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Chromium tricarbonyl-facilitated nucleophilic aromatic substitution by metal carbonyl anions. Synthesis and molecular structure of a new class of bimetallic .pi.-arene complexes

Joseph A. Heppert, Mark A. Morgenstern, Devin M. Scherubel, Fusao. Takusagawa, and Mohammad R. Shaker

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bling into the methylene. This would be inconsistent with both the spt and labeling data, and we suggest that the absence of unconstrained rotation reflects a significant agostic interaction in the isopropyl intermediate (see Schemes VI and VII).

The evidence for agostic alkyl intermediates in insertion reactions of **1**$^+$ is one of three ways in which our results complement those of Doherty and Bercaw on olefin insertion in [Nb(η-C_5Me_5)$_2$(RCH=CH_2)H] complexes.[18a] A second difference is that the availability of pure **1**$^+$-exo and **1**$^+$-endo has allowed us to monitor alkene rotation within **1**$^+$ (the Nb complexes are exclusively endo), and a third is that the neutral Nb complexes do not exhibit an equivalent of the deprotonation/protonation sequences observed with **1**$^+$. These are rapid when catalyzed by added base and have an effect on label distributions similar to that of alkene rotation.

The lack of evidence within this study for an indirect α-elimination, 1,2-hydride shift mechanism for overall β-elimination from the tungstenocene alkyls studied does not conflict with the previous evidence for chemically facile α-elimination within this system. A more reasonable interpretation is that the 1,2-hydride shift within an intermediate tungstenocene alkylidene hydride is slow: the β-carbon in the potential alkylidene intermediate must be held at some distance from the metal, and there is unlikely to be good overlap between the p orbital on the carbon that will form the alkene π-bond and the frontier orbital of the metal during the early stages of the 1,2-hydride shift. This would result in considerable unstabilized carbonium ion character in the transition state and disfavor the 1,2-hydride shift.[57] It seems probable that similar problems will arise in other systems, and we conclude that the combination of an α-elimination reaction with a 1,2-hydride shift is unlikely to be a common alternative to direct β-elimination.[58]

Acknowledgment. We thank Dr. Shaw Huang for helpful guidance in the spt experiments and the National Science Foundation for financial support. The Bruker AM-500 was purchased with the assistance of NSF Grant CHE-84-10774 to Harvard University.

Registry No. *endo*-**1**-PF_6, 114298-83-8; *exo*-**1**-PF_6, 114298-85-0; *endo*-**1**-d_5-PF_6, 114273-28-8; *exo*-**1**-d_5-PF_6, 114375-26-7; *endo*-**1**-d_6-PF_6, 114251-75-1; *exo*-**1**-d_6-PF_6, 114298-87-2; *endo*-**1**-d_7-PF_6, 114251-77-3; *exo*-**1**-d_7-PF_6, 114375-07-4; **2**, 37343-23-0; **2**-d_6, 114251-78-4; **3**-PF_6, 114251-80-8; **4**, 114251-81-9; **5**, 102977-68-4; $(CD_3)_2CHMgBr$, 99727-83-0; $(CD_3)_2CO$, 666-52-4; $(CD_3)_2CHOH$, 3976-29-2; $(CD_3)_2CHBr$, 52809-76-4; $(CD_3)_2CDMgBr$, 114251-82-0; $(CD_3)_2CDOD$, 22739-76-0; $(CD_3)_2CDBr$, 39091-63-9; $(CH_3)_2CHO$-TS, 2307-69-9; TsCl, 98-59-9; $(CH_3)_2CHOH$, 67-63-0; $(CH_3)_2CH$-MgBr, 920-39-8; [W(η-C_5H_5)$_2Cl_2$], 12184-26-8; W(η-C_5H_5)$_2$HLi, 53322-18-2.

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(57) A similar accumulation of charge on the β-carbon has been postulated for the rearrangement of electrophilic iron alkylidene species via a 1,2-hydride shift, and Brookhart has shown that alkyl substituents on the β-carbon of alkylidene complexes of the type [(η-C_5H_5)(CO)(PPh_3)-Fe=CHR]$^+$ greatly increase the rate of rearrangement to the alkene complex, presumably by stabilizing the incipient carbonium center formed in the transition state.[11c]

(58) Unless there are special factors such as the steric restraints operative in the platinacyclobutanes for which α-elimination routes to alkenes have been established: Parsons, E. J.; Jennings, P. W. *J. Am. Chem. Soc.* 1987, *109*, 3973–3977 and references therein.

Chromium Tricarbonyl Facilitated Nucleophilic Aromatic Substitution by Metal Carbonyl Anions: The Synthesis and Molecular Structure of a New Class of Bimetallic π-Arene Complexes

Joseph A. Heppert,* Mark. A. Morgenstern, Devin M. Scherubel, Fusao Takusagawa, and Mohammad R. Shaker[1]

Department of Chemistry, University of Kansas, Lawrence, Kansas 66045

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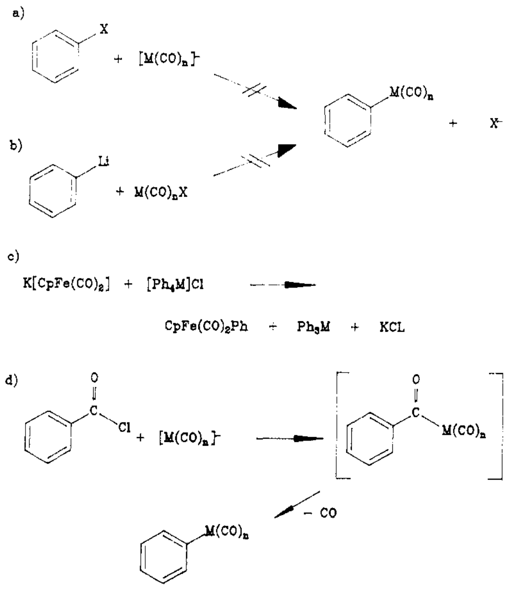
The highly nucleophilic metal carbonyl anions $[CpFe(CO)_2]^-$ and $[(C_5Me_5)Fe(CO)_2]^-$ ($C_5Me_5 \equiv Cp^*$) react with (η-XRC_6H_4)$Cr(CO)_3$ substrates in a previously unknown type of nucleophilic aromatic substitution to form (η^6-{$CpFe(CO)_2$}RC_6H_4)$Cr(CO)_3$ products. A variety of less reactive metal nucleophiles, including $[CpMo(CO)_3]^-$, $[CpNi(CO)]^-$, $[Mn(CO)_5]^-$, and $[Co(CO)_4]^-$, fail to participate in the substitution reactions. The structure of (η-{$CpFe(CO)_2$}ClC_6H_4)$Cr(CO)_3$ has been determined by X-ray crystallography. The compound crystallizes in the space group $P2_1/n$ with four molecules in the unit cell of dimensions a = 7.969 (2) Å, b = 18.982 (4) Å, c = 10.789 (2) Å, and β = 91.45 (3). Full-matrix least-squares refinement yielded R = 0.0353 for 2153 reflections. The structure shows that the conformation of the $Cr(CO)_3$ fragment is determined by a cogging of the carbonyl ligands of the $CpFe(CO)_2$ and $Cr(CO)_3$ units to avoid steric interactions, although ^1H and ^{13}C NMR studies failed to show a perceptible barrier to $Cr(CO)_3$ rotation about the Cr–$Ph_{centroid}$ vector. Certain haloarene substrates react predominantly through an apparent electron-transfer pathway to produce $[CpFe(CO)_2]_2$ and (η-RC_6H_5)$Cr(CO)_3$. The fraction of reduced products formed is dependent on (1) the reducing power of the anion ($[Cp^*Fe(CO)_2]^- \gg [CpFe(CO)_2]^-$), (2) the electron-donating ability of the R group (electron donor $\gg$ electron acceptor), (3) the substitution pattern of the arene (in general ortho $\gg$ meta $\cong$ para), and (4) the identity of the halogen leaving group ($I \gg Cl > F$).

The activation of carbon–hydrogen and carbon–halogen bonds in aromatic hydrocarbons by homogeneous transition-metal catalysts are processes of significant industrial importance.[2] A variety of Pd- and Ni-catalyzed reactions,

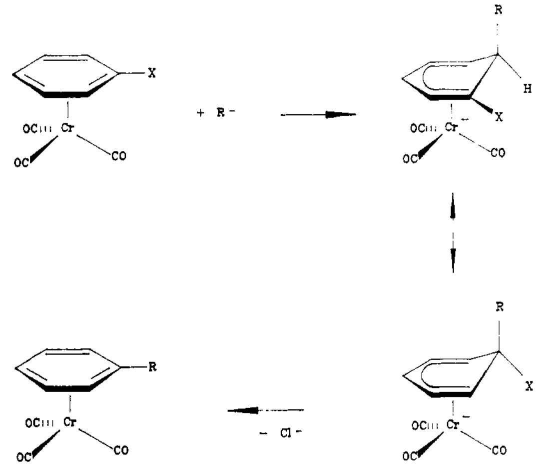
Scheme I



including selective arene oxidation,[3] arene oxidative coupling,[4] arene condensation and arene alkylation processes,[5] rely on the formation of metal–arene σ-bonds (M–C(Ar)) in reactive intermediates. The peculiar receptivity of arene C–H bonds toward activation by transition-metal complexes has been attributed to the formation of M–arene π-complexes prior to metal insertion into a C–H bond.[2a] The observation of π-bound intermediates during M–C(Ar) bond formation in cyclometalation reactions provided implicit support for this proposal,[6] and recent studies of photoinitiated C–H bond activation by rhodium complexes have confirmed the anticipated mechanism for the homogeneous activation of free arene molecules.[7]

Despite the common occurrence of organometallic compounds containing M–C(Ar) bonds, the direct synthesis of low-valent complexes containing simple σ-bound arene substituents is surprisingly difficult. This problem arises because nucleophilic substitution processes—including the reaction of metal carbonyl anions with haloarenes (Scheme Ia) and reactions between aryllithium reagents and metal carbonyl halides (Scheme Ib)—are not general routes to simple metal–arene σ-bonded complexes. Ellis[8] reported a high-yield route to $CpFe(CO)_2Ph$ by treating $K[CpFe(CO)_2]$ with $[MPh_4]Cl$ (M = P, As) (Scheme Ic). This procedure appears to be specific for $[CpFe(CO)_2]^-$ but, unfortunately, is not easily extended to include a range of substituted $[MAr_4]Cl$ derivatives. The most general route to simple σ-bonded metal–arene derivatives (Scheme Id) involves the reaction of metal carbonyl anions with benzoyl halides to produce metal–benzoyl intermediates, which are photolytically decarbonylated to form products containing a metal–arene σ-bond.[9] This method succeeds despite the low nucleophilicity of many metal anions and can, in principle, be used to synthesize numerous derivatives with functionality at the arene. A serious drawback of this process is that the decarbonylation step is frequently inefficient, presumably because of the significant kinetic barrier to migratory deinsertion in unsaturated acyl intermediates.[10]

Scheme II



In searching for new methods to synthesize complexes containing σ-bound arene substituents, we wondered whether η^6-arene or η^6-haloarene complexes would be activated toward attack by metal carbonyl nucleophiles. Semmelhack has extensively studied the factors influencing similar reactions of carbanion nucleophiles with (η^6-arene)$Cr(CO)_3$ and (η^6-haloarene)$Cr(CO)_3$ substrates.[11] Reagents such as phenyllithium, lithium acetylide, $Li[C(CH_3)_2CN]$, $Li[CH(CO_2Me)_2]$, and $Li[CH_2CO_2Me]$ react with (η^6-haloarene)$Cr(CO)_3$ complexes to irreversibly form η^5-cyclohexadienide complexes with a marked preference for the substitution at the meta site (Scheme II).[11] Over time, the cyclohexadienide complexes of the tertiary carbanions and the carbanions stabilized by two electron-withdrawing groups apparently rearrange to a gem-disubstituted intermediate, which spontaneously loses halide ion to form a neutral η^6-arene product.[11] We hoped to exploit this behavior of (η-haloarene)$Cr(CO)_3$ complexes to develop a new route to transition-metal–arene σ-bonds. In this paper, we report the first examples of $Cr(CO)_3$-mediated nucleophilic aromatic substitution by metal carbonyl anions.

Experimental Section

Reactions were performed in a water and oxygen-free environment using double-manifold Schlenk vacuum lines (equipped with vented Hg exhaust bubblers) and Kejldahl-type double-

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(1) Participant in the K.U. Summer Undergraduate Research Program. Current address: Department of Chemistry, Idaho State University, Pocatello, ID.

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schlenk glassware.[12] Solids were isolated and transferred in a dry N_2-filled Vacuum Atmospheres glovebox. All solvents were dried and deoxygenerated by refluxing over sodium benzophenone ketyl. Dioxane was predried by refluxing over CaH_2. NMR solvents were dried over activated 5-Å molecular sieves. Benzene-d_6 was deoxygenated with a dry N_2 purge, while acetone-d_6 was deoxygenated by repeated freeze–pump–thaw cycles.

^1H and ^{13}C NMR spectra were obtained on a Varian XL-300 NMR spectrometer. IR spectra were obtained as KBR pellets on an IBM IR/30S FT instrument. Low-resolution mass spectra were obtained on a Tribos Ribermag spectrometer using a direct insertion probe. Analytical data were obtained from Analytical Laboratories, Gummersback, FRG, and from Desert Analytics, Tuscon, AZ.

Preparation of Metal Carbonyl Anions. $Na[Co(CO)_4]$, $Na[Mn(CO)_5]$, $Na[CpNi(CO)]$, $Na[CpFe(CO)_2]$, and $K[(C_5Me_5)Fe(CO)_2]$ were prepared according to published procedures[13] and used without isolation. $[Me_4N][CpFe(CO)_2]$, whose synthesis is incompletely outlined in the literature, was prepared by metathesis of $K[CpFe(CO)_2]$ with $[Me_4N]Cl$. The KCl and $[Me_4N][CpFe(CO)_2]$ proved to be inseparable, and the 1:1 salt mixture was used for subsequent reactions. $[Et_4N][CpFe(CO)_2]$ was prepared by a modification of standard procedures:[13a] a 0.5% sodium amalgam (500 g) was prepared in a Schlenk-modified round-bottom flask (500 mL) containing a large magnetic stirbar. After the amalgam was washed twice with THF (20 mL), the flask was equipped with a pressure-equalized addition funnel containing $Cp_2Fe_2(CO)_4$ (15 g) dissolved in THF (350 mL). The solution was added dropwise to the flask and was stirred for 3 h. Recrystallized $[Et_4N]Br$ (17 g) was added to the flask by Schlenk addition tube, and the mixture was allowed to stir 12 h. Filtration of the resultant solution through Celite separated the product from the residual mercury and finely divided NaBr. The volume was reduced in vacuo (to 150 mL) and C_6H_6 (300 mL) was layered onto the solution. After 5 h the brown solution was decanted, leaving large red crystals of $[Et_4N][CpFe(CO)_2]$. Yield: 84% (22 g).

Preparation of (η^6-Arene)$Cr(CO)_3$ Derivatives. $(\eta^6\text{-}IC_6H_5)Cr(CO)_3$[14] was prepared according to the published method.

The synthesis of (η^6-haloarene)$Cr(CO)_3$ derivatives in refluxing Bu_2O frequently resulted in the formation of arene byproducts which were difficult to separate from the desired product. The general procedure that follows was adapted to alleviate this problem, and specific variations from the procedure are noted for each product.[15,16]

$[\eta^6\text{-}p\text{-}(CF_3)ClC_6H_4]Cr(CO)_3$ (1a). $Cr(CO)_6$ (3.4 g) was added to a Schlenk-modified round bottom (250 mL), and dioxane (120 mL) and $p\text{-}(CF_3)ClC_6H_4$ (17 mL) were added via syringe. The reaction was stirred and brought to a rapid reflux under a cover of dry N_2 gas. After 4 days, the reaction was cooled and filtered to separate unreacted $Cr(CO)_6$. After removal of the solvent in vacuo, the residue was transferred to a water-cooled sublimator and the product was sublimed as orange-yellow crystals under vacuum (100 °C, 10^{-2} Torr). Yield: 58% (2.4 g). Analytical data supported formulation of the product as $[\eta^6\text{-}p\text{-}(CF_3)ClC_6H_4]Cr(CO)_3$. IR (KBr): 1986.9, 1935.0, 1904.0 cm^{-1}. ^1H NMR spectral data (benzene-d_6, 22 °C): δ 4.66 (d, 2 H, $J_{H_AH_B}$ = 5.7 Hz), 4.19 (d, 2 H, $J_{H_AH_B}$ = 5.7 Hz).

$[\eta^6\text{-}m\text{-}(CF_3)ClC_6H_4]Cr(CO)_3$ (1b). IR (KBr): 1988.9, 1909.8 cm^{-1}. ^1H NMR spectral data (benzene-d_6, 22 °C): δ 5.00 (s, 1 H, ArH), 4.36 (d, 1 H, ArH, J_{BC} = 7.5 Hz), 4.20 (d, 1 H, ArH, J = 6.9 Hz), 3.99 (t, 1 H, AH, $J_{AB,BC}$ = 6.9 Hz).

$[\eta^6\text{-}p\text{-}(MeO_2C)ClC_6H_4]Cr(CO)_3$ (1c). Yield: 49%. IR (KBr): 1990.8, 1943.5, 1900.1, 1709.1 cm^{-1} (CO_2Me). ^1H NMR spectral data (benzene-d_6, 22 °C): δ 4.66 (d, 2 H, $J_{H_AH_B}$ = 6.6 Hz), 4.20 (d, 2 H, $J_{H_AH_B}$ = 6.6 Hz), 3.23 (s, 3 H, OCH_3).

$(\eta^6\text{-}p\text{-}F_2C_6H_4)Cr(CO)_3$ (1d). ^1H NMR spectral data (benzene-d_6, 22 °C): δ 4.36 (s, 4 H).

$(\eta^6\text{-}p\text{-}Cl_2C_6H_4)Cr(CO)_3$ (1e). IR (KBr): 1973.4, 1880.8 cm^{-1}. ^1H NMR spectral data (benzene-d_6, 22 °C): δ 4.41 (s, 4 H).

$(\eta^6\text{-}m\text{-}Cl_2C_6H_4)Cr(CO)_3$ (1f). IR (KBr): 1965.7, 1890.5 cm^{-1}. ^1H NMR spectral data (benzene-d_6, 22 °C): δ 4.73 (m, 1 H), 4.17 (m, 1 H), 4.08 (m, 2 H).

$[\eta^6\text{-}m\text{-}(CH_3O)ClC_6H_4]Cr(CO)_3$ (1g). IR (KBr): 1952.2, 1878.9 cm^{-1}. ^1H NMR spectral data (benzene-d_6, 22 °C): δ 4.72 (s, 1 H), 4.47 (t, 1 H, J = 6.6 Hz), 4.23 (d, 1 H, J = 6.3 Hz), 3.95 (d, 1 H, J = 6.3 Hz), 2.77 (s, 3 H, CH_3).

$[\eta^6\text{-}ClC_6H_5]Cr(CO)_3$ (1h). Yield: 44%. IR (KBr) 1968, 1881 cm^{-1}. ^1H NMR spectral data (benzene-d_6, 22 °C): δ 4.46 (d, 2 H, J = 5.4 Hz), 4.24 (m, 2 H, J = 5.4 Hz), 3.81 (t, 1 H, J = 5.4 Hz).

$[\eta^6\text{-}FC_6H_5]Cr(CO)_3$ (1h*). IR: 1971.5, 1880.8 cm^{-1}. ^1H NMR spectral data (benzene-d_6, 22 °C): δ 4.27 (m, 4 H), 4.63 (m, 1 H).

$[\eta^6\text{-}m\text{-}(CH_3)ClC_6H_4]Cr(CO)_3$ (1i). IR (KBr): 1971.5, 1869.3 cm^{-1}. ^1H NMR spectral data (benzene-d_6, 22 °C): δ 4.43 (m, 3 H, ArH), 3.77 (d, 1 H, ArH, J = 5.1 Hz), 1.44 (s, 3 H, CH_3).

$[\eta^6\text{-}p\text{-}(CH_3)ClC_6H_4]Cr(CO)_3$ (1j). IR (KBr): 1959.9, 1869.3 cm^{-1}. ^1H NMR spectral data (benzene-d_6, 22 °C): δ 4.69 (d, 2 H, J = 5.7 Hz), 4.18 (d, 2 H, J = 5.7 Hz), 1.32 (s, 3 H).

$[\eta^6\text{-}p\text{-}(CH_3O)ClC_6H_4]Cr(CO)_3$ (1k). IR: 1961, 1855 cm^{-1}. ^1H NMR spectral data (benzene-d_6, 22 °C): δ 4.84 (d, 2 H, ArH, J 6.9 Hz), 4.12 (d, 2 H, ArH, $J_{H_AH_B}$ = 6.9 Hz), 2.72 (s, 3 H, CH_3).

$(\eta^6\text{-}o\text{-}Cl_2C_6H_4)Cr(CO)_3$ (1l). IR: 1969.6, 1880.8 cm^{-1}. ^1H NMR spectral data (benzene-d_6, 22 °C): δ 6.11 (m, 2 H, ArH), 5.65 (m, 2 H, ArH).

$[\eta^6\text{-}o\text{-}(CH_3O)ClC_6H_4]Cr(CO)_3$ (1m). IR: 1958.0, 1890.5 cm^{-1}. ^1H NMR spectral data (benzene-d_6, 22 °C): δ 5.02 (dd, 1 H, ArH, J = 6.3, 0.9 Hz), 4.28 (td, 1 H, ArH, J = 5.7 Hz), 3.98 (d, 1 H, ArH, J = 6.3 Hz), 3.89 (t, 1 H, ArH, J = 5.7 Hz), 2.91 (s, 3 H).

$(\eta^6\text{-}C_6H_6)Cr(CO)_3$ (1n). IR: 1966, 1865 cm^{-1}. Yield: 62.2%. ^1H NMR spectra data (benzene-d_6, 22 °C): δ 4.28 (s, 6 H).

$[\eta^6\text{-}(CF_3)(C_6H_5)]Cr(CO)_3$ (1o). IR: 1967.8, 1894.3 cm^{-1}. Yield: 38%. ^1H NMR spectral data (benzene-d_6, 22 °C): δ 4.68 (d, 2 H, $J_{H_AH_B}$ = 6.6 Hz), 4.20 (t, 1 H, $J_{H_AH_B}$ = 6.3 Hz), 3.98 (t, 2 H, $J_{H_AH_B}$ = 6.6 Hz).

Synthesis of $[\eta^6\text{-}(CpFe(CO)_2]RC_6H_4]Cr(CO)_3$ Derivatives. The following general procedure was used for preparative reactions between $[CpFe(CO)_2]^-$ and (η^6-haloarene)$Cr(CO)_3$ derivatives:

$[\eta^6\text{-}p\text{-}(CF_3)\{CpFe(CO)_2\}C_6H_4]Cr(CO)_3$ (2a). $[Et_4N][CpFe(CO)_2]$ (0.39 g) and **1a** (0.40 g) were added to a 50-mL Erlenmeyer flask that was sealed with two serum caps. THF (5 mL) was added via cannula, and the flask was rapidly swirled to dissolve the reactants. The appearance of the solution rapidly changed to yellow-brown, and a light colored precipitate formed. After 8 h, the flask was opened in air, the contents were filtered, and the white solid on the frit was washed with several volumes of acetone (4-mL total). The white solid showed no features in the terminal CO stretching region of the IR spectrum. The solvent was removed in vacuo, and the residue was thoroughly extracted with cold Et_2O (10 mL, −10 °C). The Et_2O was evaporated in vacuo, and the light brown oily residue was identified by ^1H NMR spectroscopy as a 2:1 molar ratio of $[\eta^6\text{-}(CF_3)C_6H_5]Cr(CO)_3$ and $Cp_2Fe_2(CO)_4$, respectively. Small sets of resonances associated with the major product were also observed in this fraction.

The remaining yellow-orange solid was extracted into hot toluene (12 mL, 90 °C), filtered, and evaporated to saturation at 90 °C. Refrigeration at −20 °C for 8 h yielded bright orange-yellow crystals that were identified as $[\eta^6\text{-}p\text{-}(CF_3)\{CpFe(CO)_2\}C_6H_4]Cr(CO)_3$ (**2a**) by ^1H and ^{13}C NMR spectroscopy, IR spectroscopy, mass spectrometry, and elemental analysis. Yield: 39% (0.27 g). IR (KBr): 2031.3, 1993.7, 1949.3, 1887.5, 1863.5 cm^{-1}. ^1H NMR for **2a** (acetone-d_6, 20 °C): δ 5.75 (d, 2 H, Ar, $J_{H_AH_B}$ = 6.9 Hz), 5.61 (d, 2 H, Ar, $J_{H_AH_B}$ = 6.9 Hz), 5.22 (s, 5 H, Cp). ^{13}C NMR for **2a** (acetone-d_6, 20 °C, including representative coupling

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(12) Kejldahl-type Schlenk-ware can be obtained from Kontes Glass Co.

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(16) Strohmeier, W. *Z. Naturforsch.* **1962**, *175*, 627.

constants): δ 233.8 (s, $Cr(CO)_3$), 215.5 (s, $CpFe(CO)_2$), 132.5, 123.6 (s, ipso-Ar), 106.4 (dd, Ar, J_{CH} = 175 Hz, J_{CH} = 10.7 Hz). Anal. Calcd: C, 44.57; H, 1.98. Found: C, 44.81; H, 1.98. MS: *m/e* 458 (m^+), 402 (m^+ – 2CO), 374 (m^+ – 3CO), 346 (m^+ – 4CO), 318 (m^+ – 5CO). A ^1H NMR assay of the remaining mother liquor displayed a 6:1 ratio of **2a** to $Cp_2Fe_2(CO)_4$, but no attempt was made to continue fractional crystallization from this mixture.

$[\eta^6$-*m*-$(CF_3)\{CpFe(CO)_2\}C_6H_4]Cr(CO)_3$ (2b). Starting materials: **1b** (0.32 g) and $[Et_4N][CpFe(CO)_2]$ (0.385 g). Yield of **2b**: 60% (0.24 g). IR (KBr): 2019.7, 1950.3, 1893.5, 1862.0 cm^{-1}. ^1H NMR for **2b** (acetone-d_6, 20 °C): δ 5.88 (s, 1 H, Ar), 5.82 (d, 1 H, Ar, $J_{H_AH_B}$ = 6.6 Hz), 5.77 (d, 1 H, Ar, $J_{H_AH_B}$ = 6.6 Hz), 5.38 (t, 1 H, Ar, $J_{H_AH_B}$ = 6.6 Hz), 5.24 (s, 5 H, Cp). ^{13}C NMR for **2b** (acetone-d_6, 20 °C): δ 234.2 (s, $Cr(CO)_3$), 215.4 (s, $CpFe(CO)_2$), 130.1 (s, ipso-Ar), 121.6 (d, Ar), 111.6 (dt, Ar), 105.7 (dd, Ar), 92.0 (d, Ar), 87.6 (dquin, Cp). Anal. Calcd: C, 44.57; H, 1.98. Found: C, 44.46; H, 1.97. MS: *m/e* 458 (m^+), 402 (m^+ – 2CO), 374 (m^+ – 3CO), 346 (m^+ – 4CO), 318 (m^+ – 5CO).

$[\eta^6$-*p*-$(MeO_2C)\{CpFe(CO)_2\}C_6H_4]Cr(CO)_3$ (2c). Starting materials: **1c** (0.41 g) and $[Et_4N][CpFe(CO)_2]$ (0.41 g). Yield of **2c**: 63% (0.37 g). IR (KBr): 2023.6, 1975.4, 1950.3, 1893.0, 1871.2, 1714.9 cm^{-1} (CO_2Me). ^1H NMR for **2c** (acetone-d_6, 20 °C): δ 5.98 (d, 2 H, Ar, $J_{H_AH_B}$ = 7.5 Hz), 5.62 (d, 2 H, Ar, $J_{H_AH_B}$ = 7.5 Hz), 5.20 (s, 5 H, Cp), 3.81 (s, 3 H, CO_2CH_3). ^{13}C NMR for **2c** (acetone-d_6, 20 °C): δ 233.4 (s, $Cr(CO)_3$), 214.2 (s, $CpFe(CO)_2$), 196.6 (s, $CH_3OC(O)Ar$), 85.8 (dquin, Cp), 52.2 (q, CH_3O, J_{CH} = 147 Hz). Anal. Calcd: C, 48.24; H, 2.70. Found: C, 48.32; H, 2.69. MS: *m/e* 448 (m^+), 392 (m^+ – 2CO), 364 (m^+ – 3CO), 336 (m^+ – 4CO), 308 (m^+ – 5CO).

$[\eta^6$-*p*-$F\{CpFe(CO)_2\}C_6H_4]Cr(CO)_3$ (2d). Starting materials: **1d** (0.32 g) and $K[CpFe(CO)_2]$ (0.28 g). Yield of **2d**: 41% (0.22 g). IR (KBr): 2021.0, 1960.5, 1861.4 cm^{-1}. ^1H NMR for **2d** (acetone-d_6, 20 °C): δ 4.85 (m, 2 H, Ar), 4.70 (m, 2 H, Ar), 3.89 (s, 5 H, Cp). ^{13}C NMR for **2d** (acetone-d_6, 20 °C): δ 235.5 (s, $Cr(CO)_3$), 214.9 (s, $CpFe(CO)_2$), 148.7 (d, ipso-Ar, J_{CF} = 260 Hz), 113.3 (s, ipso-Ar), 109.1 (dq, Ar), 87.0 (dquin, Cp), 82.6 (dd, Ar). Anal. Calcd: C, 47.09; H, 2.22. Found: C, 47.15; H, 2.11. MS: *m/e* 408 (m^+), 352 (m^+ – 2CO), 234 (m^+ – 3CO), 296 (m^+ – 4CO), 268 (m^+ – 5CO).

$[\eta^6$-*p*-$Cl\{CpFe(CO)_2\}C_6H_4]Cr(CO)_3$ (2e). Starting materials: **1e** (0.30 g) and $K[CpFe(CO)_2]$ (0.25 g). Yield of **2e**: 22% (0.10 g). IR (KBr): 2019.7, 1971.5, 1942.6, 1863.5 cm^{-1}. ^1H NMR for **2e** (C_6D_6, 20 °C): 4.79 (m, 4 H, Ar), 3.78 (s, 5 H, Cp). ^{13}C NMR for **2e** (acetone-d_6, 20 °C): δ 234.6 (s, $Cr(CO)_3$), 214.0 (s, $CpFe(CO)_2$), 107.7 (dd, Ar), 92.8 (d, Ar), (dquin, Cp). Anal. Calcd C, 45.26; H, 2.14. Found: C, 44.82; H, 2.10. MS: *m/e* 424 (m^+), 368 (m^+ – 2CO), 340 (m^+ – 3CO), 312 (m^+ – 4CO), 284 (m^+ – 5CO).

$[\eta^6$-*m*-$Cl\{CpFe(CO)_2\}C_6H_4]Cr(CO)_3$ (2f). Starting materials: **1f** (0.39 g) and $[Et_4N][CpFe(CO)_2]$ (0.42 g). Yield of **2e**: 36% (0.21 g). IR (KBr): 2033.2, 1981.1, 1944.5, 1898.2, 1870.0 cm^{-1}. ^1H NMR for **2f** (acetone-d_6, 20 °C): δ 5.74 (s, 1 H, Ar), 5.51 (m, 2 H, Ar), 5.34 (d, 1 H, $J_{H_AH_B}$ = 7.2 Hz), 5.21 (s, 5 H, Cp). ^{13}C NMR for **2f** (acetone-d_6, 20 °C): δ 235.1 (s, $Cr(CO)_3$), 215.5 (s, $CpFe(CO)_2$), 128.1 (d, ipso-Ar), 114.9 (d, ipso-Ar), 108.3 (dd, Ar), 105.9 (dt, Ar), 96.3 (d, Ar), 90.8 (dt, Ar), 87.6 (dquin, Cp). Anal. Calcd: C, 45.26; H, 2.14; Cl, 8.35. Found: C, 44.62; H, 2.13; Cl, 8.33. MS: *m/e* 426, 424 (m^+), 370, 368 (m^+ – 2CO), 342, 340 (m^+ – 3CO), 314, 312 (m^+ – 4CO), 286, 284 (m^+ – 5CO).

$[\eta^6$-*m*-$(CH_3O)\{CpFe(CO)_2\}C_6H_4]Cr(CO)_3$ (2g). Starting materials **1g** (0.40 g) and $[Et_4N][CpFe(CO)_2]$ (0.44 g). Yield of **2g**: 36% (0.22 g). IR (KBr): 2025.5, 1969.6, 1934.8, 1850.0 cm^{-1}. ^1H NMR for **2g** (acetone-d_6, 20 °C): δ 5.54 (s, 1 H, Ar), 5.51 (m, 1 H, Ar), 5.19 (m, 1 H, Ar), 5.17 (s, 5 H, Cp), 5.11 (d, 1 H, Ar $J_{H_AH_B}$ = 6.9 Hz), 3.68 (s, 3 H, CH_3O). ^{13}C NMR for **2g** (acetone-d_6, 20 °C): δ 236.1 (s, $Cr(CO)_3$), 215.8 (s, $CpFe(CO)_2$), 102.9 (dt, Ar), 97.4 (dm, Ar), 97.1 (dd, Ar), 87.5 (dquin, Cp), 76.6 (d, Ar), 55.5 (q, OCH_3, J_{CH} = 147 Hz). Anal. Calcd: C, 48.60; H, 2.88. Found: C, 49.06; H, 3.06. MS: *m/e* 420 (m^+), 364 (m^+ – 2CO), 336 (m^+ – 3CO), 308 (m^+ – 4CO), 280 (m^+ – 5CO), 265 (m^+ – 5CO – CH_3).

$[\eta^6$-$\{CpFe(CO)_2\}C_6H_5]Cr(CO)_3$ (2h). Starting materials: **1h** (0.50 g) and $K[CpFe(CO)_2]$ (0.45 g). Yield of **2h**: 30% (0.24 g). Starting materials: **1h*** (0.50 g) and $K[CpFe(CO)_2]$ (0.47 g). Yield of **2h**: 50% (0.46 g). IR (KBr): 2019.7 1973.4, 1934.8, 1951.0 cm^{-1}. ^1H NMR for **2h** (acetone-d_6, 20 °C): δ 5.55 (dd, 2 H, Ar, $J_{H_AH_B}$ = 6.3 Hz, and $J_{H_AH_B}$ = 1.8 Hz), 5.33 (m, 3 H, Ar), 5.16 (s, 5 H, Cp). ^{13}C NMR for **2h** (acetone-d_6, 20 °C): δ 235.6 (s, $Cr(CO)_3$), 214.5 (s, $CpFe(CO)_2$), 121.6, 117.5 (s, ipso-Ar), 108.2 (dt, Ar), 94.4 (dd, Ar), 90.7 (d, Ar), 85.8 (dquin, Cp). Anal. Calcd: C, 49.26; H, 2.58. Found: C, 49.08; H, 2.97. MS: *m/e* 390 (m^+), 334 (m^+ – 2CO), 306 (m^+ – 3CO), 278 (m^+ – 4CO), 250 (m^+ – 5CO).

$[\eta^6$-*m*-$(CH_3)\{CpFe(CO)_2\}C_6H_4]Cr(CO)_3$ (2i). Starting materials: **1i** (0.34 g) and $[Et_4N][CpFe(CO)_2]$ (0.40 g). Yield of **2i**: 55% (0.29 g). IR (KBr): 2018.8, 1972.5, 1931.9, 1872.0, 1850.9 cm^{-1}. ^1H NMR for **2i** (acetone-d_6, 20 °C): δ 5.49 (s, 1 H, Ar), 5.38 (m, 3 H, Ar), 5.15 (s, 5 H, Cp), 2.07 (s, 3 H, CH_3). ^{13}C NMR for **2i** (acetone-d_6, 20 °C): δ 236.5 (s, $Cr(CO)_3$), 215.8 (s, $CpFe(CO)_2$), 132.2, 127.4 (s, ipso-Ar), 111.0 (dquin, Ar), 107.0 (dt, Ar), 97.3 (d, Ar), 92.0 (dq, Ar), 87.5 (dquin, Cp), 20.8 (q, CH_3, J_{CH} = 128 Hz). Anal. Calcd: C, 50.53; H, 2.99. Found: C, 50.81; H, 3.07. MS: *m/e* 404 (m^+), 348 (m^+ – 2CO), 320 (m^+ – 3CO), 292 (m^+ – 4CO), 264 (m^+ – 5CO).

$[\eta^6$-*p*-$(CH_3)\{CpFe(CO)_2\}C_6H_4]Cr(CO)_3$ (2j). Starting materials: **1j** (0.50 g) and $K[CpFe(CO)_2]$ (0.45 g). Yield of **2j**: 15% (0.07 g). IR (KBr): 2019.7, 1967.6, 1934.8, 1853.8 cm^{-1}. ^1H NMR for **2j** (C_6D_6, 20 °C): δ 4.97 (d, 2 H, Ar, $J_{H_AH_B}$ = 6.3 Hz), 4.50 (d, 2 H, Ar, $J_{H_AH_B}$ = 6.3 Hz), 3.90 (s, 5 H, Cp), 1.70 (s, 3 H, CH_3). ^{13}C NMR for **2j** (acetone-d_6, 20 °C): δ 236.2 ($Cr(CO)_3$), 214.5 ($CpFe(CO)_2$), 114.1 (ipso-Ar), 109.5 (Ar), 94.8 (Ar), 85.8 (Cp), 19.8 (CH_3). Anal. Calcd: C, 50.53; H, 2.99. Found: C, 49.70; H, 3.60. MS: *m/e* 404 (m^+), 348 (m^+ – 2CO), 320 (m^+ – 3CO), 292 (m^+ – 4CO), 264 (m^+ – 5CO).

$[\eta^6$-$\{(C_5Me_5)Fe(CO)_2\}C_6H_5]Cr(CO)_3$ (3). A THF solution of $K[(C_5Me_5)Fe(CO)_2]$ (1.96 g) was transferred onto solid **1h*** (1.59 g) by cannula. The mixture was stirred for 12 h. The solvent was removed in vacuo, the solid washed with ether at –10 °C, and the product extracted into hot toluene. Crystals were obtained from toluene at –20 °C. Yield: 10% (0.315 g). IR (KBr): 2001, 1953, 1944, 1933, 1872, 1848 cm^{-1}. ^1H NMR spectral data (benzene-d_6, 22 °C): δ 4.90 (d, 2 H, *o*-ArH, $J_{H_AH_B}$ = 6.3 Hz), 4.67 (t, 2 H, *m*-ArH, $J_{H_AH_B}$ = 6.3), 4.49 (t, 1 H, *p*-ArH, $J_{H_AH_B}$ = 6.3 Hz), 1.09 (s, 15 H, C_5Me_5). ^1H NMR spectral data (acetone-d_6, 22 °C): δ 5.40 (m, 4 H, *m*- and *p*-ArH), 5.27 (m, 1 H, *o*-ArH), 1.75 (s, 15 H, C_5Me_5). ^{13}C NMR data (acetone-d_6, 22 °C): δ 236.4 (s, $Cr(CO)_3$), 217.1 (s, $Cp^*Fe(CO)_2$), 138 (s, ipso-Ar), 97.5 (s, ipso-Cp*), 107.8, 97.4, 91.5 (*o*-, *m*- and *p*-Ar, J_{CH} = 174 Hz), 9.45 (q, Cp*-Me, J_{CH} = 127.3 Hz). Anal. Calcd: C, 54.80; H, 4.38. Found: C, 54.83; H, 4.54. MS: *m/e* 460 (m^+), 404 (m^+ – 2CO), 376 (m^+ – 3CO), 348 (m^+ – 4CO), 320 (m^+ – 5CO).

Reaction of 1k with $[Et_4N][CpFe(CO)_2]$. Preparative scale reactions between **1k** and $[CpFe(CO)_2]^-$ failed to yield any crystalline product. A small scale reaction between **1k** (50 mg) and $[Et_4N][CpFe(CO)_2]$ in THF was evaporated to dryness and dissolved in C_6D_6. The ^1H NMR spectrum of the resulting mixture showed that the major products of the reaction were $\{\eta^6$-$(MeO)C_6H_5\}Cr(CO)_3$ and $Cp_2Fe_2(CO)_4$ in an approximate 2:1 molar ratio. Small sets of resonances in the methoxide, cyclopentadienide, and π-arene regions of the spectrum suggested that a small amount (≤12%) of $[\eta^6$-*p*-$(MeO)\{CpFe(CO)_2\}C_6H_4]Cr(CO)_3$ was also formed. ^1H NMR data (benzene-d_6, 22 °C): δ 5.12, 5.91 (d, 2 H, ArH, $J_{H_AH_B}$ = 5.7 Hz), 4.02 (s, 5 H, Cp), 2.80 (s, 3 H, MeO).

Product Distribution Data. Data concerning product distributions were characteristically obtained by dissolving the entire product mixture of a small-scale reaction in acetone-d_6 and determining the product ratios by integration of the ^1H NMR spectrum. Typical conditions for one such reaction follows:

$[Et_4N][CpFe(CO)_2]$ (25 mg) and $(\eta$-$ClC_6H_5)Cr(CO)_3$ (20 mg) were added to a small Erhlenmeyer flask. The flask was capped with two cerum caps, and THF (25 ml) was added via syringe. After 12 h, the flask was opened in air and the contents were filtered in air through glass wool to separate a small amount of colorless powder and the supernatant liquid was evaporated to dryness. The entire sample was dissolved in acetone-d_6, and a ^1H NMR spectroscopic assay yielded the following product ratios: $[CpFe(CO)_2]_2$:$(\eta$-$C_6H_6)Cr(CO)_3$:$(\eta$-$\{CpFe(CO)_2\}C_6H_5)Cr(CO)_3$ = 1.00:1.64:11.26.

Crystallographic Study

A suitable sized crystal of $(\eta$-*p*-$\{CpFe(CO)_2\}ClC_6H_4)Cr(CO)_3$ (**2e**) was mounted on a glass fiber by using epoxy glue in air. The only observed systematic absences were $0k0$ for $k = 2n + 1$ and $h0l$

Table I. Summary of Crystal Data for 2e

empirical formula	$CrFeClC_{16}H_9O_5$
color of cryst	yellow-brown
cryst dimens, mm	0.10 × 0.07 × 0.05
space group	$P2_1/n$
cell dimens (25 °C)	
a, Å	7.969 (2)
b, Å	18.982 (4)
c, Å	10.789 (2)
β, deg	91.45 (3)
Z, molecules/cell	4
V, Å^3	1631.5 (6)
d(calcd), g/cm^3	1.728
X-ray radiatn	Mo K$\bar{\alpha}$ (λ = 0.71069 Å)
mol wt	424.54
linear abs coeff, cm^{-1}	17.912
av ω scan width, deg	0.3
scan speed, deg/min	0.5–10.0
scan width, deg	1.3 below Kα_1 and 1.3 above Kα_2
bkgd range	$^1/_6$ of scan at edges
aperture size, mm	0.5
2θ range, deg	4–45
total no. of reflctns collected	2382
no. of unique reflctns	2153
$R(F)$	0.0353
$R_w(F)$	0.0455
goodness of fit for last cycle	1.0797
max Δ/σ for last cycle	0.09

for $h + l = 2n + 1$, unambiguously identifying the space group as $P2_1/n$. Data were collected on a Syntex $P2_1$ diffractometer using a θ–2θ scan procedure. Since a ψ-scan of the data did not show any significant intensity change, the data were not corrected for absorption. All of the observed reflections were used for the structure determination and refinement. The structure was solved by the heavy-atom method. All hydrogen atoms were located in a difference electron density map and were introduced into the full-matrix least-squares refinement with isotropic thermal parameters. The $\Sigma w(|F_o| - |F_c|)^2$ is minimized, for $w = 1/\sigma(F_o)^2$. The final difference electron density map was featureless (±0.18 e/Å^3). Atomic scattering factors were taken from the *International Tables for X-ray Crystallography* (1974). All calculations were performed on a Honeywell 66/6000 computer at the University of Kansas using programs of the KUDNA system (Takusagawa, 1984). A summary of the experimental details is collected in Table I.

Results and Discussion

Reactions of $[CpFe(CO)_2]^-$ with (η^6-Haloarene)Cr$(CO)_3$ Derivatives. Potassium and tetraethylammonium salts of $[CpFe(CO)_2]^-$ participate in nucleophilic attack on $(\eta^6\text{-}RClC_6H_4)Cr(CO)_3$ substrates, producing $[\eta^6\text{-}\{CpFe(CO)_2\}RC_6H_4]Cr(CO)_3$ derivatives (eq 1).[17] The products

$$M[CpFe(CO)_2] + (\eta^6\text{-}RClC_6H_4)Cr(CO)_3 \xrightarrow{THF} [\eta^6\text{-}\{CpFe(CO)_2\}RC_6H_4]Cr(CO)_3 + MCl \quad (1)$$

$$M = Na^+, [Et_4N]^+$$

are yellow or yellow-orange crystalline solids that are isolated by fractional crystallization from toluene. Purification of the products can also be achieved by fractional sublimation of $[CpFe(CO)_2]_2$ contaminant at 50 °C (10^{-5} Torr), followed by sublimation of the bright yellow bimetallic complex at 100 °C. All of the bimetallic arene derivatives can be handled in nondeaerated solvents for short periods of time without substantial decomposition.

The potassium salt of $[(C_5Me_5)Fe(CO)_2]^-$ reacts with $(\eta\text{-}FC_6H_5)Cr(CO)_3$ to produce $[\eta^6\text{-}\{(C_5Me_5)Fe(CO)_2\}C_6H_5]Cr(CO)_3$ (**3**), as shown in eq 2. The overall

$$K[(C_5Me_5)Fe(CO)_2] + (\eta\text{-}FC_6H_5)Cr(CO)_3 \xrightarrow[22\ °C]{THF} [\eta\text{-}\{(C_5Me_5)Fe(CO)_2\}C_6H_5]Cr(CO)_3 + KF \quad (2)$$

yield of **3** has only been optimized to 10%, and the reaction is specific for the fluorobenzene substrate. Reactions employing $(\eta\text{-}ClC_6H_5)Cr(CO)_3$ result in the isolation of $[(C_5Me_5)Fe(CO)_2]_2$ and $(\eta\text{-}C_6H_6)Cr(CO)_3$ in a 1:1 molar ratio.

The infrared spectra of the bimetallic products contain three distinct groups of terminal CO stretching bands. A single sharp band appears in the range 2035–2015 cm^{-1}, and a single broad band, which resolves into two bands in a few instances, appears near 1890–1850 cm^{-1}. The third region of the spectra, 1975–1935 cm^{-1}, contains either one or two bands, which appear on preliminary inspection to shift randomly over a range of frequencies. Despite the reduced symmetry undoubtedly imposed by the solid state, the following reasonable correspondences between the observed CO stretching bands and the expected molecular vibrational modes can be developed: (1) The high-energy band near 2020 cm^{-1} in all of the spectra corresponds to the high-energy stretching mode of the $CpFe(CO)_2$ fragment. This assignment is supported by comparing the spectra of the coupled products with the spectra of known $CpFe(CO)_2R$ derivatives[9] and through the relative insensitivity of the energy of this band to changing substitution at the arene. (2) A low-energy absorption, which may appear as one or two bands between 1895 and 1850 cm^{-1}, represents the band of nominal E symmetry associated with the $Cr(CO)_3$ unit. This band, which is highlighted for each derivative, appears in the approximate energy region expected for the E symmetry CO vibration of a $Cr(CO)_3$ fragment[16] and, like the corresponding band in the π-haloarene precursors, shifts from higher energy (1875 cm^{-1}) in the presence of electron-withdrawing groups to lower energy (1860 cm^{-1}) in the presence of electron-donating methyl substituents. This band is consistently shifted to lower energy in the $CpFe(CO)_2$-substituted products as compared with the chloroarene precursors, suggesting that the $CpFe(CO)_2$ unit is electron-donating to the arene ring *by comparison with* the Cl group. (3) The remaining bands in the region between 1975 and 1935 cm^{-1} must, therefore, represent the remaining two modes of molecular vibration, one each from $CpFe(CO)_2$ and $Cr(CO)_3$. The band that consistently appears near 1950 cm^{-1} in each isomer could tentatively be assigned to the low-energy vibration of the $CpFe(CO)_2$ fragment, which is expected to show only a small shift with varying substitution at the arene. The remaining bands, which are also highlighted, slowly shift from 1995 to 1970 cm^{-1} as more strongly electron-releasing substituents are added to the arene. The direction in which these bands shift is apparently consistent with the behavior expected of the remaining vibrational band of the $Cr(CO)_3$ unit. Unfortunately, the assignment of bands in this third region to a unique metal carbonyl fragment may be invalid because their similar energies probably result in significant mixing of the expected vibrational modes of the separate metal fragments.

These proposed assignments can be cross-checked by comparing the spectrum of **2h** with that of its pentamethylcyclopentadienyl analogue **3**, both of which are shown in Figure 1. As expected, the 2019.7 cm^{-1} band associated with the $CpFe(CO)_2$ unit of **2h** shifts to 2001 cm^{-1} in the presence of the electron-releasing C_5Me_5 unit of **3**, while one of the bands that results from the $Cr(CO)_3$ fragment is essentially unshifted from 1850 cm^{-1} in both

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[17] Another researcher has reported the preparation of **2h** by reaction of $Cr(CO)_6$ and $CpFe(CO)_2Ph$ in refluxing Bu_2O. Although complete analytical data was not provided, the IR spectrum of **2h** corresponds closely to that of the reported product: Nesmeyanov, A. N.; Polovyanyuk, I. V.; Nakarova, L. G. *Dokl. Akad. Nauk SSSR* **1976**, *230*, 1351.

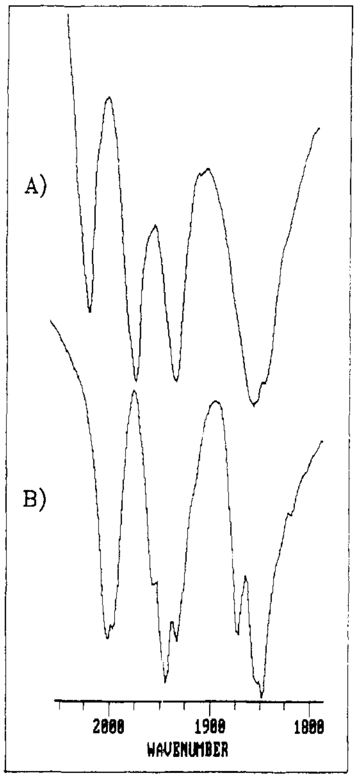
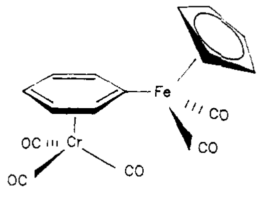


Figure 1. IR spectra (as KBr pellets) of the terminal CO stretching region for (A) (η-{CpFe(CO)$_2$}C$_6$H$_5$)Cr(CO)$_3$ (**2h**) and (B) (η-{Cp*Fe(CO)$_2$}C$_6$H$_5$)Cr(CO)$_3$ (**3**).

spectra. The remaining vibrational bands are more difficult to assign. The 1973.4 cm^{-1} band of **2h**, tentatively assigned to the Cr(CO)$_3$ fragment, apparently shows a large unexpected shift to 1948 cm^{-1}, and the remaining band originally assigned to the CpFe(CO)$_2$ fragment appears near 1935 cm^{-1} in both compounds. These inconsistencies support the assumption that vibrational modes associated with the two metal carbonyl fragments mix in the 1995–1935 cm^{-1} region.

The ^{1}H and ^{13}C NMR spectra of the products indicate that a single substitutional isomer is formed in each reaction and that the products result from direct replacement of the halogen atom in the precursor complex. The absence of rearranged products argues strongly against the possibility of benzyne and metal hydride intermediates acting in the substitution process. As with all chromium π-arene derivatives, the positions of the arene proton resonances in the products lie between δ 5.0 and δ 3.5 in benzene-d_6, shifting to between δ 6.2 and δ 4.5 in acetone-d_6.

The ^{13}C NMR spectra show two distinct resonances for the carbonyl ligands, with the resonance near 230 ppm representing the Cr(CO)$_3$ fragment and the resonance near 215 ppm arising from the CpFe(CO)$_2$ unit. The equivalence of the carbonyl ligands of the Cr(CO)$_3$ fragment at 20 °C indicates that rotation about the Cr–Ph$_{\text{cent.}}$ vector is rapid. Similar free rotation is not, however, required to generate equivalent carbonyl ligands in the CpFe(CO)$_2$ fragment. The static structure I generates the mirror plane through the iron center necessary to produce equivalent CO ligands. In fact, it might be expected that the CpFe(CO)$_2$ or Cp*Fe(CO)$_2$ units would display some preference for placing the cyclopentadienide ligand in an anti conformation with respect to the Cr(CO)$_3$ unit (see the discussion of the X-ray structure below). Variable-temperature ^{1}H and ^{13}C NMR spectra show no evidence for freezing out an asymmetric rotomer of **2h** or **3** at temperatures approaching −90 °C. Significant temperature dependent chemical shifts involving the *m*- and *o*-arene proton resonances do occur over this range, suggesting that some changes in the average relative position of the arene and the CpFe(CO)$_2$ unit are occurring. For example, the arene proton resonances of **3** undergo a dramatic change from an apparent ABCBA pattern to an AA′BB′M pattern over the range of 0–20 °C. On the basis of these spectroscopic data, we can *infer* that there is a low barrier to rotation about the Fe–C$_{\text{arene}}$ bond, that certain rotational isomers of the compound are slightly energetically preferred, and that the rotational conformers become completely averaged near room temperature.



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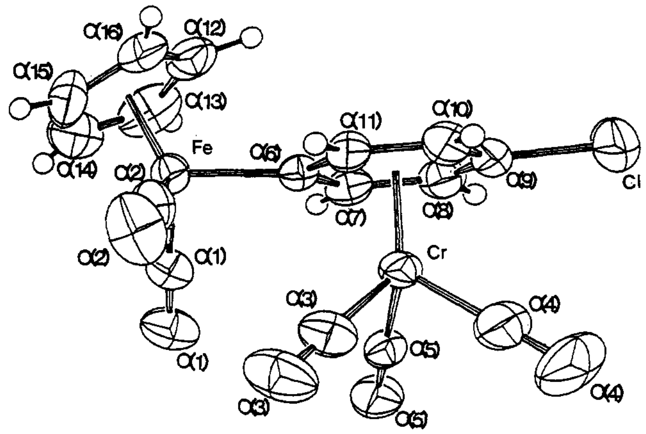
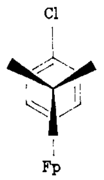


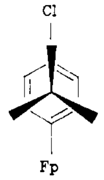
Figure 2. ORTEP representation of the molecular structure of [η-*p*-{CpFe(CO)$_2$}ClC$_6$H$_4$]Cr(CO)$_3$ (**2e**).

Molecular Structure of 2e. An ORTEP representation of the molecular structure of (η-*p*-{CpFe(CO)$_2$}ClC$_6$H$_4$)Cr(CO)$_3$ (**2e**) is shown in Figure 2. The atomic coordinates and isotropic thermal parameters are listed in Table II, and selected bond distances and angles are collected in Table III, respectively. The general features of the molecular structure are consistent with those proposed from spectroscopic data. The Cr–Fe distance of 3.943 (1) Å is, as expected, too long for any direct M–M interaction. The Cr–C$_{\text{arene}}$ distances are identical within experimental error, and the Cr–Ph–C(6) and Cr–Ph–C(9) angles of 91.4 (2) and 89.3 (2)°, respectively, indicated that the Cr–Ph vector is nearly normal to the approximate plane of the arene ring. The 1.990 (4) Å Fe–C(6) bond distance is characteristic of Fe–C$_{sp^2}$ single-bond distances, and the other structural features of the iron unit are similar to those found in CpFe(CO)$_2$R complexes.[9] These structural features suggest that the molecule has adopted a preferred conformation to relieve steric interactions between the CpFe(CO)$_2$ and Cr(CO)$_3$ units.

Two stick-figure drawings of the molecule, representing a view from above the arene plane and a view down the Fe–C(6) bond, are shown in Figure 3. The top view shows that the Cr(CO)$_3$ fragment lies in a pseudo-staggered geometry, experiencing an approximate at 39° clockwise rotation from the fully staggered structure II and a 21° *anticlockwise rotation from the alternate staggered* structure III. A fully eclipsed geometry is the preferred structure for substituted (η^6-arene)Cr(CO)$_3$ molecules, with



II



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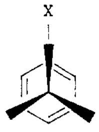
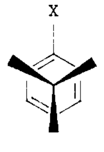
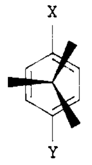


IV



V



VI

the syn-eclipsed conformation IV being adopted for electron-donating functional groups and the anti-eclipsed conformation V being favored for electron-withdrawing groups.[18] The fully staggered structure VI is normally adopted by disubstituted π-complexes in which steric interactions interfere with the ability of the $Cr(CO)_3$ fragment to achieve a preferred eclipsed geometry.[18] As the IR spectroscopic data implies that the $CpFe(CO)_2$ unit is electron-donating with respect to the Cl group, the preferred rotational isomer of **2e** is represented by the fully staggered structure II. The approximate 39° clockwise rotation from III observed in the structure of **2e** suggests that steric factors are largely responsible for determining the conformation of the $Cr(CO)_3$ fragment.

The view down the Fe–C(6) vector reveals the origin of this effect. As is expected due to steric considerations, the cyclopentadienide ligand is anti to the $Cr(CO)_3$ unit. The entire $CpFe(CO)_2$ fragment is rotated by approximately 11° anticlockwise from a strict anti configuration to allow the CO ligands of the iron unit to straddle the single adjacent CO ligand of the $Cr(CO)_3$ fragment. This cogging effect evidentally provides a minimum steric contact between the two metal carbonyl moieties and acts to define the conformational structure of the $Cr(CO)_3$ unit.

Reactions of Other Transition-Metal Anions with (η^6-$RClC_6H_4$)$Cr(CO)_3$ Substrates. Other monoanions, including $Na[Co(CO)_4]$, $Na[Mn(CO)_5]$, $Na[CpMo(CO)_3]$, and $Na[CpNi(CO)]$, fail to react with (η-XC_6H_5)$Cr(CO)_3$ substrates (X = F, Cl, I) in ether solution. In addition, $[CpMo(CO)_3]^-$ fails to react with **1h** over a 20-h period in refluxing THF. These results are not surprising, considering that three of the anions lie at least a factor of 8 lower than $[CpFe(CO)_2]^-$ on King's nucleophilicity scale.[19] The steric bulk of the anion apparently does not account for the failure of these substitution reactions because the two-coordinate $[CpNi(CO)]^-$ moiety, which lies only a factor of 2 below $[CpFe(CO)_2]^-$ in nucleophilicity, is among those reagents that forms no substitution products. It is also possible that the thermal decomposition of $[CpNi(CO)]^-$ to $Cp_3Ni_3(CO)_2$ may occur too rapidly to allow the nucleophilic aromatic substitution reaction to effectively compete.[20]

Table II. Fractional Coordinates and Equivalent Isotropic Thermal Parameters for 2e

atom	*x*	*y*	*z*	*B*, Å^2
Fe	0.93967 (8)	0.65914 (3)	0.83724 (6)	3.47
Cr	0.99964 (8)	0.86415 (4)	0.79975 (6)	3.25
Cl	1.2580 (2)	0.96339 (8)	1.0119 (2)	7.35
O(1)	0.6216 (5)	0.7218 (2)	0.7603 (4)	6.39
O(2)	1.0824 (6)	0.6572 (3)	0.5945 (4)	7.23
O(3)	0.9496 (6)	0.8147 (3)	0.5391 (4)	7.50
O(4)	1.0724 (6)	1.0080 (3)	0.7058 (6)	8.90
O(5)	0.6386 (4)	0.9067 (2)	0.8007 (3)	5.03
C(1)	0.7472 (6)	0.6968 (3)	0.7902 (4)	4.36
C(2)	1.0269 (7)	0.6597 (3)	0.6886 (6)	4.91
C(3)	0.9685 (6)	0.8340 (3)	0.6408 (5)	4.73
C(4)	1.0470 (6)	0.9518 (3)	0.7417 (6)	5.31
C(5)	0.7782 (6)	0.8898 (2)	0.7991 (4)	3.54
C(6)	1.0315 (5)	0.7538 (2)	0.8800 (4)	3.20
C(7)	0.9474 (6)	0.7986 (2)	0.9628 (4)	3.63
C(8)	1.0171 (7)	0.8630 (3)	1.0048 (5)	4.23
C(9)	1.1695 (7)	0.8848 (3)	0.9606 (5)	4.56
C(10)	1.2554 (6)	0.8437 (3)	0.8768 (6)	4.37
C(11)	1.1862 (5)	0.7794 (2)	0.8364 (4)	3.41
C(12)	1.0389 (8)	0.6289 (3)	1.0125 (5)	4.93
C(13)	0.870 (1)	0.6154 (5)	1.0044 (8)	6.68
C(14)	0.839 (1)	0.5675 (5)	0.9106 (9)	8.29
C(15)	0.993 (1)	0.5513 (5)	0.8558 (7)	6.91
C(16)	1.1135 (8)	0.5907 (3)	0.9212 (6)	5.41
PH[a]	1.101180	0.820570	0.920250	
CP[a]	0.970810	0.590760	0.940900	

[a] PH and CP are center positions of benzene and cyclopentadiene rings, respectively.

Table III. Selected Bond Distances (Å) and Angles (deg) for 2e[a]

	Bond Distances		
Fe–C(1)	1.755 (5)	O(3)–C(3)	1.164 (7)
Fe–C(2)	1.764 (6)	O(4)–C(4)	1.155 (8)
Fe–C(6)	1.990 (4)	O(5)–C(5)	1.158 (6)
Fe–CP	1.727 (1)	C(6)–C(7)	1.414 (6)
Cr–C(3)	1.819 (6)	C(6)–C(11)	1.417 (6)
Cr–C(4)	1.821 (6)	C(7)–C(8)	1.413 (7)
Cr–C(5)	1.830 (5)	C(8)–C(9)	1.379 (8)
Cr–PH	1.725 (1)	C(9)–C(10)	1.388 (7)
Cl–C(9)	1.735 (5)	C(10)–C(11)	1.404 (7)
O(1)–C(1)	1.147 (6)	C–C(Cp)	1.386 (av)
O(2)–C(2)	1.119 (7)		
	Bond Angles		
C(1)–Fe–C(2)	95.52 (24)	Fe–C(6)–C(7)	120.79 (31)
C(1)–Fe–C(6)	90.73 (20)	Fe–C(6)–C(11)	123.42 (31)
C(1)–Fe–CP	127.11 (17)	Fe–C(6)–PH	175.71 (27)
C(2)–Fe–C(6)	93.11 (21)	Cl–C(9)–C(8)	120.16 (39)
C(3)–Cr–C(4)	89.30 (26)	Cl–C(9)–PH	178.69 (36)
C(3)–Cr–C(5)	88.37 (21)	C–C–C	119.63 (av)
C(3)–Cr–PH	127.58 (18)	Cr–PH–C(6)	91.42 (16)
C(4)–Cr–C(5)	87.93 (21)	Cr–PH–C(9)	89.30 (21)
C(4)–Cr–PH	126.88 (18)	Fe–Cp–C	89.99 (av)
C(5)–Cr–PH	124.35 (14)		

[a] Estimated standard deviations are given in parentheses.

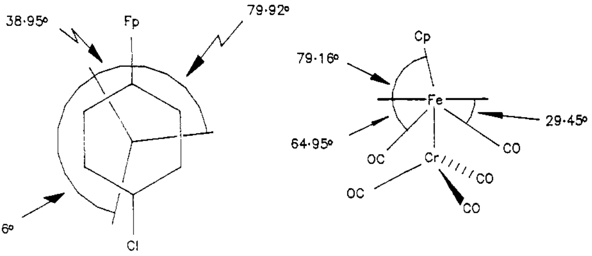


Figure 3. Stick figures of **2e** showing views down (a) the Ph_{cent}–Cr axis and (b) the Fe–C(8) axis.

Preliminary studies indicate that both $Na_2[Fe(CO)_4]$[21] and $Na_2[Cr(CO)_5]$[22] react with (η-haloarene)$Cr(CO)_3$ substrates to produce $Na[(\eta^6\text{-}\{(CO)_nM\}C_6H_5)Cr(CO)_3]$ derivatives (M = Cr, n = 5; M = Fe, n = 4). These results are in accord with the expected higher nucleophilicities of the

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Table IV. Product Distributions as a Percentage of Total Arene Products by ^{1}H NMR Spectroscopy (Acetone-d_6, 20 °C) for Reactions between [Et$_4$N][CpFe(CO)$_2$] and (η-Chloroanisole)Cr(CO)$_3$ or (η-Chlorobenzotrifluoride)Cr(CO)$_3$

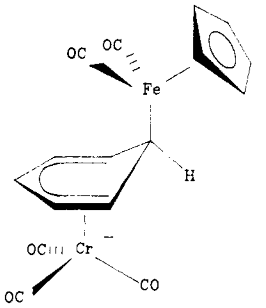
substrate	% substitutn	% reductn
(η-*p*-(CF$_3$)ClC$_6$H$_4$)Cr(CO)$_3$ (**1a**)	92	8
(η-*m*-(CF$_3$)ClC$_6$H$_4$)Cr(CO)$_3$ (**1b**)	92	8
(η-*p*-(MeO)ClC$_6$H$_4$)Cr(CO)$_3$ (**1k**)	12	88
(η-*m*-(MeO)ClC$_6$H$_4$)Cr(CO)$_3$ (**1g**)	81	19

dianion reagents.[19] Although many of the general features of these substitution reactions appear similar to those of [CpFe(CO)$_2$]$^-$ and [Cp*Fe(CO)$_2$]$^-$, the details of the syntheses and structures of the tetracarbonyl ferrate and pentacarbonyl chromate reagents are still under study.

Reactions with Other π-Arene Substrates. The [CpFe(CO)$_2$]$^-$ and [CpMo(CO)$_3$]$^-$ nucleophiles react with other π-arene substrates, such as (η-C$_6$H$_6$)Mn(CO)$_3$$^+$, ($\eta$-ClC$_6H_5$)Mn(CO)$_3$$^+$, and ($\eta^6$-C$_6H_6$)$_2$Fe^{2+}, to produce [CpFe(CO)$_2$]$_2$ and [CpMo(CO)$_3$]$_2$, respectively, as the only identifiable organometallic products.[23] The cationic arene complexes evidentally act as strong oxidizing agents, producing only radical-derived products.

In the absence of halogen substituents, (η-Ar)Cr(CO)$_3$ derivatives (Ar = C$_6$H$_6$, (MeO)C$_6$H$_5$, CF$_3$C$_6$H$_5$) do not form isolable substitution products with [CpFe(CO)$_2$]$^-$. This does not rule out the presence of an η^5-cyclohexadienide intermediate, shown in eq 3, which exists in rapid equilibrium with the starting reagents. Semmelhack observed exactly this type of equilibrium with (η-arene)Cr(CO)$_3$ substrates for a class of carbon-based nucleophiles with pK_a > 20.[11] If such an equilibrium exists for [CpFe(CO)$_2$]$^-$, either it must lie overwhelmingly toward the reactants or the cyclopentadienide intermediate must be rapidly converted back to reactants in the absense of coordinating solvents.

$$(\eta\text{-C}_6\text{H}_6)\text{Cr(CO)}_3 + [\text{CpFe(CO)}_2]^- \rightleftharpoons$$



(3)

Distributions of the Substituted and Reduced Products. The starting reagents are always partitioned between two sets of final products; the (η-{CpFe(CO)$_2$}-RC$_6$H$_4$)Cr(CO)$_3$ substitution product, and the apparent products of reduction of the haloarene substrate, (η-RC$_6$H$_5$)Cr(CO)$_3$, and [CpFe(CO)$_2$]$_2$. The identity of functional groups on the haloarene substrate and the substitution pattern of the arene strongly influence whether the reaction proceeds principally to form the substituted product or the reduced products. Product distribution data from reactions employing chloroanisole and chlorobenzotrifluoride derivatives are listed in Table IV. Only small quantities of η^6-CF$_3$C$_6$H$_5$ byproduct were detected in syntheses involving either the meta- or para-substituted chlorobenzotrifluoride substrates, and relatively small quantities of η^6-anisole reduction product were found for the *m*-chloroanisole reactant. In contrast, dehalogenation was the principle reaction pathway for the *p*-chloroanisole derivative. Only a small set of ^{1}H NMR resonances, representing < 12% of the overall product, could be attributed to [η-*p*-{CpFe(CO)$_2$}(MeO)C$_6$H$_4$]Cr(CO)$_3$. In the cases studied thus far, the reactions of complexes bearing electron-withdrawing substituents, such as *m*- and *p*-CF$_3$ and *m*-MeO groups, result in the formation of high percentages of substitution products, while substrates bearing electron-donating substituents, such as the *p*-MeO group, react to form larger quantities of reduced products.

Table V. Product Distributions (Normalized to [CpFe(CO)$_2$]$_2$) by ^{1}H NMR Spectroscopy (Acetone-d_6, 22 °C) for Reactions between (η-Chlorobenzene)Cr(CO)$_3$ and M[CpFe(CO)$_2$]

M$^+$	[CpFe(CO)$_2$]$_2$	(η-C$_6$H$_6$)-Cr(CO)$_3$	[η-{CpFe-(CO)$_2$}C$_6$H$_5$]-Cr(CO)$_3$
Na$^+$	1.00	1.04	2.90
K$^+$	1.00	1.04	3.02
[Me$_4$N]$^{+a}$	1.00	0.82	0.80
[Et$_4$N]$^+$	1.00	1.64	5.63

[a] [Me$_4$N][CpFe(CO)$_2$] was used as a 1:1 mixture with KCl.

Steric factors also strongly influence the substitution process. All of the ortho-disubstituted arene derivatives tested, including *o*-Cl$_2$C$_6$H$_4$ and *o*-(MeO)ClC$_6$H$_4$ complexes, are substantially reductively dehalogenated by [CpFe(CO)$_2$]$^-$. Reactions between the dichlorinated isomers **1e** and **1f** and 2 equiv of iron nucleophile also failed to yield isolable quantities of bis-CpFe(CO)$_2$-substituted products. The major detectable products of these reactions are [CpFe(CO)$_2$]$_2$, (η-ClC$_6$H$_5$)Cr(CO)$_3$, and (η-C$_6$H$_6$)Cr(CO)$_3$.

The identity of the halogen leaving group on the arene ring has a significant influence on the product distribution. Consistently higher yields of the substituted product **2h** are obtained from the fluorobenzene substrate, as compared with the chlorobenzene substrate, while (η-IC$_6$H$_5$)-Cr(CO)$_3$ forms only the products resulting from dehalogenation, (η-C$_6$H$_6$)Cr(CO)$_3$ and [CpFe(CO)$_2$]$_2$, in a nominal 2:1 molar ratio.

Surprisingly, varying the identity of the countercation also has a significant effect on the product distribution. Not all aspects of the counterion influence, summarized in Table V, are well-understood, but the following points are apparent: (1) Changing from metallic counterions to the [Et$_4$N]$^+$ ion results in the formation of a substantially higher percentage of the substituted product. (2) A significant decrease in the [CpFe(CO)$_2$]$_2$:(η-C$_6$H$_6$)Cr(CO)$_3$ byproduct ratio also occurs with the [Et$_4$N]$^+$ counterion. The first observation probably stems from the ability of sodium and potassium ions to form more intimate ion pairs with the iron anion than can the noncoordinating [Et$_4$N]$^+$ ion. Darensbourg[25] has noted that tight ion paring with the M–H bond of anionic transition metal hydrides results in an increased degree of SET character during the transfer of the hydride. By analogy, our observed product distributions suggest that Na$^+$ and K$^+$ salts of [CpFe(CO)$_2$]$^-$ may show enhanced SET reactivity, resulting in the formation of a larger percentage of reduced products from these salts than from the corresponding [Et$_4$N]$^+$ salt. The second observation amounts to a dramatic change in the

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Scheme III

$$(\eta\text{-XRC}_6\text{H}_4)\text{Cr(CO)}_3 + [\text{CpFe(CO)}_2]^- \rightarrow [(\eta\text{-XRC}_6\text{H}_4)\text{Cr(CO)}_3]^{\bullet -} + \text{CpFe(CO)}_2^{\bullet}$$
$$[(\eta\text{-XRC}_6\text{H}_4)\text{Cr(CO)}_3]^{\bullet -} \rightarrow (\eta\text{-RC}_6\text{H}_4)\text{Cr(CO)}_3^{\bullet} + \text{X}^-$$
$$2\text{CpFe(CO)}_2^{\bullet} \rightarrow [\text{CpFe(CO)}_2]_2$$

$[Et_4N]^+$ absent

$$2(\eta\text{-RC}_6\text{H}_4)\text{Cr(CO)}_3^{\bullet} \rightarrow (\eta\text{-RC}_6\text{H}_5)\text{Cr(CO)}_3 + [(\eta\text{-RC}_6\text{H}_3)\text{Cr(CO)}_3]_n$$

$[Et_4N]^+$ present

$$2(\eta\text{-RC}_6\text{H}_4)\text{Cr(CO)}_3^{\bullet} + \text{Et}_4\text{N}^+ \rightarrow (\eta\text{-RC}_6\text{H}_5)\text{Cr(CO)}_3 + [\text{Et}_3\text{N}]^{\bullet +} + \text{C}_2\text{H}_4$$

Scheme IV

$$(\eta\text{-XRC}_6\text{H}_4)\text{Cr(CO)}_3 + [\text{CpFe(CO)}_2]^- \rightarrow [(\eta\text{-RC}_6\text{H}_4)\text{Cr(CO)}_3]^- + \text{CpFe(CO)}_2\text{X}$$
$$\text{CpFe(CO)}_2\text{X} + \text{CpFe(CO)}_2^- \rightarrow [\text{CpFe(CO)}_2]_2 + \text{X}^-$$

$[Et_4N]^+$ present

$$[(\eta\text{-RC}_6\text{H}_4)\text{Cr(CO)}_3]^- + [\text{Et}_4\text{N}]^+ \rightarrow (\eta\text{-RC}_6\text{H}_5)\text{Cr(CO)}_3 + \text{Et}_3\text{N} + \text{C}_2\text{H}_4$$

$[Et_4N]^+$ absent

$$[(\eta\text{-RC}_6\text{H}_4)\text{Cr(CO)}_3]^- + (\eta\text{-ClRC}_6\text{H}_4)\text{Cr(CO)}_3 \rightarrow (\eta\text{-RC}_6\text{H}_5)\text{Cr(CO)}_3 + [(\eta\text{-ClRC}_6\text{H}_3)\text{Cr(CO)}_3]^-$$
$$[(\eta\text{-ClRC}_6\text{H}_3)\text{Cr(CO)}_3]^- \rightarrow \text{Cl}^- + [(\eta\text{-RC}_6\text{H}_3)\text{Cr(CO)}_3]_n$$

stoichiometry of the dehalogenation process from an approximate 1:1 molar ratio of $[CpFe(CO)_2]_2$:(η-C_6H_6)$Cr(CO)_3$ formed in the presence of metallic counterions to an approximate 1:2 molar ratio for $[Et_4N]^+$ salts. These trends are observed in numerous reactions of metal carbonyl nucleophiles with haloarene substrates. For example, K[Cp*Fe(CO)$_2$] completely dehalogenates (η-ClC_6H_5)$Cr(CO)_3$, resulting in a 1.00:1.16 molar ratio of [Cp*Fe(CO)$_2$]$_2$:(η-C_6H_6)$Cr(CO)_3$ products, while $[Et_4N][CpFe(CO)_2]$ exhaustively dehalogenates (η-IC_6H_5)$Cr(CO)_3$, resulting in a 1.00:1.84 ratio of $[CpFe(CO)_2]_2$:(η-C_6H_6)$Cr(CO)_3$ products. In addition, while reactions involving the $[Et_4N]^+$ salt are stoichiometric, dehalogenation reactions employing sodium or potassium salts of $[CpFe(CO)_2]^-$ produce substantial quantities of intractable byproducts. These intractable residues evidentally contain intact (η-arene)$Cr(CO)_3$ units, as they display the CO stretching bands characteristic of the $Cr(CO)_3$ fragment.[26] This observation suggests that in the absence of the $[Et_4N]^+$ ion, the η-haloarene substrates are partially consumed as a proton or hydrogen atom source, leaving approximately half of the anticipated reduced arene byproduct as an intractable polymer.[26]

On the basis of the known chemistry of haloarenes in radical chain substitution reactions,[27a] the observed increases in the quantity of dehalogenated products formed in reactions employing metallic counterions, and the propensity of $[CpFe(CO)_2]^-$ to act as a reducing agent,[27b] it appears likely that the $[CpFe(CO)_2]_2$ and (η-RC_6H_5)$Cr(CO)_3$ byproducts result from an electron-transfer reaction. A set of equations representing a proposed electron-transfer-initiated dehalogenation process are outlined in Scheme III. A similar haloarene radical anion intermediate is proposed in radical chain carried nucleophilic aromatic substitution reactions in liquid ammonia.[27a] An alternate pathway for dehalogenation involves a direct attack of the nucleophile at the halogen atom, leading initially to formation of $CpFe(CO)_2X$ and the arene-centered carbanion $[(\eta\text{-}C_6H_5)Cr(CO)_3]^-$. A hypothetical dehalogenation scheme incorporating this process is shown in Scheme IV. The order of increasing ease of dehalogenation of the halide substrates ($I \gg Cl > F$), shown on Table IV, is consistent with this scheme.

Unfortunately, the addition of hydrogen atom and hydrogen ion donor molecules such as 1,4-cyclohexadiene, triphenylmethane, and methanol to the substitution reactions interferes with the primary reaction by directly converting substantial quantities of the $[CpFe(CO)_2]^-$ nucleophile to $[CpFe(CO)_2]_2$. As a consequence, no reliable information could be obtained about the effect of these reagents on the product distributions. However, ^2H NMR spectroscopic assays of a reaction between $[Et_4N][CpFe(CO)_2]$ and (η-*p*-$MeClC_6H_4$)$Cr(CO)_3$, performed in the presence of stoichiometric quantities of either CH_3OD or CD_3OD, displayed deuterium incorporation into the 4-position of the (η-toluene)$Cr(CO)_3$ reduction product from both alcohols. This result appears most consistent with the formation of the reduced arent product through hydrogen ion abstraction by an arene-based carbanion.

More detailed studies of product distributions, reagent stoichiometry, and substitution rates are currently underway to define both the mechanism of the substitution reaction, the identities of the intermediates in the dehalogenation process, and the relationship between the substitution and dehalogenation processes.

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Registry No. **1a**, 107067-36-7; **1b**, 114636-07-6; **1c**, 12241-54-2; **1d**, 56213-60-6; **1e**, 86409-62-3; **1f**, 86409-61-2; **1g**, 77490-87-0; **1h**, 12082-03-0; **1h***, 12082-05-2; **1i**, 33411-11-9; **1j**, 12116-24-4; **1k**, 77490-88-1; **1l**, 70140-19-1; **1m**, 77502-82-0; **1n**, 12082-08-5; **1o**, 60429-40-5; **2a**, 114636-08-7; **2b**, 114636-09-8; **2c**, 114636-10-1; **2d**, 114636-11-2; **2e**, 114636-12-3; **2f**, 114636-13-4; **2g**, 114636-14-5; **2h**, 62010-71-3; **2i**, 114636-15-6; **2j**, 114636-16-7; **3**, 114636-17-8; [η^6-(MeO)C_6H_5]$Cr(CO)_3$, 12116-44-8; [η^6-*p*-(MeO){CpFe(CO)$_2$}C_6H_4]$Cr(CO)_3$, 114636-19-0; $[Me_4N][CpFe(CO)_2]$, 114636-18-9; $[Et_4N][CpFe(CO)_2]$, 57812-16-5; $K[CpFe(CO)_2]$, 60039-75-0; $Cp_2Fe_2(CO)_4$, 12154-95-9; $K[(C_5Me_5)Fe(CO)_2]$, 59654-59-0; $[Me_4N]Cl$, 75-57-0; $[Et_4N]Br$, 71-91-0; $Cr(CO)_6$, 13007-92-6.

Supplementary Material Available: A complete listing of atomic and positional parameters including anisotropic thermal parameters and bond distances and angles involving H atoms for the structure of **2e** (16 pages); a listing of structure factors (13 pages). Ordering information is given on any current masthead page.

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