centroid distance of 1.680(1) Å. Infrared spectroscopic, electrochemical, and metrical data for **6** lead to the conclusion that hexachlorobenzene is the most electron-poor arene thus far coordinated to a Cr(CO)$_3$ fragment.

Introduction

Decreasing the availability of the arene π electrons for dative coordination to transition metal d orbitals, by attaching highly electron-withdrawing ring substituents, presents an operational test of structural limits within an important class of π complexes.[2,3] Relatively electron-poor arenes generally will not displace other ligands such as carbonyl, ethers, and nitriles from the low-valent precursors in standard thermal substitution reactions. Furthermore, highly electronegative substituents such as halo, carboalkoxy, perfluoroalkyl, or nitro are incompatible with the harsh conditions required for *in-situ* reduction of metal halides as in the Fischer–Hafner synthesis of (η^6-C_6H_6)$_2$Cr.[4] While considerable attention has recently been directed toward perhalogenated η^5-cyclopentadienyl (Cp) complexes,[5] partly because of their decreased susceptibility to oxidative decomposition, similar efforts to prepare perhalogenated η^6-arene complexes have been largely restricted to metal atom synthesis.[6] Although examples of (η^6-arene)$_2$M complexes (M = Cr, V) bearing two or more electron-withdrawing substituents (chloro, fluoro, or trifluoromethyl) on each arene are readily prepared by the latter method,[7] the development of rational solution methods for the π-complexation of electron-poor arenes remains particularly important to the chemistry of non-homoleptic species such as (η^6-arene)Cr(CO)$_3$ for which metal atom synthesis is much less applicable.[8]

Our laboratory has demonstrated a long-standing interest in the interpretation of ring substituent electronic effects in transition metal η^5-cyclopentadienide (Cp) species using X-ray photoelectron spectroscopy (XPS or ESCA) among other analytical methods.[9] Recently, we have expanded this project to include the closely-related η^6-arene complexes represented by (η^6-arene)Cr(CO)$_3$ and (η^5-arene)Fe(η^5-C_5H_5)PF$_6$.[10] In selecting particular (η^6-arene)Cr(CO)$_3$ species for study, we recognized that very few of the hundreds of previously reported examples bear two or more electron-withdrawing substituents on the carbocyclic ligand and none, to our knowledge, bears more than three.[11] Previously, we demonstrated the balanced electronic effects of methyl and chloro substitution in (η^5-$C_5(CH_3)_5$)(η^5-C_5Cl_5)Ru by recording the same Ru ($3d_{5/2}$) binding energy for this complex as for (η^5-C_5H_5)$_2$Ru, within experimental error.[9f] The series of methylated complexes

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[†] Deceased April 21, 1993.

[⊛] Abstract published in *Advance ACS Abstracts,* March 15, 1994.

(1) (a) National Science Foundation Predoctoral Fellow, 1987–1990. (b) Author to whom correspondence should be addressed at: Department of Chemistry, Northwestern University, Evanston, IL 60208-3113.

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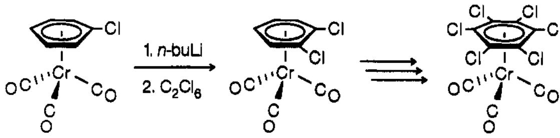
0276-7333/94/2313-1934$04.50/0

Scheme 1



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[η^6-$C_6(CH_3)_nH_{6-n}$]$Cr(CO)_3$ (n = 0–6) was already available *via* published procedures, so that our interest in preparing the chlorinated series (η^6-$C_6H_{6-n}Cl_n$)$Cr(CO)_3$ (n = 1–6) was further motivated by the opportunity to seek a meaningful comparison of the electronic effects of (η^6-arene) and Cp substituents on their respective coordinated metal fragments.

Our synthetic approach (Scheme 1) envisioned a chlorination procedure in which the readily available (η^6-C_6H_5Cl)$Cr(CO)_3$ (**1**) would be lithiated with n-butyllithium,[12] followed by treatment of the intermediate (η^6-1,2-ClC_6H_4Li)$Cr(CO)_3$ (**8**) with C_2Cl_6 to afford **2**. Stepwise repetition of this procedure would furnish the series (η^6-$C_6Cl_nH_{6-n}$)-$Cr(CO)_3$. Our strategy was based on previous work which showed that species such as **8** could be treated with electrophiles (E^+), affording (η^6-1,2-ClC_6H_4E)$Cr(CO)_3$.[12] The chlorination of **8** with C_2Cl_6 was, however, not reported, even though C_2Cl_6 had already been used in an analogous preparation of decachloroferrocene.[13]

We wish to present here our unforeseen observation that the first reaction proposed in Scheme 1 afforded not only the desired product **2** *but all five of the homologs* ***2–6***, obviating execution of the remainder of the sequence. Infrared spectroscopy, cyclic voltammetry, and structural analysis were then employed to demonstrate the electronic effects of increasing chloro substitution in (η^6-arene)Cr-$(CO)_3$ complexes.

Experimental Section

General Considerations. All manipulations were carried out under an atmosphere of nitrogen or argon following standard drybox and Schlenk techniques.[14] Solvents and starting materials were purified by accepted procedures.[15] Infrared spectra were recorded on a Mattson Polaris FT-IR; $\tilde{\nu}_{CO}$ values for solutions of (η^6-arene)$Cr(CO)_3$ species were determined at a resolution of 0.5 cm^{-1}. All ^1H NMR spectra were recorded at 300 MHz (^{13}C NMR at 75 MHz) except where otherwise indicated; all ^{13}C NMR spectra are broad-band ^1H decoupled. Elemental analyses were performed by Scandinavian Microanalytical Laboratory (Herlev, Denmark). Crystallographic analysis was carried out by Professor Doyle Britton at the University of Minnesota X-ray Diffraction Service Laboratory. Tricarbonyl(η^6-chlorobenzene)chromium (**1**), tricarbonyl(η^6-1,2-dichlorobenzene)chromium (**2**), (η^6-benzene)tricarbonylchromium (**10**), tricarbonyl(η^6-1,4-dimethylbenzene)chromium (**12**), tricarbonyl(η^6-1,2,3,4-tetramethylbenzene)-chromium (**14**), tricarbonyl(η^6-pentamethylbenzene)chromium (**15**), and tricarbonyl(η^6-hexamethylbenzene)chromium (**16**) were prepared following a general procedure,[16] and tricarbonyl(η^6-toluene)chromium (**11**) and tricarbonyl(η^6-mesitylene)chromium (**13**) were purchased from Aldrich and recrystallized prior to use. The identities and purities of previously reported materials were confirmed by melting points, infrared spectra, and ^1H and ^{13}C NMR spectra, as indicated below.

Chlorination of Tricarbonyl(η^6-chlorobenzene)chromium. A solution of n-butyllithium in hexanes (7.1 mL, 2.5 M, 17.8 mmol) was added in one portion, with stirring, to 75 mL of tetrahydrofuran maintained at −78 °C. After stirring for 0.5 h, a solution of tricarbonyl(η^6-chlorobenzene)chromium (**1**, 4.00 g, 16.1 mmol) in tetrahydrofuran (25 mL), maintained at −78 °C, was added in small portions via cannula. The resulting yellow-orange solution was stirred for 1 h at −78 °C and then added as quickly as possible, via cannula, to a rapidly stirred solution of hexachloroethane (4.20 g, 17.7 mmol) in tetrahydrofuran (75 mL) maintained at −78 °C. After stirring the resulting solution for 1 h at −78 °C, the cooling bath was withdrawn, and the volatile components were removed *in vacuo*. The orange-brown residue was taken up in 25 mL of dichloromethane and filtered through diatomaceous earth. The yellow-orange filtrate was evaporated to afford a viscous yellow oil, which was subjected to silica gel chromatography. Three bands were eluted with pentane/ether and evaporated to afford yellow residues, from which individual products were isolated, as described below. All chromatographic separations were carried out under nitrogen and monitored by FT-IR in the $\tilde{\nu}_{CO}^{A}$ region of 1970–2030 cm^{-1}.[17]

Tricarbonyl(η^6-hexachlorobenzene)chromium (6). The first band eluted from the silica gel chromatographic separation of the crude chlorination reaction mixture was found to contain primarily **6** and **5** with a small amount of **4**. This mixture was separated by flash chromatography on silica gel (2 × 25 cm), eluting with pentane. An initial yellow band afforded an orange crystalline solid, which was recrystallized from hexanes to afford 104 mg (0.247 mol, 1.5%) of **6** in three crops of yellow prisms: mp (sealed capillary) 165.0–167.5 °C; IR (methylcyclohexane) $\tilde{\nu}_{CO}$ = 2013, 1969 cm^{-1}; IR (dichloromethane) $\tilde{\nu}_{CO}$ = 2009, 1957 cm^{-1}; IR (KBr) 2012, 1962, 1933, 1282, 688, 640, 603, 452 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) showed no signals; ^{13}C NMR (125 MHz, $CDCl_3$) δ 106.56, 225.81; HRMS (CI using CH_4) m/e calcd for $C_9Cl_6CrO_3$ 417.7384, found 417.7408. Anal. Calcd for $C_9Cl_6CrO_3$: C, 25.69; H, 0.00; Cl, 50.55. Found: C, 25.84; H, 0.11; Cl, 50.08.

Tricarbonyl(η^6-pentachlorobenzene)chromium (5). From the flash chromatographic separation described for the isolation of **6** above, a second yellow band was eluted with pentane and evaporated to afford a yellow crystalline solid, which was recrystallized from pentane to yield 165 mg (0.427 mmol, 2.7%) of **5** in three crops of yellow prisms: mp (sealed capillary) 107.5–108.0 °C; IR (methylcyclohexane) $\tilde{\nu}_{CO}$ = 2009, 1962 cm^{-1}; IR (dichloromethane) $\tilde{\nu}_{CO}$ = 2004, 1949 cm^{-1}; IR (KBr) 3082, 2925, 2001, 1940, 1353, 1340, 1277, 1163, 1141, 807, 697, 641, 630, 612, 604, 449 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.84 (s); ^{13}C NMR ($CDCl_3$) δ 226.86, 110.47, 108.27, 104.60, 87.02; HRMS (EI) m/e calcd for $C_9HCl_5CrO_3$ 383.7773, found 383.7770. Anal. Calcd for $C_9HCl_5CrO_3$: C, 27.98; H, 0.26; Cl, 45.88. Found: C, 28.08; H, 0.30; Cl, 45.57.

Tricarbonyl(η^6-tetrachlorobenzene)chromium (4). The second band eluted from the silica gel chromatographic separation of the crude chlorination reaction was found to contain primarily **4** and **3** with small amounts of **5**, **2**, and **1**. This mixture was separated by thin layer chromatography on silica gel (20 cm × 20 cm × 0.5 mm with preadsorbant), carried out in a nitrogen drybox, eluting with pentane. The yellow band appearing at the highest R_f contained less than 5 mg of **5** and was discarded. The second yellow band was extracted with ether, and the solvent was evaporated to afford a yellow solid, which was recrystallized from pentane to yield 95 mg of **4** as yellow rods: mp (sealed

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capillary) 105.5–106.5 °C; IR (methylcyclohexane) $\tilde{\nu}_{CO}$ = 2005, 1953 cm^{-1}; IR (dichloromethane) 1998, 1937 cm^{-1}; IR (KBr) 3090, 1987, 1918, 1393, 1290, 1151, 1112, 842, 833, 760, 699, 651, 638, 632, 615, 536, 520, 460, 452 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 5.55 (s); ^{13}C NMR (CDCl$_3$) δ 228.05, 108.92, 107.04, 88.16; HRMS (EI) *m/e* calcd for $C_9H_2Cl_4CrO_3$ 349.8163, found 349.8169. Anal. Calcd for $C_9H_2Cl_4CrO_3$: C, 30.72; H, 0.57; Cl, 40.30. Found: C, 30.81; H, 0.65; Cl, 40.03.

Tricarbonyl(η^6-trichlorobenzene)chromium (3). From the thin layer chromatogram described for the isolation of 4, the broad yellow band at the baseline was recovered, extracted with ether, and evaporated to afford a yellow residue which consisted of 1–3 in an approximate ratio of 1:3:3, respectively. This residue was subjected to flash chromatography on silica gel (2 × 30 cm). The first yellow band was eluted with hexanes, and removal of the solvent afforded 3, which was recrystallized from hexanes to afford 22.3 mg (0.07 mmol, 0.4%) of yellow prisms: mp (sealed capillary) 92–98 °C dec; IR (methylcyclohexane) $\tilde{\nu}_{CO}$ = 2001, 1948, 1944; IR (dichloromethane) $\tilde{\nu}_{CO}$ = 1992, 1926 cm^{-1}; IR (KBr) 3092, 3087, 1980, 1633, 1490, 1467, 1400, 1369, 1350, 1177, 1145, 1138, 839, 784, 658, 637, 619, 535, 466 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$) δ 5.40 (d, ^3J = 6.4 Hz, 2 H), 5.29 (t, ^3J = 6.1 Hz, 1 H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 229.18, 111.57, 106.83, 89.24, 88.19; HRMS (EI) *m/e* calcd for $C_9H_3Cl_3CrO_3$ 315.8553, found 315.8540. Anal. Calcd for $C_9H_3Cl_3CrO_3$: C, 34.05; H, 0.95; Cl, 33.50. Found: C, 34.33; H, 1.05; Cl, 32.22.

Identification of Tricarbonyl(η^6-dichlorobenzene)chromium (2) and Tricarbonyl(η^6-chlorobenzene)chromium (1). The third band eluted from the silica gel chromatographic separation of the crude chlorination reaction was found to contain a mixture of complexes 2 and 1 in a 5:1 ratio. Spectra of the mixture were assigned by comparison to authentic samples prepared by a general method.[16] Data for 2 (yellow prisms from hexanes): mp (sealed capillary) 88–90 °C (lit.[18] mp 88 °C); IR (methylcyclohexane) $\tilde{\nu}_{CO}$ = 1995, 1936, 1933 cm^{-1}; IR (dichloromethane) $\tilde{\nu}_{CO}$ = 1985, 1915 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 5.65 (m, 2 H), 5.18 (m, 2 H); ^{13}C NMR (CDCl$_3$) δ 230.21, 109.47, 91.80, 89.26. Data for 1 (yellow needles from benzene/hexane): mp (sealed capillary) 100.5–101.5 °C (lit.[16] mp 101–102 °C); IR (methylcyclohexane) $\tilde{\nu}_{CO}$ = 1990, 1926; IR (dichloromethane) $\tilde{\nu}_{CO}$ = 1979, 1905 cm^{-1}; ^{1}H NMR (C$_6$D$_6$) δ 4.50 (dd, ^3J = 6.6 Hz, ^4J = 0.9 Hz, 2 H), 4.29 (t, ^3J = 6.4 Hz, 2 H), 3.87 (tt, ^3J = 6.2 Hz, ^4J = 0.9 Hz, 1 H); ^{13}C NMR (C$_6$D$_6$) δ 232.02, 112.69, 92.93, 90.62, 87.58.

(η^6-Benzene)tricarbonylchromium (10). Yellow prisms from benzene/hexanes: mp 159.0–161.0 °C (lit.[19] 161.5–163.0 °C); IR (methylcyclohexane) $\tilde{\nu}_{CO}$ = 1983, 1915 cm^{-1}; IR (dichloromethane) $\tilde{\nu}_{CO}$ = 1971, 1891 cm^{-1}; ^{1}H NMR (C$_6$D$_6$) δ 4.29 (s, 6 H); ^{13}C NMR (C$_6$D$_6$) δ 233.28, 92.36.

Tricarbonyl(η^6-toluene)chromium (11). Yellow prisms from hexanes: mp 81.5–83.0 °C (lit.[19] mp 80–81 °C); IR (methylcyclohexane) $\tilde{\nu}_{CO}$ = 1983, 1915 cm^{-1}; IR (dichloromethane) $\tilde{\nu}_{CO}$ = 1967, 1887 cm^{-1}; ^{1}H NMR (C$_6$D$_6$) δ 4.54 (t, ^3J = 6.7 Hz, 2 H), 4.25 (m, 3 H), 1.53 (s, 3H); ^{13}C NMR (C$_6$D$_6$) δ 233.28, 92.36.

Tricarbonyl(η^6-1,4-dimethylbenzene)chromium (12). Yellow rods from hexanes: mp 96.5–98.0 °C (lit.[19] mp 97–98 °C); IR (methylcyclohexane) $\tilde{\nu}_{CO}$ = 1974, 1904 cm^{-1}; IR (dichloromethane) $\tilde{\nu}_{CO}$ = 1963, 1880 cm^{-1}; ^{1}H NMR (C$_6$D$_6$) δ 4.44 (s, 4 H), 1.53 (s, 6 H); ^{13}C NMR (C$_6$D$_6$) δ 234.16, 106.37, 94.13, 19.74.

Tricarbonyl(η^6-1,3,5-trimethylbenzene)chromium (13). Yellow rods from benzene/hexanes: mp 167.0–169.0 °C (lit.[19] mp 172–174 °C); IR (methylcyclohexane) $\tilde{\nu}_{CO}$ = 1970, 1900 cm^{-1}; IR (dichloromethane) $\tilde{\nu}_{CO}$ = 1959, 1878 cm^{-1}; ^{1}H NMR (C$_6$D$_6$) δ 4.08 (s, 3 H), 1.67 (s, 9 H); ^{13}C NMR (C$_6$D$_6$) δ 236.53, 110.50, 91.32, 20.24.

Tricarbonyl(η^6-1,2,4,5-tetramethylbenzene)chromium (14). Yellow plates from benzene/hexanes: mp 116.5–118.0 °C (lit.[20] mp 115–117 °C); IR (methylcyclohexane) $\tilde{\nu}_{CO}$ = 1965, 1896, 1889 cm^{-1}; IR (dichloromethane) $\tilde{\nu}_{CO}$ = 1955, 1869 cm^{-1}; ^{1}H NMR (C$_6$D$_6$) δ 4.58 (s, 2 H), 1.60 (s, 12 H); ^{13}C NMR (C$_6$D$_6$) δ 235.03, 106.17, 97.64, 17.69.

Tricarbonyl(η^6-pentamethylbenzene)chromium (15). Yellow plates from hexanes: mp 101.5–102.0 °C (lit.[20] mp 101–102 °C); IR (methylcyclohexane) $\tilde{\nu}_{CO}$ = 1961, 1888 cm^{-1}; IR (dichloromethane) 1950, 1866 cm^{-1}; ^{1}H NMR (C$_6$D$_6$) δ 4.52 (s, 1 H), 1.75 (s, 3 H), 1.72 (s, 6 H), 1.62 (s, 6 H); ^{13}C NMR (C$_6$D$_6$) δ 235.43, 108.50, 107.06, 105.16, 95.91, 19.56, 16.04, 15.38.

Tricarbonyl(η^6-hexamethylbenzene)chromium (16). Yellow prisms from benzene/hexanes: mp 190–195 °C dec (lit.[19] mp 211–213 dec); IR (methylcyclohexane) $\tilde{\nu}_{CO}$ = 1957, 1883; IR (dichloromethane) 1946, 1861 cm^{-1}; ^{1}H NMR (C$_6$D$_6$) δ 1.73 (s, 18 H); ^{13}C NMR (C$_6$D$_6$) δ 235.81, 105.94, 16.63.

Electrochemical Experiments. Cyclic voltammetry was performed using a Princeton Applied Research Model 273 potentiostat at room temperature. The three-electrode configuration comprised a highly polished glassy carbon disk working electrode (A = 0.07 cm^2), an AgCl/Ag reference electrode containing 1.0 M aqueous KCl, and a platinum counter electrode. The working component was separated from the reference compartment by a modified Luggin capillary. All three compartments contained a 0.10 M solution of tetra-*n*-butylammonium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (TBA$^+$TFPB$^-$).[21] The analyses were carried out using 0.75–1.0 mL of 0.5 mM solutions of the organometallic species using dichloromethane (distilled from P_4O_{10} under argon) as solvent. About 0.1 g of alumina (Fisher Brockman Activity I, 60–200 mesh, activated overnight in a 300 °C furnace) was added to the working compartment as an internal dessicant to improve the reversibility of the cyclic voltammograms;[11] the cell was entirely assembled in a nitrogen glovebox. Potentials were recorded against the aqueous AgCl/Ag electrode (not corrected for the junction potential) and calibrated after each series of experiments against the ferrocenium/ferrocene (Fc$^+$/Fc) couple (TBA$^+$TFPB$^-$/CH$_2$Cl$_2$). Thus, the $E^{\circ\prime}$ values for the Fc$^+$/Fc couple ranged from 440 to 500 mV but were defined at the previously reported[22] value of 470 mV vs SCE with ΔE ($E_{pa} - E_{pc}$) values ranging from 86 to 97 mV. The potentials are the averages of values obtained from three scans (500 mV/s) on the same solution and are reported vs SCE.

X-ray Structure Determination. A plate crystal of 6 was grown by cooling a concentrated dichloromethane solution of 6 to −25 °C overnight in a drybox freezer. A crystal of 6 was mounted on a glass fiber, and unit cell parameters and an orientation matrix for data collection were obtained from 22 carefully centered reflections in the range 25.26 < 2θ < 53.60°. The centrosymmetric space group $P\bar{1}$ (No. 2) was selected and later confirmed by refinement. Additional crystal data for 6 are collected in Table 1. The structures were solved by direct methods,[23] and all atoms were refined anisotropically. Calculations were carried out using the TEXSAN software.[24]

Results and Discussion

Synthesis. The starting material 1 was conveniently prepared by thermal reaction of chlorobenzene with hexacarbonylchromium.[16] Lithiation of 1 with butyllithium in tetrahydrofuran (THF) at −78 °C afforded (η^6-2-chlorolithiobenzene)tricarbonylchromium (8),[12] which was not isolated but added directly to a THF solution of hexachloroethane at −78 °C. This "inverse addition" procedure, if carried out quickly to avoid thermal de-

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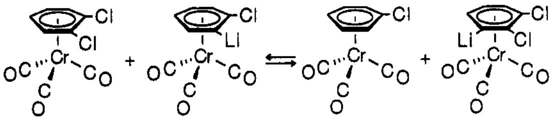
Table 1. Crystal Data for (η^6-C_6Cl_6)Cr(CO)$_3$ (6)

(a) Crystal Parameters	
empirical formula	$CrC_9Cl_6O_3$
fw	420.81
cryst color, habit	yellow, plate
cryst dimens (mm)	0.450 × 0.350 × 0.150
cryst class	triclinic
no. of reflns used for unit cell determination [2θ range (deg)]	22 (25.3–53.6)
θ scan FWHM	0.00
space group	$P\bar{1}$ (No. 2)
a (Å)	7.538(2)
b (Å)	7.734(3)
c (Å)	13.511(3)
α (deg)	75.26(2)
β (deg)	74.48(2)
γ (deg)	60.94(2)
V (Å^3)	656.1(8)
Z	2
d_{calc} (g cm^{-3})	2.130
$\mu_{MoK\alpha}$ (cm^{-1})	20.80
(b) Data Collection	
diffractometer	Enraf-Nonius CAD-4
monochromator	graphite
radiation [λ (Å)]	Mo Kα (0.710 69)
temp (°C)	−101
attenuator	Zr foil (factor = 17.8)
take-off angle (deg)	2.8
scan type	ω
scan rate (deg/min in ω)	16.5
scan width (deg)	1.20 + 0.35 tan θ
$2\theta_{max}$ (deg)	51.9
no. of reflns collected	3148
no. of ind reflns	2581
(c) Solution and Refinement	
no. observns ($I > 2.00\sigma(I)$)	2244
no. variables	172
N_o/N_v	13.05
$R(F)$	0.053
$R_w(F)$	0.069
goodness of fit	1.99
max peak in final diff map (e/Å^3)	1.93
min peak in final diff map (e/Å^3)	−0.69
max shift/error in final cycle	0.08

composition of the lithio species,[25] resulted in the best observed conversions to higher ring-chlorinated products. The crude product mixture was analyzed in filtered methylcyclohexane solution by FT-IR spectroscopy in the region 1970–2030 cm^{-1} (symmetric CO stretching, $\tilde{\nu}_{CO}^{A}$). Several partly overlapping bands with distinct maxima separated by ~5 cm^{-1} were observed and assigned to higher ring-chlorinated species;[17] reference values of $\tilde{\nu}_{CO}^{A}$ for 1 and 2 were independently measured (*vide supra*). Silica gel chromatographic separation of the crude mixture afforded significant yields of 2–6 as well as the unreacted starting material 1. Although yields of the higher ring-chlorinated species could be improved somewhat by resubmitting the crude product mixture to two more lithiation–chlorination cycles prior to chromatographic separation, the analytical samples reported here were obtained from the initial product mixture.

Two aspects of the chlorination reaction deserve further attention. First, products resulting from di-, tri-, tetra- and pentachlorination are evident after treatment of the intermediate 8 with 1 equiv of hexachloroethane. Second, regioisomers of 2–4 were not observed. The presence of polylithiated 1 after treatment of 1 with only 1 equiv of *n*-butyllithium is unlikely.[26] A possible alternative rationalization, illustrated in Scheme 2, invokes rapid proton transfer between neutral and ring-lithiated η^6-arene complexes during the reaction with hexachloroethane. As the chlorination of lithiated species proceeds, increasingly chlorinated η^6-arenes result from proton transfer. Apparently, the *ortho* selectivity of the initial lithiation with *n*-butyllithium is maintained throughout the proposed proton-exchange processes.

Scheme 2



The new substances 3–6 exhibited varying degrees of thermal stability. The perchlorinated species 6 could be melted and resolidified (mp 165.0–167.5 °C) two or three times before a reduction in melting point was observed.[27] Also, 6 was relatively stable to air in the solid state, but air-exposed solutions decomposed rapidly. In contrast, 3 decomposed rapidly below 100 °C in a sealed capillary, and the solid was quite air-sensitive. Finally, although adequate carbon/hydrogen analyses could be readily obtained for 3–6, halogen analyses varied between individual samples taken from the same source and were invariably lower than the calculated values.

Infrared Spectroscopic Analysis. Infrared absorption band positions in metal carbonyl species have been extensively investigated as a method for determining electronic effects on CO-containing organometallic fragments. Within an isostructural series,[28] a higher CO stretching wavenumber ($\tilde{\nu}_{CO}$) implies higher C–O bond order as a result of diminished back-bonding from a relatively electron-poor metal fragment ($d\pi_{metal} - p\pi^{*}_{CO}$). Accordingly, $\tilde{\nu}_{CO}$ values for 1 through 6 and the reference compounds 10–16 were determined by FT-IR and are recorded in Table 2. Methylcyclohexane and dichloromethane were used as solvents for the FT-IR experiments: Methylcyclohexane was used to minimize the broadening and red-shifting of absorption bands observed for more polar solvents like dichloromethane,[29] while $\tilde{\nu}_{CO}$ values were obtained in the latter solvent for comparison to previously reported data.[11]

The symmetric stretching wavenumbers $\tilde{\nu}_{CO}^{A}$ are plotted in Figure 1 versus the number of chloro and methyl substituents. The average effect of each chloro substituent increases $\tilde{\nu}_{CO}^{A}$ by 4.9 ± 0.1 cm^{-1} ($r^2 = 0.989$), while the average effect of each methyl decreases $\tilde{\nu}_{CO}^{A}$ by 4.3 ± 0.1 cm^{-1} ($r^2 = 0.999$). Thus, the electron-donating effect of methyl substituents in (η^6-arene)Cr(CO)$_3$ species *balances* the electron-withdrawing influence of chloro, as determined by infrared spectroscopic analysis, as was observed

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(27) The products were also moderately stable toward preparative gas-liquid partition chromatography using a 24 × $^3/_{16}$ in. copper column packed with Analabs SE-30 (10% on nonacid washed Chromasorb-W) installed in a Varian Aerograph 90-P instrument with injector and thermal conductivity detector temperatures of 180 °C and oven temperatures of 90–150 °C; the carrier gas was helium (Linde, used as received).

(28) Methods to compare nonisostructural metal carbonyl species, differing in the metal atom and the spacial arrangement of ligands, have been developed: (a) Bursten, B. E.; Green, M. R. *Prog. Inorg. Chem.* **1988**, *38*, 477. (b) Cotton, F. A.; Kraihanzel, C. S. *J. Am. Chem. Soc.* **1962**, *84*, 4432. (c) Graham, W. A. G. *Inorg. Chem.* **1968**, *7*, 315. (d) Haas, H.; Sheline, R. K. *J. Chem. Phys.* **1967**, *47*, 2996.

(29) Red-shifting is primarily due to Lewis acidic interaction of solvent with carbonyl ligands. (a) Adams, D. M. *Metal-Ligand and Related Vibrations*; Edward Arnold: London, 1967. (b) Herzberg, G. *Molecular Spectra and Molecular Structure*; Van Nostrand: New York, 1945; Vol. II, p 534.

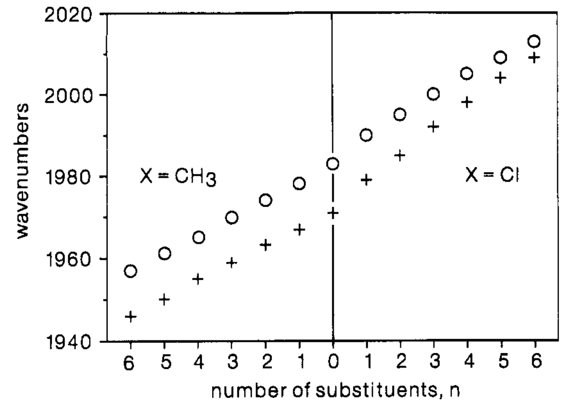

Figure 1. $\tilde{\nu}_{CO}^{A}$ values for 1–6 and 10–16 in methylcyclohexane (O) and dichloromethane (+) solution. Data are taken from Table 2.

Table 2. Wavenumbers of Carbonyl Stretching in $(\eta^6\text{-arene})Cr(CO)_3$ Complexes

		$\tilde{\nu}_{CO}$ ($\pm$1 cm^{-1})			
		methylcyclohexane		dichloromethane	
	substituents	A	E	A	E
1	Cl	1990	1926	1979	1905
2	1,2-Cl$_2$	1995	1936 1933	1985	1915
3	1,2,3-Cl$_3$	2001	1948 1944	1992	1926
4	1,2,3,4-Cl$_4$	2005	1953	1998	1937
5	Cl$_5$	2009	1962	2004	1949
6	Cl$_6$	2013	1969	2009	1957
10	H	1983	1915	1971	1891
11	CH$_3$	1978	1909	1967	1887
12	1,4-(CH$_3$)$_2$	1974	1904	1963	1880
13	1,3,5-(CH$_3$)$_3$	1970	1900	1959	1878
14	1,2,4,5-(CH$_3$)$_4$	1965	1896 1889	1955	1869
15	(CH$_3$)$_5$	1961	1888	1950	1866
16	(CH$_3$)$_6$	1957	1883	1946	1861

for substituted ruthenocenes.[30] The $\tilde{\nu}_{CO}^{A}$ value for **6** is especially noteworthy in exceeding all other published values for neutral $(\eta^6\text{-arene})Cr(CO)_3$ species. The second highest $\tilde{\nu}_{CO}^{A}$ value of which we are aware is 2003 cm^{-1}, recently reported for (η^6-1,3,5-tricarbomethoxybenzene)tricarbonylchromium in dichloromethane,[11] while a typical range for this parameter is about 1950–2000 cm^{-1}. These data imply that the chromium center in **6** is more electron-deficient than in any other $(\eta^6\text{-arene})Cr(CO)_3$ complex.

Crystal Structure of 6. ORTEP side and top views of the molecular structure of **6** are shown in Figures 2 and 3, respectively. In the crystalline state, **6** adopts the familiar "piano stool" structure (Figure 2) in the expected[31] staggered arrangement of the Cr(CO)$_3$ tripod with respect to the η^6-arene carbon atoms (Figure 3). Selected bond lengths and average intramolecular angles are collected in Tables 3 and 4, respectively; complete tables of crystal data and metrical parameters are deposited in the supplementary material.

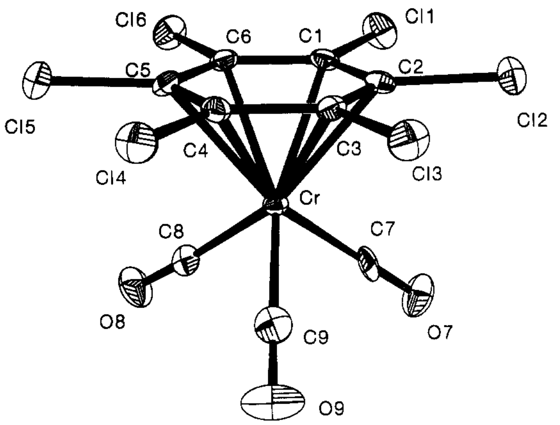

Figure 2. Side view ORTEP diagram of $(\eta^6\text{-}C_6Cl_6)Cr(CO)_3$ (**6**), showing 50% probability thermal ellipsoids.

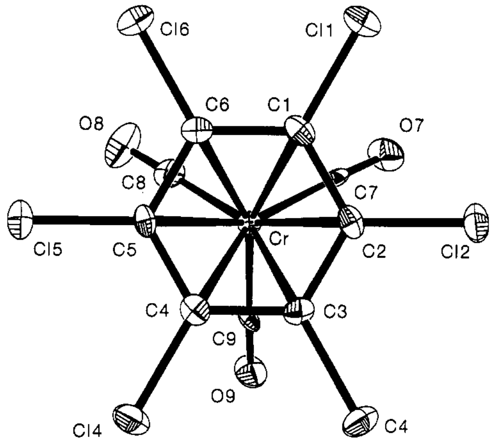

Figure 3. Top view ORTEP diagram of $(\eta^6\text{-}C_6Cl_6)Cr(CO)_3$ (**6**), showing 50% probability thermal ellipsoids.

Table 3. Selected Intramolecular Distances (Å) for $(\eta^6\text{-}C_6Cl_6)Cr(CO)_3$ (6)

Cr–C1	2.205(5)	C4–Cl4	1.725(5)
Cr–C2	2.206(5)	C5–Cl5	1.720(4)
Cr–C3	2.205(5)	C6–Cl6	1.719(5)
Cr–C4	2.196(5)	C1–C2	1.427(7)
Cr–C5	2.194(5)	C2–C3	1.409(6)
Cr–C6	2.194(5)	C3–C4	1.428(6)
Cr–C7	1.884(5)	C4–C5	1.402(6)
Cr–C8	1.865(6)	C5–C6	1.432(6)
Cr–C9	1.889(5)	C6–C1	1.427(6)
C1–Cl1	1.713(5)	C7–O7	1.126(6)
C2–Cl2	1.713(5)	C8–O8	1.133(7)
C3–Cl3	1.715(5)	C9–O9	1.118(6)

Table 4. Average Intramolecular Angles (deg) for $(\eta^6\text{-}C_6Cl_6)Cr(CO)_3$ (6)

intraarene angle C–C–C	120.1(4)
intercarbonyl angle C–Cr–C	88.4(2)
intracarbonyl angle Cr–C–O	177.6(4)
halogen–arene torsional angle Cl–C–C–C	178.0(4)

The most noteworthy feature of the molecular structure of **6** is the extremely short distance 1.680(5) Å from the chromium atom to the η^6-arene centroid, which is apparently the present limiting value for all structurally characterized $(\eta^6\text{-arene})Cr(CO)_3$ complexes. The second shortest chromium to arene centroid distance of which we are aware is 1.706(3) Å, recently reported[35] for $[\eta^6\text{-}1,4\text{-}C_6H_4(COOCH_3)_2]Cr(CO)_3$ (**17**). The corresponding value

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(30) The precision of this comparison is limited by the experimental errors of measuring core electron binding energies (CBEs) by XPS. However, it is important to note that CBEs are intrinsically a more direct probe of metal-centered electron richness than ligand vibrational parameters. Unfortunately, an analysis of CBEs for **1–6** was vitiated by the instability of these compounds under the conditions of the XPS experiment in our laboratory.

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(32) Byers, B. P.; Hall, M. B. *Inorg. Chem.* **1987**, *26*, 2186.

(33) The long Cr–CO distance of 1.879(7) Å in **6** also suggests weak back-bonding to the CO ligands, indicative of an electron-deficient metal center. This distance lies barely within 3σ of the corresponding Cr–CO distance of 1.861(2) Å, also reported for **17**.

(34) For a discussion of bond alternation in $(\eta^6\text{-arene})Cr(CO)_3$ complexes, see ref 32. Crystal structure of $(\eta^6\text{-}C_6H_6)Cr(CO)_3$: Rees, B.; Coppens, P. *Acta Crystallogr. Sect. B* **1973**, *29*, 2515.

(35) Hunter, A. D.; Shilliday, L.; Furey, W. S.; Zaworotko, M. J. *Organometallics* **1992**, *11*, 1550.

Table 5. Electrochemical Data for (η^6-$C_6Cl_nH_{6-n}$)$Cr(CO)_3$

complex	no. of Cl substituents (n)	$E^{\circ\prime}$ (mV)[a]	ΔE ($E_{pa} - E_{pc}$) (mV)	i_{pc}/i_{pa}
10	0	884	71	0.92
		877[b]	84[b]	0.91[b]
1	1	1018	131	0.78
		987[b]	89[b]	0.75[b]
2	2	1097	132	0.77
		1140[b]	irrev	irrev
4	4	1260	145	0.68
5	5	1337	130	0.67
6	6	1442	120	0.35

[a] Determined in 0.10 M TBA^+TFPB^-/dichloromethane solution using Fc^+/Fc (470 mV vs SCE) as an external standard. All potentials reported vs SCE. [b] Recorded in 0.1 M $TBA^+PF_6^-$ (data taken from ref 11).

in **6** is significantly (about 5σ) shorter. In [η^6-$C_6(CH_3)_6$]$Cr(CO)_3$ (**16**), a value of 1.730(3) Å[32] was observed, while a typical range for this parameter in (η^6-arene)$Cr(CO)_3$ complexes is 1.70–1.74 Å.[33] These data corroborate our infrared spectroscopic evidence, suggesting that (η^6-C_6Cl_6)$Cr(CO)_3$ is the most electron-poor (η^6-arene)$Cr(CO)_3$ complex reported to date.

In other respects, **6** displays an unexceptional structure. The six η^6-arene carbon atoms are coplanar (less than 1σ deviation from the C_6 least squares plane), and the six C–C–C angles within the ring are all within 0.6° of 120°. The least squares planes defined by (a) the six η^6-arene carbon atoms, (b), the three carbonyl carbon atoms, and (c) the three carbonyl oxygen atoms are all parallel within 2°. Uniform $Cr-C_{arene}$ distances (well within 2σ of the average 2.200 Å) confirm the hexahapticity of the C_6Cl_6 ligand in crystalline **6**. The C–C bond alternation within the η^6-arene is questionably significant at the 3σ level: Those C–C bonds which intersect the projected Cr–CO bonds (C1–C2, C3–C4, and C5–C6 in Figure 3) average 1.429(7) Å, while the others (C2–C3, C4–C5, and C6–C1) average 1.409(6) Å. The magnitude of C–C bond alternation is virtually identical with that for the unsubstituted benzene complex **10**.[34] The six chlorine atoms lie 0.04–0.06 Å from the C_6 least squares plane on the side distal to the $Cr(CO)_3$ fragment, so that when viewed from the *top* as in Figure 3, the C_6Cl_6 unit forms a very shallow concave bowl; the character and magnitude of this distortion is normal for η^6-arene complexes.[11,35]

Cyclic Voltammetry. A detailed study of oxidation potentials measured by cyclic voltammetry (CV) for (η^6-arene)$Cr(CO)_3$ complexes (eq 1) was recently reported by

$$(\eta^6\text{-arene})Cr(CO)_3 \rightleftharpoons (\eta^6\text{-arene})Cr(CO)_3^{\bullet +} + e^- \qquad (1)$$

Hunter and co-workers.[11] However, their investigation of electron-deficient species was hampered by the observation of irreversible oxidations when two or more electron-withdrawing groups were present on the η^6-arene ligand. Using methods developed by Mann and co-workers, we have obtained quasi-reversible CV data for **10**, **1**, **2**, and **4**–**6** (a sufficient quantity of pure **3** was not available at the time the CV experiments were carried out). These electrochemical data are summarized in Table 5. The major improvements implemented here were the use of Mann's electrolyte, tetra-*n*-butylammonium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate or TBA^+TFPB^-, and a faster scan rate of 500 mV/s. These conditions furnished ΔE and i_{pc}/i_{pa} values typical for quasi-reversible oxidation with the exception of **6**, which shows a relatively weak cathodic wave.

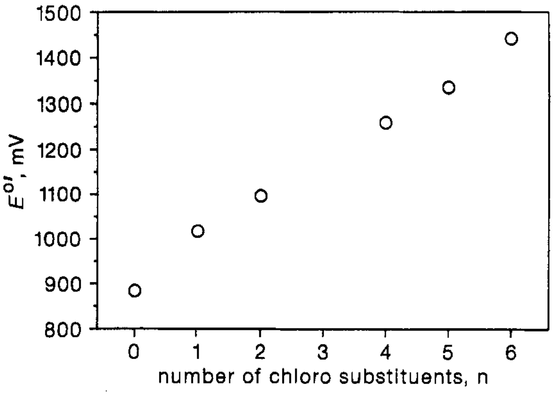

Figure 4. $E^{\circ\prime}$ of oxidation for (η^6-$C_6Cl_nH_{6-n}$)$Cr(CO)_3$ determined by cyclic voltammetry. Data are taken from Table 5.

The $E^{\circ\prime}$ values are plotted against the number of chloro substituents in Figure 4. The linear relationship suggested by Figure 4 ($r^2 = 0.994$) is particularly striking, considering Hunter's observation of electronic "saturation" effects in $E^{\circ\prime}$ data when several electron-releasing substituents were present on the η^6-arene ligand.[11] The additive effect of each chloro substituent raised $E^{\circ\prime}$ by 88 ± 4 mV. Average effects of 110, 150, and 208 mV per substituent had been previously reported for chloro, carbomethoxy, and trifluoromethyl.[11] The $E^{\circ\prime}$ value for **6** is the highest observed for any (η^6-arene)$Cr(CO)_3$ species. For the sake of comparison, the second highest value observed is 1380 mV (irreversible) for [η^6-$C_6H_3(COOCH_3)_3$]$Cr(CO)_3$, while the typical range for (η^6-arene)$Cr(CO)_3$ species is about 400–1400 mV.[11] A higher $E^{\circ\prime}$ value implies a more electron-deficient organometallic complex.

Conclusions

The described chlorination of **1** affords not only **2** but also meaningful yields of higher chlorinated species **3**–**6** as a mixture which is readily separated chromatographically. The latter complexes represent novel stable examples of (η^6-arene)$Cr(CO)_3$ species bearing several electron-withdrawing substituents. X-ray structural, infrared spectroscopic, and electrochemical data demonstrate that the electron-deficiency of the chromium center in (η^6-C_6Cl_6)$Cr(CO)_3$ (**6**) is unprecedented within this important class of organometallic complexes.

Acknowledgment. We wish to thank Professor Doyle Britton for X-ray crystallographic analysis and Dr. John R. Sowa, Jr., for the electrochemical analyses. This work was funded by the National Science Foundation under CHE-8921744-06.

Supplementary Material Available: Textual description of experimental procedures, tables of atomic coordinates, anisotropic thermal parameters, intramolecular distances and angles, conformational angles, least squares planes, and intermolecular distances, and packing diagrams (ORTEP, 50.0% probability ellipsoids; see ref 1 in supplementary material) for compound **6** (25 pages). Ordering information is given on any current masthead page.

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