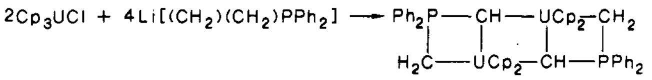
or of a Cp* ligand by an ylide moiety. This behavior should be contrasted to reactions of Cp_3AnCl with $Li[(CH_2)(CH_2)PRR']$ where no evidence of $Cp_2An(ylide)Cl$ has been observed and where products are very dependent upon the metal and reaction stoichiometry. With Cp_3UCl several complexes have been characterized:[1-3,37-40] and with

$$Cp_3UCl + 1Li[(CH_2)(CH_2)PRR'] \longrightarrow Cp_3U{=}CHP(CH_3)RR'$$



$$Cp_3UCl + 3Li[(CH_2)(CH_2)PRR'] \longrightarrow CpU[(CH_2)(CH_2)PRR']_3$$

the Cp_3ThCl system two chelating ylides can be attached to a Cp_2Th fragment:[55]

$$Cp_3ThCl + 2Li[(CH_2)(CH_2)PPh_2] \rightarrow Cp_2Th[(CH_2)(CH_2)PPh_2]_2$$

Perhaps these differences reflect the greater basicity of Cp*, which makes it less prone to dissociate, and the greater size of this ligand, which prevents the variety of coordination modes encountered with the Cp system.

While there are similarities between the Cp^*_2An complexes and Cp_2M complexes of early transition metals,[21,22] 1 and 2 are more thermally stable than their transition-metal counterparts. Both 1 and 2 survive heating to at least 100 °C for several hours while $Cp_2(H)Zr[(CH_2)(CH_2)P(Me)_2]$ rapidly decomposes at 85 °C, $Cp_2(Cl)Zr[(CH_2)(CH_2)P(Me)_2]$ rearranges smoothly to $Cp_2(Cl)Zr{=}CHP(Me)_3$ within 12 h at 50 °C,[9] and $Cp_2(Cl)Zr[(CH_2)(CH_2)P(NEt_2)_2]$, whose structure is analogous to 1, is in equilibrium with $[Cp_2(Cl)Zr{=}CHP(NEt_2)_2(Me)]$.[6,22] These data indicate that the ylide ligand is more prone to serve as a monodentate $[CHPR_3]^-$ ligand with $Cp_2(X)M$ complexes than with the analogous $Cp^*_2(X)An$ complexes.

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Registry No. 1a, 119743-15-6; 1b, 119743-16-7; 1c, 119743-17-8; 2a, 119743-18-9; 2b, 119743-19-0; 2c, 119743-20-3; $Cp^*_2UCl_2$, 67506-89-2; $Li[(OH_2)(CH_2)p(Me)(Ph)]$, 59983-61-8; $Cp^*_2ThCl_2$, 67506-88-1; $Li[(CH_2)(CH_2)p(Me)_2]$, 21752-68-1; $Li[(CH_2)(CH_2)P(Ph)_2]$, 59983-62-9.

Supplementary Material Available: Tables of positional and thermal parameters for the hydrogen atoms of the monoclonic form of 1a, intramolecular nonbonded distances for 1a and 1b, positional and thermal parameters of anisotropically refined non-hydrogen atoms of the triclinic form of 1a, positional and thermal parameters of isotropically refined non-hydrogen atoms of the triclinic form of 1a, and bond lengths and angles for the triclinic form of 1a (5 pages); listings of observed and calculated structure factors for the triclinic form of 1a, the monoclinic form of 1a, and 1b (40 pages). Ordering information is given on any current masthead page.

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[55] Gilje, J. W.; Cramer, R. E.; Hitt, J.; Chung, T. D. Y., unpublished results.

Competitive Nucleophilic Aromatic Substitution and Haloarene Reduction in the Synthesis of Bimetallic π-Arene Complexes: The Structural Characterization of $[Et_4N][(\eta^6\text{-}\{(CO)_5W\}C_6H_5)Cr(CO)_3]$

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

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

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Collman's reagent, $[Fe(CO)_4]^{2-}$, reacts with $(\eta^6\text{-}ClC_6H_5)Cr(CO)_3$ to produce $[(\eta^6\text{-}\{(CO)_4Fe\}C_6H_5)Cr(CO)_3]^-$ in THF/*N*-methyl-2-pyrrolidinone solvents, while $[M(CO)_5]^{2-}$ (M = Cr or W) reacts with $(\eta^6\text{-}FC_6H_5)Cr(CO)_3$ in THF at 0 °C to form analogous $[(\eta^6\text{-}\{(CO)_5M\}C_6H_5)Cr(CO)_3]^-$ complexes. The products are isolated as yellow-orange crystalline $[Et_4N]^+$ salts from acetone or methylene chloride and are somewhat air sensitive in both solution and the solid state. Spectroscopic data indicate that the molecules adopt a classical η^6-arene structure, as opposed to the alternate possible η^5-cyclohexadienide carbene valence form. This supposition is confirmed by an X-ray crystallographic study of $[Et_4N][(\eta^6\text{-}\{(CO)_5W\}C_6H_5)Cr(CO)_3]$, which displays a typical $W\text{–}C_{Ar}$ σ-bond interaction and a minimal distortion of the planarity of the arene. The reaction of $[M(CO)_5]^{2-}$ (M = Cr or W) with $(\eta^6\text{-}ClC_6H_5)Cr(CO)_3$ results in the exhaustive reductive dehalogenation of the chlorobenzene substrate to $(\eta^6\text{-}C_6H_6)Cr(CO)_3$. This later reaction is in keeping with anticipated higher reactivity and reducing power of the $[M(CO)_5]^{2-}$ anions. Crystal data for $[Et_4N][(\eta^6\text{-}\{(CO)_5W\}C_6H_5)Cr(CO)_3]$ at 20 °C: $a = 11.599$ (3) Å, $b = 10.562$ (2) Å, $c = 20.369$ (5) Å, $Z = 4$, $D_{calcd} = 1.782$, space group $Pca2_1$ and $R(F) = 0.0352$, $R_w(F) = 0.0583$ for 1698 reflections.

Introduction

Complexes bearing $(\eta^6\text{-arene})Cr(CO)_3$ subunits have been widely studied because of the unique modes of reactivity that the $Cr(CO)_3$ template engenders in the arene ligand.[2] Although the increased electrophilicity of the aromatic carbon centers is among the most interesting and widely exploited facets of (π-arene)chromium chemistry,

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[1] Summer participant, University of Kansas Undergraduate Research Program. Current address: Department of Chemistry, Idaho State University, Pocatello, ID.

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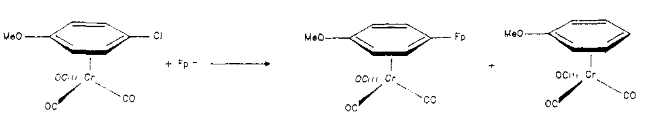
Scheme I



it still remains relatively poorly understood.[3] Little is known about the factors that influence the reactivity of carbanions with (η^6-arene)Cr(CO)$_3$ substrate except that the observed chemistry varies from nucleophilic attack by bases with p$K_a \geq 20$,[4] to deprotonation by strong bases such as *n*-BuLi and lithium diisopropylamide (LDA),[5] to metal–acyl formation by other strong bases such as PhLi.[6] Some understanding of the regiochemistry of nucleophile addition to the arene has been developed by correlating the directing influence of the arene substituents (and their effect on the conformational preference of the Cr(CO)$_3$ subunit) with the identity of the aromatic carbon centers on which the LUMO is principally localized.[7] Certainly, one of the most intriguing aspects of (π-arene)chromium chemistry is the nucleophilic displacement of halide ligands by alkoxides and certain carbanions.[8] Although it has been demonstrated that a kinetically formed meta- or para-disubstituted cyclohexadienide intermediate must rearrange to a gem-disubstituted isomer prior to halide loss, the mechanism of this unusual migration has never been exhaustively investigated.

We have recently observed a new type of nucleophile-induced activation of carbon–halogen (C–X) bonds in (η^6-arene)Cr(CO)$_3$ substrates.[9] Cyclopentadienyl iron dicarbonyl anions ([CpFe(CO)$_2$]$^-$) were found to react with (π-haloarene)chromium substrates to form new bimetallic products (η^6-{CpFe(CO)$_2$}arene)Cr(CO)$_3$ and dehalogenation products (η^6-arene)Cr(CO)$_3$ in parallel nucleophilic substitution and reduction reactions (Scheme I). These reactions were the first reported observation of a reductive dehalogenation pathway operating in (η^6-haloarene)Cr(CO)$_3$ chemistry. Whether a reaction between [CpFe(CO)$_2$]$^-$ and an arene complex produces more bimetallic or dehalogenated product depends on various attributes of both the nucleophile and arene substrate including (1) the reducing power of the nucleophile (in order of increasing dehalogenation [Cp*Fe(CO)$_2$]$^-$ $\gg$ [CpFe(CO)$_2$]$^-$), (2) the counterion associated with the nucleophile (Na$^+$ > K$^+$ > [Et$_4$N]$^+$), (3) the identity of the halogen substituent (I $\gg$ Cl > F), and (4) the identity and regiochemistry of substituents on the aromatic ring (electron donating $\gg$ H > electron withdrawing). These trends, together with additional experimental data gained about the [CpFe(CO)$_2$]$^-$ reactions, suggest that the reductive dehalogenation proceeds through an electron-transfer pathway.

This suggestion is hardly surprising, considering that recent detailed mechanistic studies of nucleophilic aromatic substitution in non-π-bound arene substrates have identified a strong component of electron-transfer character.[10,11] The classical mechanism of nucleophilic aromatic substitution in liquid ammonia (S$_{\mathrm{NAr}}$2) defined by Bunnett proceeds through a radical chain-initiated by a single electron-transfer (SET) process.[10] The fragmentation of the C–X bond in the radical anion intermediate proposed by Bunnett is consistent with negative ion mass spectrometric results that define this as the major decomposition pathway.[12] More recently, the nucleophilic hydroxylation of both halogenated and non-halogenated nitroaromatic molecules in aqueous solution has been demonstrated to proceed through a non-radical-chain SET process.[11]

The importance of extending metal-mediated dehalogenation reactions to either free or π-bound aromatic substrates lies in the significant role of haloaromatic compounds as environmental pollutants.[13] Polychlorinated aromatic hydrocarbons (PCAH's) such as pentachlorophenol (PCP) and polychlorinated biphenyls (PCB's) were highly attractive materials for industrial applications because of their resistance to chemical or biological degradation, high thermal stability, attractive dielectric behavior, and useful biocidal properties. Unfortunately, later studies determined that the partial oxidation or hydrolysis of these molecules can convert PCP and PCB's into more toxic polychlorodibenzodioxins and polychlorodibenzofurans. A major effort is now centered around developing safe methods for the disposal of PCAH's. Current methods for destroying these wastes—including high-temperature combustion, uncatalyzed reductive dehalogenation, and dehalogenation by concentrated caustic solutions—all create distinct and potentially serious environmental problems.[14] Clearly new technologies aimed at developing catalytic methods for the dehalogenation of PCAH's should be of strategic importance in solving these problems.

On the basis of the unique chemistry we encountered in reactions between [CpFe(CO)$_2$]$^-$ and (η^6-haloarene)Cr(CO)$_3$ complexes, we have initiated an investigation of the reactions of other metal-derived nucleophiles with the (π-arene)chromium substrates. The purposes of these studies are threefold: (1) to build new and unusual heterobimetallic organometallic complexes, (2) to generate additional evidence for the SET character of the reaction mechanisms, and (3) to develop more efficient reagents for the dehalogenation of chloroaromatic substrates. In this paper, we present an account of our further studies that have initially focused on the reaction between more highly nucleophilic carbonyl metalate dianions ([Cr(CO)$_5$]$^{2-}$, [Fe(CO)$_4$]$^{2-}$, [W(CO)$_5$]$^{2-}$) and (η-haloarene)Cr(CO)$_3$ substrates. A brief preliminary account of the reaction between [Fe(CO)$_4$]$^{2-}$ (Collman's reagent) and (η^6-ClC$_6$H$_5$)Cr(CO)$_3$ has already appeared.[15]

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Experimental Section

All reactions were performed by using modified Kejldahl Schlenk glassware and double-manifold Schlenk vacuum lines. Solid reagents were isolated in a nitrogen-filled Vacuum Atmosphere drybox. Water was deaerated via a nitrogen purge prior to use. All organic solvents were distilled from Na/benzophenone and stored over activated 5-Å molecular sieves prior to use, except for *N*-methyl-2-pyrrolidinone, which was dried over 5-Å molecular sieves and degassed by using a purge of dry nitrogen gas. Acetone-d_6 was dried over 5-Å molecular sieves and degassed by using freeze–pump–thaw cycles prior to use. $(\eta^6\text{-FC}_6H_5)Cr(CO)_3$ and $(\eta^6\text{-ClC}_6H_5)Cr(CO)_3$ were prepared by using published procedures.[9] $Na_2[Fe(CO)_4]\cdot{}^1/_2$(dioxane) was used as purchased from Aldrich.

^1H and $^{13}C\{^1H\}$ NMR spectra were acquired on a Varian FX-300 spectrometer, with ^1H resonances referenced against the protio impurity in acetone-d_6 and ^{13}C resonances referenced against the methyl resonance of acetone-d_6. IR spectra were collected on an IBM FT IR-20. Elemental analyses were obtained from Desert Analytics, Tuscon, AZ.

Preparation of $M(CO)_5(NMe_3)$ Derivatives. $Cr(CO)_5(NMe_3)$ was prepared by a modification of standard procedure.[16] $Cr(CO)_6$ (2.1 g) and $Me_3NO\cdot 2H_2O$ (1.5 g) were placed in a Schlenk-modified round-bottom flask (250 mL) containing a large stir bar. After THF (100 mL) was added, the solution was frozen and NMe_3 (17 mL) was added in vacuo. The solution was warmed to room temperature and stirred for 75 min and then warmed to 40 °C for 1 h while stirring. The solvent was removed, and a vacuum was maintained over the greenish residue for 2 h to remove residual chromium hexacarbonyl. The solid was extracted into two volumes (100 mL) of hexanes, filtered through Celite, and collected in a Schlenk-modified round-bottom flask. The solution was reduced in volume until a super-saturated solution was obtained. After 24 h at −20 °C, the solution was decanted from long needlelike golden yellow crystals of the product.

$W(CO)_5(NMe_3)$ was prepared by a modification of standard procedure.[17] $W(CO)_6$ (.704 g total) was divided between a pair of quartz reaction tubes that were then sealed with septa and degassed by nitrogen purge. THF (25 mL) was added to a round-bottom flask and frozen at −196 °C, and NMe_3 (5 mL) was added in vacuo. The solution was warmed to room temperature and was transferred onto the $W(CO)_6$. The quartz reaction tubes were placed in a Rayonet photochemical reactor and photolyzed for 12 h while under slight positive pressure of argon supplied by a cannula. The solutions were transferred to a Schlenk flask (50 mL); the solvent was removed in vacuo. The solid was extracted into two volumes (20 mL) of hexanes and collected in a Schlenk flask (50 mL). The solution was reduced in volume until a super-saturated solution was obtained. After 18 h at −78 °C the solution was decanted and yellow crystals of the product were collected.

Preparation of Metal Carbonyl Dianions. The following general procedure was adapted from the published method[17] and used for the preparation of $K_2Cr(CO)_5$ and $K_2W(CO)_5$.

$K_2Cr(CO)_5$. $Cr(CO)_5(NMe_3)$ (0.306 g) was placed in a Schlenk flask (25 mL), dissolved in THF (15 mL), and cooled to −78 °C. Potassium metal (0.112 g) and naphthalene (500 mg) were placed in a Schlenk flask (25 mL) and dissolved in THF (15 mL). The potassium naphthalide solution was transferred dropwise onto the $Cr(CO)_5(NMe_3)$ solution until a green color persisted. The temperature was then raised to 0 °C and the solvent removed in vacuo. The solid was washed with two portions of Et_2O (10 mL) and then dried briefly in vacuo. The solid was then dissolved in THF at −20 °C and used without isolation.

$K_2[W(CO)_5]$ starting materials: $W(CO)_5(NMe_3)$ (0.246 g), K (0.059 g), naphthalene (0.200 g), and Et_2O (5 mL, 15 mL).

Reaction of $K_2[Cr(CO)_5]$ with $(\eta^6\text{-FC}_6H_5)Cr(CO)_3$. A THF solution of $K_2[Cr(CO)_5]$ (1.22 mmol) at 0 °C was transferred onto solid $(\eta^6\text{-FC}_6H_5)Cr(CO)_3$ (0.289 g) by cannula. The mixture was stirred for 12 h. The solvent was removed in vacuo and the solid dissolved in water and filtered through Celite filter aid. An aqueous solution of $[Et_4N]Br$ (0.256 g) was added, precipitating a light yellow solid. The solid $[Et_4N][(\eta^6\text{-}\{(CO)_5Cr\}C_6H_5)Cr(CO)_3]$ was isolated by decanting the water and recrystallizing at −20 °C from CH_2Cl_2; yield 0.217 g (32.7%). ^1H NMR data (acetone-d_6, 20 °C): δ 5.66 (2 H, d, *o*-Ar), 5.20 (2 H, t, *m*-Ar), 5.12 (1 H, t, *p*-Ar), 3.49 (8 H, q, NCH_2CH_3), 1.39 (12 H, t, NCH_2CH_3). $^{13}C\{^1H\}$ NMR data (acetone-d_6, 19 °C): δ 238 ($Cr(CO)_3$), 226 ($Cr(CO)_5$), 111, 96, 91 (Ar), 53, 7.5 (NCH_2CH_3). IR spectrum (KBr, cm^{-1}, carbonyl stretching region): 2040.0, 1944.5, 1917.5, 1888.5, 1867.3, 1840.3, 1824.9. Anal. Calcd: C, 49.35; H, 4.71; N, 2.62. Found: C, 49.15, H, 4.72; N, 2.82.

Reaction of $K_2[W(CO)_5]$ with $(\eta^6\text{-FC}_6H_5)Cr(CO)_3$. A THF solution of $K_2[W(CO)_5]$ (0.642 mmol) at 0 °C was transferred onto solid $(\eta\text{-FC}_6H_5)Cr(CO)_3$ (0.149 g) by cannula. The mixture was stirred for 12 h. The solvent was removed in vacuo and the solid dissolved in water and filtered through Celite filter aid. Aqueous $[Et_4N]Br$ (0.135 g) was added, precipitating a light yellow solid. The solid $[Et_4N][(\eta^6\text{-}\{(CO)_5W\}C_6H_5)Cr(CO)_3]$ was isolated by decanting the water and crystallizing at −20 °C from CH_2Cl_2; yield 0.0463 g (10.7%). ^1H NMR data (acetone-d_6, 20 °C): δ 5.80 (2 H, m, Ar), 5.19 (3 H, m, Ar), 3.48 (3 H, q, NCH_2CH_3), 1.38 (12 H, t, NCH_2CH_3). $^{13}C\{^1H\}$ NMR data (acetone-d_6, 19 °C): δ 238 ($Cr(CO)_3$), 203 ($W(CO)_5$), 113, 97, 92 (Ar), 53, 7.4 (NCH_2CH_3). IR spectrum (KBr, cm^{-1}, carbonyl stretching region): 2048.7, 1886.6, 1859.6, 1850.0, 1842.2, 1819.1, 1808.3. Anal. Calcd: C, 39.60; H, 3.78; N, 2.10. Found: C, 39.71; H, 3.85, N, 2.17.

Reaction of $Na_2[Fe(CO)_4]\cdot$1.5Dioxane with $(\eta^6\text{-ClC}_6H_5)Cr(CO)_3$. $(\eta^6\text{-ClC}_6H_5)Cr(CO)_3$ (0.275 g, 1.1 mmol) and $Na_2[Fe(CO)_4]\cdot$1.5dioxane (0.381 g, 1.1 mmol) were placed in a small Schlenk flask to which THF (10 mL) was added via syringe. As 1-methyl-2-pyrolidinone (4 mL) was added dropwise to the stirred THF slurry, the solution clarified and became a pale red color with significant warming. After the solution was stirred 20 h, the THF was removed in vacuo and deaerated water (15 mL) was added to the oily residue. The aqueous solution was filtered to separate a small quantity of yellow solid and an aqueous solution of $[Et_4N]Br$ (0.23 g, 1.1 mmol) was added to the filtrate. A pale yellow solid formed from this mixture, and, after filtration from the bulk of the solution, the residue was twice recrystallized at −20 °C from CH_2Cl_2 to yield pure $[Et_4N][(\eta^6\text{-}\{(CO)_4Fe\}C_6H_5)Cr(CO)_3]$, yield (as crystals) 41% (0.23 g). ^1H NMR (acetone-d_6, 20 °C): δ 5.69 (d, 2 H, *o*-ar), 5.26 (t, 2 H, *m*-Ar), 5.09 (t, 1 H, *p*-Ar), 3.48 (q, 9 H, NCH_2CH_3), 1.39 (t, 12 H, NCH_2CH_3) ^{13}C NMR (acetone-d_6, 19 °C): δ 237.5 ($Cr(CO)_3$), 220.8 ($Fe(CO)_4$), 110.4, 96.6, 90.0 (Ar, partial), 52.0, 7.5 (NCH_2CH_3). IR spectrum (KBr, cm^{-1}, carbonyl stretching region): 2016, 1938, 1923, 1900, 1877, 1852, 1830. Anal. Calcd: C, 49.33; H, 4.93; N, 2.74. Found: C, 49.26; H, 4.95; N, 2.72.

Reaction of $K_2[W(CO)_5]$ and $K_2[Cr(CO)_5]$ with $(\eta^6\text{-ClC}_6H_5)Cr(CO)_3$. Reactions between $K_2W(CO)_5$ and $(\eta^6\text{-ClC}_6H_5)Cr(CO)_3$ and between $K_2Cr(CO)_5$ and $(\eta^6\text{-ClC}_6H_5)Cr(CO)_3$ failed to yield any $[Et_4N][(\eta^6\text{-}\{(CO)_nM\}C_6H_5)Cr(CO)_3]$ product. Instead, a large amount of H_2O-insoluble material collected after aqueous workup was identified by ^1H NMR spectroscopy and IR spectrophotometry as $(\eta^6\text{-C}_6H_6)Cr(CO)_3$. Typical yields of reduced product: 98% (starting, $(\eta^6\text{-ClC}_6H_5)Cr(CO)_3$ (0.151 g); isolated, $(\eta^6\text{-C}_6H_6)Cr(CO)_3$ (0.131 g)).

Crystallographic Study. A suitably sized crystal of $[Et_4N][(\eta^6\text{-}\{(CO)_5W\}C_6H_5)Cr(CO)_3]$ was mounted on top of a glass fiber by using epoxy glue. Cell constants were determined by using 15 reflections widely scattered throughout reciprocal space. Preliminary data indicated an orthorhombic cell with systematic absences $0kl$ for $l = 2n + 1$, $h0l$ for $h = 2n + 1$, and $00l$ for $l = 2n + 1$, identifying the space group as $Pca2_1$ or $Pcam$. A space group assignment of $Pca2_1$ was confirmed by subsequent structure determination and refinement. Data were collected through two octants of space (to $2\theta = 45°$) on a Syntex P2$_1$ diffractometer using a θ–2θ scan procedure. Two reflections were monitored every 100 measurements for intensity changes. A semiempirical ψ-scan technique was used to correct for absorption (correction factor range 0.955–1.045). Reflections with $F_o^2 < 0.20(F_o^2)$ were reset to $F_o^2 = 0.20(F_o^2)$. The $\sigma(F_o^2)$ and $\sigma(F_o)$ values were defined as $\sigma(F_o^2) = [\sigma^2_{\text{count}} + (0.02F_o^2)^2]^{1/2}$ and $\sigma(F_o) = \sigma(F_o^2)/2F_o$. A total of 1698 independent F_o data were used for the structure determination and refinement, and the structure was solved by the heavy-atom method. Anomalous dispersion corrections were used

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Table I. Summary of Crystal Data for $[Et_4N][(\eta\text{-}\{(CO)_5W\}C_6H_5)Cr(CO)_3]$

empirical formula	$WCrC_{22}H_{25}NO_8$
color of cryst	orange
cryst dimens, mm	0.3 × 0.3 × 0.4
space group	$Pca2_1$
cell dimens (25 °C)	
a, Å	11.599 (3)
b, Å	10.562 (2)
c, Å	20.369 (5)
Z, molecules/cell	4
V, Å^3	2495.4 (1)
d(calcd), g/cm^3	1.782
X-ray radiatn	Mo Kα (λ = 0.709 26 Å)
MW	669.64
linear abs coeff, cm^{-1}	54.3678
av ω scan width, deg	0.3
scan speed, deg/min	1.0–20.0
scan width, deg + dispersn	1.2 below Kα and 1.2 above Kα
bkgd range	$^1/_6$ of scan at edges
aperture size, mm	0.5
2θ range, deg	4–45
total no. of reflctns collected	3998
no. of unique intensities	1698
$R(F)$	0.0352
$R_w(F)$	0.0583
goodness of fit for last cycle	0.7496
max Δ/σ for last cycle	0.21

for the W and Cr atoms. Hydrogen atoms were not located in the difference electron density map and *consequently were not included in the refinement*. The structure was refined by using anisotropic thermal parameters. The $\sum w(|F_o| - |F_c|)^2$ is minimized, for $w = 1/\sigma(F_o)^2$. The full-matrix least-squares refinement was converged to R = 0.035, R_w = 0.058, and S = 0.749. The largest peak found in the final difference Fourier map was near the W atom (+0.90 e/Å^3). Atomic scattering factors were taken from ref 34. All calculations were performed on a VAX/8650 computer at the University of Kansas using programs of the KUDNA system (Takusagawa, 1984). A summary of the experimental details is collected Table I.

Results

Synthesis and Characterization of $[Et_4N][(\eta^6\text{-}\{(CO)_nM\}C_6H_5)Cr(CO)_3]$ (n = 4, M = Fe; n = 5, M = Cr, W). $[(\eta^6\text{-}\{(CO)_4Fe\}C_6H_5)Cr(CO)_3]^-$ was prepared by a stoichiometric reaction between $Na_2[Fe(CO)_4]$ and $(\eta^6\text{-}XC_6H_5)Cr(CO)_3$ (X = F or Cl) in 2:1 THF/NMP (NMP = N-methyl-2-pyrrolidinone) (eq 1). The yellow product

$$Na_2[Fe(CO)_4] + (\eta^6\text{-}XC_6H_5Cr(CO)_3) \xrightarrow[\text{THF/NMP}]{20\ °C} Na[(\eta^6\text{-}\{(CO)_4Fe\}C_6H_5)Cr(CO)_3] + NaX \quad (1)$$

was isolated from reaction byproducts by extraction into deaerated water and precipitation with an equimolar solution of $[Et_4N]Br$. Recrystallization of the resulting yellow powder from acetone or methylene chloride produced yellow needlelike crystals of $[Et_4N][(\eta^6\text{-}\{(CO)_4Fe\}C_6H_5)Cr(CO)_3]$. The 300-MHz ^1H NMR spectrum of the product displays a characteristic aa′mm′x pattern with the ortho, meta, and para resonances appearing at 5.69, 5.26, and 5.09 ppm, respectively. The IR spectrum of the product shows bands characteristic of the $Cr(CO)_3$ and $\{Fe(CO)_4\}^-$ fragments in the vicinity of 1930 and 1879 cm^{-1} and at 2016 cm^{-1}, respectively.

The reaction between $Na_2[Fe(CO)_4]$ and $(\eta^6\text{-}ClC_6H_5)Cr(CO)_3$ does not proceed in neat THF at ambient temperature but is rapid and exothermic on addition of an equal volume of N-methyl-2-pyrrolidinone (NMP). Although only moderate amounts of the nucleophilic substitution product $[(\eta^6\text{-}\{(CO)_4Fe\}C_6H_5)Cr(CO)_3]^-$ were isolated, a ^1H NMR assay in acetone-d_6 indicates that the reaction was complete within 2 h. The other major organometallic product isolated was a water-insoluble yellow powder that was unequivocally identified by ^1H NMR spectroscopy and IR spectrophotometry as $(\eta^6\text{-}C_6H_6)Cr(CO)_3$.[18] The corresponding iron-containing byproduct was not isolated; however, we assume from the pale red color exhibited by the aqueous solution that it is not $[Fe_3(CO)_{11}]^{2-}$, the normal product of $[Fe(CO)_4]^{2-}$ oxidation which is an intense brown-red color.[19] Similarly, $Na_2[Fe(CO)_4]$ and the fluoroarene substrate $(\eta^6\text{-}FC_6H_5)Cr(CO)_3$ fail to react in neat THF and show only slight <20% conversion to $[(\eta^6\text{-}\{(CO)_4Fe\}C_6H_5)Cr(CO)_3]^-$ over 12 h in 1:1 THF/NMP solvents. Reduction products such as $(\eta^6\text{-}C_6H_6)Cr(CO)_3]$ and $[Fe_2(CO)_8]^{2-}$ were not observed as byproducts of reactions between $[Fe(CO)_4]^{2-}$ and the fluoroarene substrate. Unreacted $(\eta^6\text{-}FC_6H_5)Cr(CO)_3$ was the only organometallic product recovered after an aqueous workup.

Synthesis and Characterization of $[(\eta^6\text{-}\{(CO)_5M\}C_6H_5)Cr(CO)_3]^-$ (M = Cr or W). The $[(\eta^6\text{-}\{(CO)_5M\}C_6H_5)Cr(CO)_3]^-$ (M = Cr or W) products were prepared by reactions between $(\eta^6\text{-}FC_6H_5)Cr(CO)_3$ and $Na_2[M(CO)_5]$ at 0 °C in THF (eq 2). The products were

$$K_2[M(CO)_5] + (\eta^6\text{-}FC_6H_5)Cr(CO)_3 \xrightarrow{0\ °C} K[(\eta^6\text{-}\{(CO)_5M\}C_6H_5)Cr(CO)_3] + KF \quad (2)$$

$$M = Cr \text{ or } W$$

isolated as $[Et_4N]^+$ salts by a procedure similar to that used in the isolation of $[Et_4N][(\eta^6\text{-}\{(CO)_4Fe\}C_6H_5)Cr(CO)_3]$, except that the products frequently required repeated recrystallization to remove residual Cr- or W-containing byproducts. Both of the resulting Cr_2 and CrW monoanions displayed ^1H NMR spectra typical of monosubstituted (η^6-arene)chromium complexes, with ortho hydrogen resonances at 5.66 and 5.80 ppm, respectively. The IR spectra of the products were effectively the sum of the A_1, B_2, and E bonds of the $M(CO)_5$ unit and the nominal A_1 and E_2 symmetry bands of the $Cr(CO)_3$ fragment.

Reactions between either of the pentacarbonyl dianions and $(\eta^6\text{-}ClC_6H_5)Cr(CO)_3]$ failed to yield detectable quantities of $[(\eta^6\text{-}\{(CO)_5M\}C_6H_5)Cr(CO)_3]^-$ products. Extraction of these reactions with water resulted in the separation of yellow alkane-soluble powder that was identified as $(\eta^6\text{-}C_6H_6)Cr(CO)_3$. Adding $[Et_4N]Br$ to the aqueous extract resulted in the precipitation of yellow microcrystalline powders that were purified by fractional crystallization from CH_2Cl_2. The yellow needlelike crystals of one product were identified as $[Et_4N][[W_2H(CO)_{10}]$ by ^1H NMR spectroscopy and IR spectrophotometry.[20]

Although the reactions of the tungsten and chromium anions with $(\eta^6\text{-}FC_6H_5)Cr(CO)_3$ proceed smoothly to form the bimetallic products, the appearance of the solutions as the reactions progressed suggested that the $[Cr(CO)_5]^{2-}$ nucleophile reacted more rapidly than its W cogener. This trend was checked by testing the relative reactivities of $[Cr(CO)_5]^{2-}$ and $[W(CO)_5]^{2-}$ with MeI. The reaction between $[Cr(CO)_5]^{2-}$ and MeI in THF at 0 °C showed no further change in appearance after 2 min, while the reaction between MeI and $[W(CO)_5]^{2-}$ continued to change in appearance over a 30-min period.

The $[Et_4N][(\eta^6\text{-}\{(CO)_5Cr\}C_6H_5)Cr(CO)_3]$ and $[Et_4N][(\eta^6\text{-}\{(CO)_4Fe\}C_6H_5)Cr(CO)_3]$ products displayed the

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[18] Crystalline samples isolated from reactions were identified by comparison with the ^1H NMR and IR spectra of analytically pure samples, prepared according to the published procedure (ref 9).

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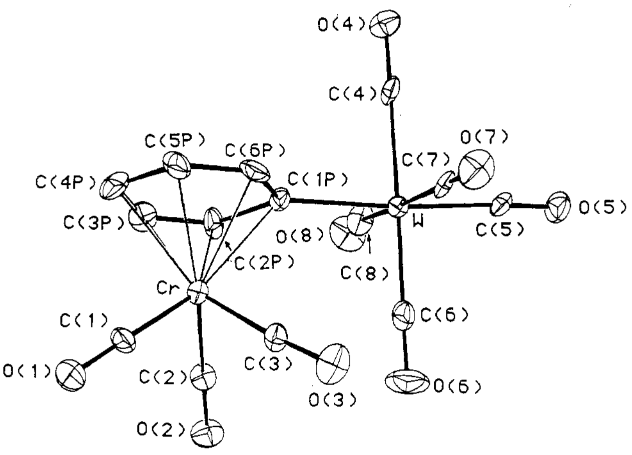

Figure 1. An ORTEP view of the molecular structure of $[(\eta^6\text{-}\{(CO)_5W\}C_6H_5)Cr(CO)_3]^-$ determined by X-ray crystallography, showing the atom numbering scheme.

greatest sensitivity to air. Crystals sealed in glass ampules or stored in an inert-atmosphere box had a minimum life expectancy of several months, but the same crystals rapidly acquired a greenish cast in air. This observation is suggestive of oxidation at the (π-arene)chromium unit. Crystals displaying a discoloration gave unsatisfactory elemental analyses, indicating that the decomposition was significant. In contrast, crystals of $[Et_4N][(\eta^6\text{-}\{(CO)_5W\}C_6H_5)Cr(CO)_3]$ were handled without exclusion of air during mounting for the X-ray crystallographic study and proved to be quite stable to a laboratory atmosphere during several days of data analysis.

The new Cr_2 and CrW products also displayed significantly different behavior on crystallization. Like the $[\eta^6\text{-}(\{(CO)_4Fe\}C_6H_5)Cr(CO)_3]^-$ complex, the $[(\eta^6\text{-}\{(CO)_5Cr\}C_6H_5)Cr(CO)_3]^-$ product crystallized as nearly unidimensional needles, while the $[\eta^6\text{-}(\{(CO)_5W\}C_6H_5)Cr(CO)_3]^-$ product crystallizes as equidimensional cubes. For this reason, an X-ray crystallographic study of $[Et_4N][(\eta^6\text{-}\{(CO)_5W\}C_6H_5)Cr(CO)_3]$ was undertaken to determine the exact nature of the $W\text{-}C_{arene}$ σ- and $Cr\text{-}C_{arene}$ π-bonding interactions.

Crystal Structure of $[Et_4N][(\eta^6\text{-}\{(CO)_5W\}C_6H_5)Cr(CO)_3]$. An ORTEP representation of the structure of the $[(\eta^6\text{-}\{(CO)_5W\}C_6H_5)Cr(CO)_3]^-$ ion determined by X-ray crystallography is shown in Figure 1. The atomic coordinates for the molecule, as well as selected bond distances and angles, are collected in Tables II and III, respectively.

The general structural features of the $(\eta^6\text{-}C_6H_5)Cr(CO)_3$ and $[W(CO)_5]^-$ subunits are common to those found in simple mononuclear derivatives. The $(\eta^6\text{-arene})Cr(CO)_3$ fragment shows the usual pseudooctahedral symmetry, with the $C_{CO}\text{-}Cr\text{-}C_{CO}$ angles averaging 89.5°. The Cr–CENT vector (CENT represents the calculated centroid of the aromatic ring) is approximately normal to the plane of the arene ligand with $Cr\text{-}CENT\text{-}C_{AR}$ angles averaging an ideal 90.0° and the Cr–CENT distance of 1.779 (3) Å being only slightly longer than the average chromium-arene centroid distance of 1.73 Å.[21] The $Ar[W(CO)_5]^-$ fragment also shows the anticipated pseduooctahedral structure. The $W\text{-}C_{trans\text{-}CO}$ distance of 2.038 (12) Å is marginally shorter than the average $W\text{-}C_{cis\text{-}CO}$ distance of 2.051 Å, reflecting the fact that the trans CO is opposite a poorer π-acceptor ligand than carbon monoxide. Given the quality of the structure, however, it is quite surprising that the W–C distance of the trans carbonyl ligand is equivalent within statistical error to several of the cis-carbonyl ligands and is significantly longer than the W–C(6) distance of 1.913 (17) Å.[22]

Table II. Fractional Coordinates and Equivalent Isotropic Thermal Parameters for $[Et_4N][(\eta\text{-}\{(CO)_5W\}C_6H_5)Cr(CO)_3]$

atom	x	y	z	B, Å^2
W	0.12643 (3)	0.33817 (3)	0.222220 (0)	2.93
Cr	0.3183 (1)	0.2072 (2)	0.0627 (1)	3.28
C(1)	0.393 (1)	0.192 (2)	−0.0138 (9)	4.62
C(2)	0.1955 (9)	0.123 (1)	0.0308 (6)	3.45
C(3)	0.252 (1)	0.352 (1)	0.0333 (6)	3.61
C(4)	0.219 (1)	0.328 (1)	0.3106 (8)	3.87
C(5)	−0.0065 (9)	0.414 (1)	0.2747 (7)	3.66
C(6)	0.032 (1)	0.331 (1)	0.1453 (9)	4.55
C(7)	0.1879 (8)	0.512 (1)	0.2015 (5)	3.60
C(8)	0.063 (1)	0.166 (1)	0.252 (1)	5.65
O(1)	0.440 (1)	0.177 (1)	−0.0655 (7)	6.29
O(2)	0.1148 (8)	0.074 (1)	0.0054 (6)	5.31
O(3)	0.2056 (8)	0.4460 (9)	0.0192 (6)	6.30
O(4)	0.2736 (9)	0.3223 (9)	0.3598 (6)	5.16
O(5)	−0.0855 (9)	0.4550 (9)	0.3015 (5)	5.81
O(6)	−0.024 (2)	0.331 (1)	0.0978 (7)	9.27
O(7)	0.2207 (9)	0.6142 (9)	0.1915 (7)	6.75
O(8)	0.016 (1)	0.078 (1)	0.2638 (7)	7.58
C(1P)	0.2777 (8)	0.250 (1)	0.1739 (6)	3.25
C(2P)	0.284 (1)	0.110 (1)	0.1590 (7)	4.41
C(3P)	0.377 (1)	0.060 (2)	0.1316 (8)	6.30
C(4P)	0.479 (1)	0.124 (2)	0.1143 (9)	6.08
C(5P)	0.474 (1)	0.261 (2)	0.1229 (8)	5.94
C(6P)	0.381 (1)	0.316 (2)	0.152 (1)	4.70
N(+)	0.6603 (9)	0.2318 (8)	0.3988 (5)	3.35
C(1+)	0.661 (1)	0.371 (1)	0.3971 (7)	4.66
C(2+)	0.561 (1)	0.445 (1)	0.4340 (8)	5.39
C(3+)	0.552 (1)	0.181 (1)	0.3685 (9)	4.96
C(4+)	0.531 (1)	0.219 (1)	0.2951 (7)	5.38
C(5+)	0.762 (1)	0.188 (1)	0.3600 (9)	5.59
C(6+)	0.774 (1)	0.037 (1)	0.358 (1)	6.67
C(7+)	0.662 (2)	0.183 (1)	0.4683 (9)	4.13
C(8+)	0.768 (1)	0.226 (2)	0.5088 (8)	5.89

Table III. Selected Bond Distances (Å) and Angles (deg) for $[Et_4N][(\eta\text{-}\{(CO)_5W\}C_6H_5)Cr(CO)_3]$[a]

	Bond Distances		
W–C(5)	2.038 (12)	Cr–CENTR	1.779 (3)
$W\text{-}C_{cis\text{-}CO}$	2.051 (av)	C(1P)–C(2P)	1.51 (2)
W–C(1P)	2.217 (11)	C(1P)–C(6P)	1.46 (2)
$Cr\text{-}C_{CO}$	1.807 (av)	C(2P)–C(3P)	1.32 (2)
Cr–C(1P)	2.357 (13)	C(3P)–C(4P)	1.41 (2)
Cr–C(4P)	2.315 (15)	C(4P)–C(5P)	1.46 (3)
$Cr\text{-}C_{o,m\text{-}Ar}$	2.245 (av)	C(5P)–C(6P)	1.36 (2)
	Bond Angles		
C(4)–W–C(5)	87.5 (5)	C(4)–W–C(1P)	87.4 (5)
C(5)–W–C(6)	90.7 (6)	C(6)–W–C(1P)	94.2 (6)
C(5)–W–C(7)	91.2 (4)	C(7)–W–C(1P)	90.6 (4)
C(5)–W–C(8)	85.4 (6)	C(8)–W–C(1P)	92.4 (5)
C(5)–W–C(1P)	174.7 (5)	$C_{CO}\text{-}Cr\text{-}C_{CO}$	89.5 (av)
C(4)–W–C(7)	92.6 (4)	W–C(1P)–CENTR	178.2 (7)
C(4)–W–C(8)	83.4 (7)	Cr–CENTR–C(1P)	91.7 (5)
C(6)–W–C(7)	93.8 (5)	$Cr\text{-}CENTR\text{-}C_{Ar}$	90.0 (av)
C(6)–W–C(8)	90.1 (7)		

[a] The symbol "CENTR" represents the calculated centroid of the arene ring. Esd's in parentheses.

Two relevant details of the molecule that bear examination are the W–C(1P) interaction, which defines the bonding between the $[W(CO)_5]^-$ and $(\eta^6\text{-}C_6H_5)Cr(CO)_3$ subunits, and the interrelationship between the conformations of the $Cr(CO)_3$ and $[W(CO)_5]^-$ moieties.

A variety of aspects of the X-ray structure indicate that there is no substantial multiple-bond character in the W–C(1P) interaction. At first inspection, the W–C(1P)

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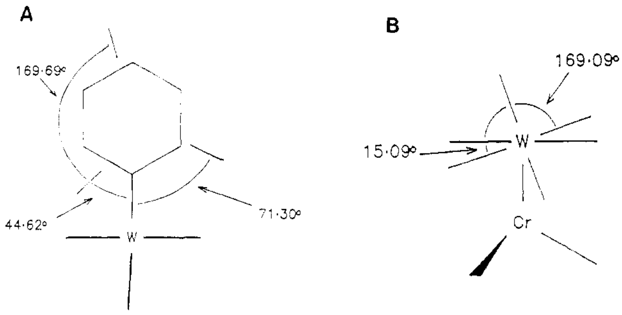

Figure 2. Stick figure drawings of $[(\eta\text{-}\{(CO)_5W\}C_6H_5)Cr(CO)_3]^-$ showing views down (a) the arene centroid-to-Cr vector and (b) the W-to-arene carbon vector, including selected dihedral angles.

distance of 2.217 (11) Å appears to be significantly shorter than the 2.34 (1) Å W–C distance representing the simple σ-bond of $[(CO)_5W\{CH(OCH_3)Ph\}]^-$.[22] However, the sum of the 3σ values for the two W–C bond distances in question (3σ = 0.03 Å for each bond) together with the expected 0.04 Å contraction of the W–C distance on moving from the W–C_{sp^3} bond of $[(CO)_5W\{CH(OMe)Ph\}]^-$ to the W–C_{sp^2} bond of $[(CO)_5W\{(\eta^6\text{-}C_6H_5)Cr(CO)_3\}]^-$[23] brings the two bonds to within 0.02 Å of being statistically identical. Typical bond distances for bona fide W–C double bonds (e.g. $(CO)_5W(CPh_2)$) are in the range of 2.14 Å.[24]

Further support for the lack of W–C multiple-bond character can be derived from the geometry of the Cr–arene–W bridge interaction. The existence of a significant degree of multiple-bond character between a π-bound aromatic carbon and an atom in a benzylic environment should be accompanied by an elevation of the multiply bound carbon out of the plane of the arene ring. This structural feature is similar to the distortions observed in η^5-cyclohexandienide complexes,[25] η^3-cyclobutadienone complexes,[26] and $Cp_2Zr[(\eta^6\text{-}OC_6H_5)Cr(CO)_3]_2$,[27] in which a small amount of C–O multiple-bond character is observed. The $[(\eta^6\text{-}\{(CO)_5W\}C_6H_5)Cr(CO)_3]^-$ moiety shows extremely little evidence of such a distortion, having a virtually linear W–C(1P)–CENT angle of 178.2 (7) Å and a nearly perpendicular Cr–CENT–C(1P) angle of 91.7 (5)°. In fact, the entire arene ligand is remarkably planar (Cr–CENT–C_{AR} = 90.0° (av)), considering the potential bulk of $[W(CO)_5]^-$ unit. The only structural feature consistent with any degree of W-to-arene π-donation is the unusually long W–$C_{trans\text{-}CO}$ distance.

The interaction between the $Cr(CO)_3$ and $[W(CO)_5]^-$ units is another noteworthy structural feature. Like other bimetallic (π-arene)chromium complexes prepared in our laboratory, the variable-temperature ^{13}C NMR spectra of the $[\eta^6\text{-}(\{(CO)_nM\}C_6H_5)Cr(CO)_3]^-$ molecules display no tendency to adopt a static conformation at temperatures approaching −50 °C. Still, several aspects of the structure do indicate that the two metal carbonyl fragments a mutually staggered orientation in order to avoid steric interactions in the solid state.

Figure 2 shows stick figure views of $[(\eta^6\text{-}\{(CO)_5W\}C_6H_5)Cr(CO)_3]^-$ down the arene centroid-to-chromium vector (Figure 2a) and down the tungsten-to-aromatic carbon vector (Figure 2b). When vectors representing the two carbonyl ligands (CO(3) and CO(2)) adjacent to the $W(CO)_5$ fragment are projected into the plane of the arene ligand, the angle subtended by these vectors is 155.9° (Figure 2a). The conformation of the $Cr(CO)_3$ fragment is slipped anticlockwise by 13.4° from the position that would allow these two proximal carbonyls to exactly stagger the $W(CO)_5$ fragment. In an effort to minimize interactions between the two metal carbonyl fragments, the $W(CO)_5$ fragment is rotated approximately 15° out of the plane of the arene ligand, allowing the carbonyl ligand (CO(6)) adjacent to the $Cr(CO)_3$ fragment to slip between the two proximal chromium-bound carbonyl ligands.

Discussion

Structural Considerations. The X-ray crystallographic study of $[Et_4N][(\eta^6\text{-}\{(CO)_5W\}C_6H_5)Cr(CO)_3]$ showed little evidence of a significant contribution by a valence structure containing a W–C_{Ar} multiple bond. This structural feature appears to be common to all of the $[(\eta^6\text{-}\{(CO)_nM\}C_6H_5)Cr(CO)_3]^-$ derivatives based on other spectroscopic data. Each of the $[(\eta^6\text{-}\{(CO)_nM\}C_6H_5)Cr(CO)_3]^-$ molecules possesses a highest frequency, CO stretch of nominal A_1 symmetry characteristic of mononuclear $[RM(CO)_n]^-$ complexes in which the $M(CO)_n$ fragment bears a full 1− charge.[22,28] In addition, the ortho hydrogen resonances of all three derivatives fall in the usual range between δ 6.0 and δ 4.6 for (η^6-arene)$Cr(CO)_3$ complexes in acetone solvent.[9] Molecules that adopt the η^5-pentadienide structure characteristically display resonances representing the "ortho" hydrogens in the range δ 3.0–1.5.[25] Although examples of (π-arene)chromium complexes containing M–C_{Ar} multiple bonds have not yet been characterized, we expect that a significant distortion of the planarity of the arene ligand in these molecules should result in accompanying shifts of the *o*-arene resonances to somewhat higher field than is ordinarily observed.

The expectation that the $[(\eta^6\text{-}\{(CO)_nM\}C_6H_5)Cr(CO)_3]^-$ complexes should at least conceptually be able to adopt an η^5-cyclohexadienide carbene valence structure stems from the well-known ability of (η-arene)chromium functional groups to stabilize benzylic anions.[29] Reike has dramatized this effect by the synthesis of $[(\eta^5,\eta^{5'}\text{-}trans\text{-stilbene})\{Cr(CO)_3\}_2]^{2-}$, which adopts a bis($\eta^5$-cyclohexadienide olefin) structure in solution.[30] By contrast, we have found spectroscopic evidence that $[(\eta^6\text{-phenoxide})Cr(CO)_3]^-$ and $[(\eta^6\text{-2,6-dimethylphenoxide})Cr(CO)_3]^-$ adopt structures containing simple C_{Ar}–O σ-bonds and have no significant delocalization of negative charge onto the $Cr(CO)_3$ moiety.[27] It appears that while other molecules such as $Cp_2Zr[(\eta^6\text{-}OC_6H_5)Cr(CO)_3]_2$ can display small contributions of a η^5 valence structure, the majority of molecules bearing benzylic atoms or functional groups that adequately support a 1−charge will adopt the normal η^6 structure.

Reactivity of the $[M(CO)_n]^{2-}$ Reagents. The different solvent systems used for reactions employing the group 6

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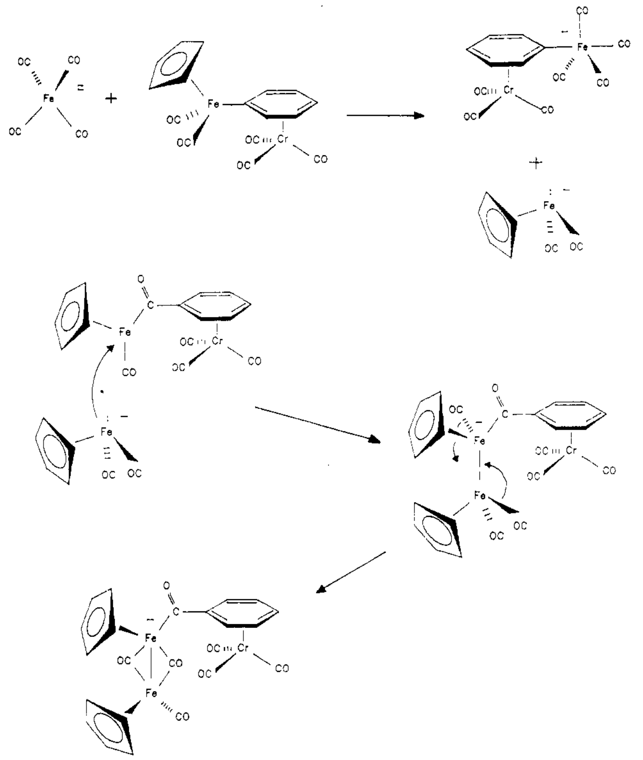
tungsten and chromium nucleophiles, as compared with those employing the group 8 iron anion, make a direct comparison of the nucleophilicity impossible. We had expected the $[Cr(CO)_5]^{2-}$ and $[W(CO)_5]^{2-}$ reagents to be qualitatively more reactive than the strongly ion paired $[Fe(CO)_4]^{2-}$ reagent, and the greater reactivity of the former two anions with $(\eta^6\text{-}FC_6H_5)Cr(CO)_3$ confirms this hypothesis. In a reversal of the classical trend of reactivity of (π-haloarene)chromium complexes, we previously observed that $[CpFe(CO)_2]^-$ reacted as much as an order of magnitude more slowly with fluoroarene substrates than with analogous chloroarene complexes.[9] This is exactly the reactivity trend observed in reactions between $[Fe(CO)_4]^{2-}$ and the $(\eta^6\text{-}ClC_6H_5)Cr(CO)_3$ and $(\eta^6\text{-}FC_6H_5)Cr(CO)_3$ substrates. In addition, just as reactions between $[Cp^*Fe(CO)_2]^-$ (expected to be both a stronger nucleophile and a better reducing agent than $[CpFe(CO)_2]^-$) and $(\eta^6\text{-}ClC_6H_5)Cr(CO)_3$ produced only $(\eta^6\text{-}C_6H_6)Cr(CO)_3$,[9] reactions between the chlorobenzene complex and $[W(CO)_5]^{2-}$ and $[Cr(CO)_5]^{2-}$ formed only the $(\eta^6\text{-}C_6H_6)Cr(CO)_3$ byproduct. Like $[Cp^*Fe(CO)_2]^-$, the chromium and tungsten dianions produced products of nucleophilic substitution on reaction with $(\eta^6\text{-}FC_6H_5)Cr(CO)_3$.

$(\eta^6\text{-}C_6H_5)Cr(CO)_3$ Fragment Transfer. The $[(\eta^6\text{-}C_6H_5)Cr(CO)_3]$ unit becomes involved in an intriguing example of competitive alkyl group transfer between two nucleophiles, which affords an interesting, albeit not overly efficient, alternate route to $[(\eta^6\text{-}\{(CO)_4Fe\}C_6H_5)Cr(CO)_3]^-$. A stoichiometric reaction between $[Fe(CO)_4]^{2-}$ and $(\eta^6\text{-}\{CpFe(CO)_2\}C_6H_5)Cr(CO)_3$ results in the formation of half of an equivalent of $[(\eta^6\text{-}\{(CO)_4Fe\}C_6H_5)Cr(CO)_3]^-$ and half of an equivalent of $[(\eta^6\text{-}\{Cp_2Fe_2(CO)_3\}OCC_6H_5)Cr(CO)_3]^-$ (eq 3).[31] The latter molecule is analogous to the simple

$$\{Fe(CO)_4]^{2-} + 2(\eta^6\text{-}FpC_6H_5)Cr(CO)_3 \rightarrow [(\eta^6\text{-}\{(CO)_4Fe\}C_6H_5)Cr(CO)_3]^- + [(\eta^6\text{-}\{Cp_2(CO)_3Fe_2\}OCC_6H_5)Cr(CO)_3]^- \quad (3)$$

dinuclear acyl $[Cp_2Fe_2(\mu\text{-}CO)_2(CO)(COPh)]^-$ isolated nearly 10 years ago.[32] A plausible pathway for this transformation is shown in Scheme II. The initial step in the reaction must involve the transfer of the $(\eta^6\text{-}C_6H_5)Cr(CO)_3$ substituent from a $CpFe(CO)_2$ unit to a $[Fe(CO)_4]^-$ moiety. This transfer results in the formation of an equivalent of $[CpFe(CO)_2]^-$. The liberated $[CpFe(CO)_2]^-$ must then react more rapidly with a remaining molecule of $(\eta^6\text{-}\{CpFe(CO)_2\}C_6H_5)Cr(CO)_3$ to produce the new iron acyl product than the $[Fe(CO)_4]^{2-}$ nucleophile reacts with $(\eta^6\text{-}\{CpFe(CO)_2\}C_6H_5)Cr(CO)_3$ to convert the entire pool of starting reagents to $[(\eta^6\text{-}\{(CO)_4Fe\}C_6H_5)Cr(CO)_3]^-$.

Scheme II



Scheme III

(a)

$$[M(CO)_n]^{2-} + (\eta\text{-}ClC_6H_5)Cr(CO)_3 \rightarrow [ClM(CO)_n]^- + [(\eta\text{-}C_6H_5)Cr(CO)_3]^-$$
$$[(\eta\text{-}C_6H_5)Cr(CO)_3]^- + [H]^+{}_{solv} \rightarrow (\eta\text{-}C_6H_6)Cr(CO)_3$$

(b)

$$[M(CO)_n]^{2-} + (\eta\text{-}ClC_6H_5)Cr(CO)_3 \rightarrow [(\eta\text{-}ClC_6H_5)Cr(CO)_3]^{\bullet-} + [M(CO)_n]^{\bullet-}$$
$$[(\eta\text{-}ClC_6H_5)Cr(CO)_3]^{\bullet-} \rightarrow [(\eta\text{-}C_6H_5)Cr(CO)_3]^{\bullet} + Cl^-$$
$$[(\eta\text{-}C_6H_5)Cr(CO)_3]^{\bullet} + [H]^{\bullet}{}_{solv} \rightarrow (\eta\text{-}C_6H_6)Cr(CO)_3$$
$$2[M(CO)_n]^{\bullet-} \rightarrow [M_2(CO)_{2n}]^{2-}$$

Reductive Dehalogenation of the (η-Chlorobenzene)$Cr(CO)_3$ Substrates by $[M(CO)_5]^{2-}$ (M = Cr and W). From the observed products of the dehalogenation reaction we infer that the dehalogenation process occurs either through (a) halide transfer from the (π-arene)chromium substrate to the metal nucleophile followed by hydrogen ion abstraction by the $[(\eta^6\text{-arene})Cr(CO)_3]^-$ moiety (Scheme IIIa) or (b) single electron transfer by the nucleophile to form $[(\eta^6\text{-}ClC_6H_5)Cr(CO)_3]^{\bullet-}$, which subsequently fragments via loss of halide ion and abstracts a hydrogen atom from the solvent (Scheme IIIb). Of these two pathways, the second is certainly consistent with the observed products, because $[M_2(CO)_{10}]^{2-}$, the proposed product of nucleophile oxidation, hydrolyzes on aqueous workup to form the observed $[M_2H(CO)_{10}]^-$ byproduct.[20]

It is interesting to note that both the anticipated reactivity of the carbonyl metalate dianions and the propensity of the dianions to reduce $(\eta^6\text{-}ClC_6H_5)Cr(CO)_3$ increase in the order Cr ≥ W ≫ Fe. It is tempting to infer that a SET process is responsible for the reductive dehalogenation of the arene, although no direct evidence for radical intermediates or correlation of the extent of arene dehalogenation with a known scale of reducing ability for $[Fe(CO)_4]^{2-}$, $[W(CO)_5]^{2-}$, and $[Cr(CO)_5]^{2-}$ is currently possible. It is plausible, however, that all of these nucleophiles can display significant SET character in their reactions because $[CpFe(CO)_2]^-$ (generally thought to be

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(31) The $[Et_4N][(\eta^5\text{-}\{Cp_2Fe(CO)_3\}COC_6H_5)Cr(CO)_3]$ complex observed in reactions between $[Fe(CO)_4]^{2-}$ and $(\eta^6\text{-}\{CpFe(CO)_2\}C_6H_5)Cr(CO)_3$ was identified by comparison with an authentic product obtained in the following manner: $(\eta^6\text{-}\{CpFe(CO)_2\}C_6H_5)Cr(CO)_3$ (0.485 g) and $[Et_4N][CpFe(CO)_2]$ (0.405 g) were added to a small Schlenk and dissolved in THF (15 mL). After being stirred for 2 days the solution was filtered through Celite and evaporated to dryness and the resulting solids were extracted with benzene. The solid residue was dissolved CH_2Cl_2, and ether was layered onto the resulting solution. Within minutes, yellow-brown microcrystals of $[Et_4N][(\eta^6\text{-}\{Cp_2Fe_2(CO)_3\}COC_6H_5)Cr(CO)_3]$ formed and were isolated by filtration; yield 69% (0.60 g). ^1H and ^{13}C NMR spectra of the product (25 °C) was consistent with the presence of a 1:3.2 ratio of the cis and trans isomers. Structural data are not yet available for an unequivocal identification of the identity of the major isomer. A complete account of the synthesis, characterization, and reactivity of these derivatives will be an integral part of another publication. ^1H NMR spectrum (major and minor isomers, acetone-d_6, 23 °C): δ 6.14 (2 H, d, J = 5.1 Hz, $o\text{-}Ar_{minor}$), 4.84 (2 H, t, J = 4.8 Hz, $m\text{-}Ar_{minor}$), 5.07 (1 H, t, J = 4.9 Hz, $p\text{-}Ar_{minor}$), 4.36, 4.12 (5 H, s, Cp_{minor}), 5.94 (2 H, d, J = 5.1 Hz, $o\text{-}Ar_{major}$), 4.72 (2 H, t, J = 5.0 Hz, $m\text{-}Ar_{major}$), 4.88 (1 H, t, J = 5.1 Hz, $p\text{-}Ar_{major}$), 4.46, 4.43 (5 H, s, Cp_{major}), 3.46 (3 H, q, $N(CH_2CH_3)_4$), 1.37 (12 H, t, $N(CH_2CH_3)_4$). IR (KBr, carbonyl region, cm^{-1}): 2016 (CO), 1935 (s), 1902 (s), 1848 (s), 1813 (s), 1700 (s).

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a less potent nucleophile than these dianions) has been shown to cyclize radical traps in reactions with primary alkyl halides.[33]

Despite various difficulties in defining the mechanism of the observed reductive dehalogenation, we find the clean rapid reduction of $(\eta^6\text{-ClC}_6\text{H}_5)\text{Cr(CO)}_3$ to $(\eta^6\text{-C}_6\text{H}_6)\text{Cr(CO)}_3$ to be an encouraging result. We are currently investigating the reactivity of the $[\text{M(CO)}_5]^{2-}$ reagents and related transition-metal-derived nucleophiles with othe haloarene substrates and with the intention of developing transition-metal-initiated homogeneous methods for dehalogenating PCAH's. A detailed study of the mechanism of the reductive dehalogenation process has also been initiated.

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Supplementary Material Available: Complete tables of the structural data for $[\text{Et}_4\text{N}][(\eta^6\text{-}\{(\text{CO})_5\text{W}\}\text{C}_6\text{H}_5)\text{Cr(CO)}_3]$ including (1) fractional coordinates and isotropic thermal parameters, (2) anisotropic thermal parameters, (3) bond distances, and (4) bond angles (12 pages); a $F_o - F_c$ list (10 pages). Ordering information is given on any current masthead page.

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Reactivity and Complexation of Dimethylsilylene Photogenerated from Dodecamethylcyclohexasilane. A Kinetic Study by Laser Flash Photolysis[1]

G. Levin,[2a,b] P. K. Das,*[,2c] C. Bilgrien,[2a] and C. L. Lee[2a]

Dow Corning Corporation, Midland, Michigan 48640, and Radiation Laboratory, University of Notre Dame, Notre Dame, Indiana 46556

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Under 266-nm laser flash photolysis, the photodecomposition of dodecamethylcyclohexasilane in cyclohexane leads to the formation of a transient intermediate ($\lambda_{\max}$ = 465 nm) that is best assigned as dimethylsilylene. The assignment is based on the spectral similarity with an analogous photoproduct previously observed and identified in low-temperature matrices as well as on the pattern of reactivity with trapping agents in fluid solutions at room temperature. The transient species is unusually reactive toward alcohols and reagents containing Si—H, Sn—H, C=C, and C≡C bonds. For example, the bimolecular rate constants (k_r) for its reaction with ethanol and tri-*n*-propylsilane are 9.2×10^9 and 2.9×10^9 $\text{M}^{-1}\,\text{s}^{-1}$, respectively. From static photolysis experiments, the ratio between these two rate constants is obtained as 2.6, which is in reasonably good agreement with the flash photolysis result. In the presence of submillimolar tetrahydrofuran (THF), dimethylsilylene ($\lambda_{\max}$ = 465 nm) disappears with pseudo-first-order kinetics and a new transient ($\lambda_{\max}$ = 310 nm), assigned as a dimethylsilylene–THF complex, appears concomitantly. The reactivity of the complex toward trapping agents is considerably lower than that of the "free" silylene (for example, k_r's for the complex are 1.9×10^8 and 8.6×10^5 $\text{M}^{-1}\,\text{s}^{-1}$ with ethanol and tri-*n*-propylsilane as quencher, respectively). The facile complex formation between dimethylsilylene and compounds containing lone pair(s) of electrons is found to be a general behavior.

Introduction

The photodecomposition of compounds containing the silicon–silicon bond constitutes a research area that is currently very active. One of the intermediates observed in such a photodecomposition reaction contains the divalent silicon. Atwell and Weyenberg[3] showed that the thermolysis of alkoxydisilanes at temperatures as low as 498 K resulted in the formation of organosilylenes. However, compared to thermolysis, the photolysis technique became preferable for generation of divalent silicon as the latter is more suitable for mechanistic studies.[4-11] West, Michl, and Drahnak[4] were the first to record the UV–visible spectrum of dimethylsilylene ($\lambda_{\max} \cong 450$ nm)

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