π-Donor Interactions and the Origin of Arene Nonplanarity in Heterobimetallic (η^6-arene)$Cr(CO)_3$ Complexes Having σ-Bonded Organometallic Substituents: X-ray Crystal Structures of (η^6-C_6H_5((η^5-C_5H_4Me)$Fe(CO)_2$))$Cr(CO)_3$, (η^6-C_6H_5((η^5-indenyl)$Fe(CO)_2$))$Cr(CO)_3$, and (η^6-1,4-C_6H_4Me((η^5-C_5H_5)$Fe(CO)_2$))$Cr(CO)_3$[1]

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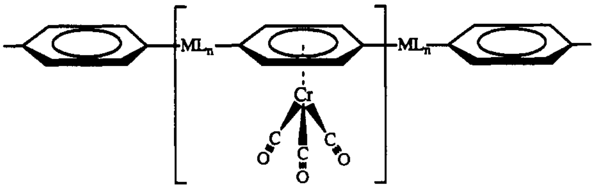
The syntheses and X-ray crystal structures of the three title complexes (η^6-C_6H_5Fp')$Cr(CO)_3$ ($C_{17}H_{12}O_5CrFe$; $a = 7.599$ (2) Å, $b = 15.054$ (4) Å, $c = 14.448$ (3) Å, $\beta = 99.90$ (2)°, $V = 1628$ Å^3; monoclinic; $P2_1/c$; $Z = 4$), (η^6-$C_6H_5Fp^{\ddagger}$)$Cr(CO)_3$ ($C_{20}H_{12}O_5CrFe$; $a = 8.024$ (1) Å, $b = 19.471$ (4) Å, $c = 11.780$ (2) Å, $\beta = 104.88$ (1)°, $V = 1778$ Å^3; monoclinic, $P2_1/n$; $Z = 4$), and (η^6-1,4-C_6H_4MeFp)$Cr(CO)_3$ ($C_{17}H_{12}O_5CrFe$; $a = 7.9042$ (7) Å, $b = 19.112$ (2) Å, $c = 10.8860$ (8) Å, $\beta = 90.981$ (7)°, $V = 1644$ Å^3, monoclinic; $P2_1/n$; $Z = 4$) were determined. They each display nonplanar benzene rings with the Fe atoms and the ipso carbon atoms to which they are bonded being bent substantially away from the $Cr(CO)_3$ centers. Comparison of these structural data to those calculated for related (η^6-arene)$Cr(CO)_3$ complexes having transition-metal and main-group π-donor and π-acceptor substituents indicates that this structural distortion is due primarily to the π-electron donation from the Fe centers to the aromatic rings rather than being due to the steric bulk of the iron-containing substituents.

Introduction

During our studies of organometallic oligomers and polymers[4] and their metal carbonyl model complexes[2,5] we became interested in determining whether the addition of 12-electron organometallic groups (e.g. $Cr(CO)_3$) to such species, e.g. would modify the degree of electronic conjugation down their backbones.[6,7] Since the synthesis and characterization of such polymeric materials are generally much more difficult than they are for structurally related low-molecular-weight species, we decided to begin these studies by investigating discrete bi- and trimetallic model complexes having the same structures as the repeating units of these hypothetical polymers (e.g. (η^6-C_6H_5Fp)$Cr(CO)_3$ (**1**) and (η^6-1,4-$C_6H_4Fp_2$)$Cr(CO)_3$ (**2**)).[2,5c–e] During the course of these studies, a variety of apparently anomalous spectroscopic, electrochemical, and crystallographic data indicating substantial metal–metal interactions and arene nonplanarity (e.g. the complex (η^6-1,3,5-$C_6H_3Fp_3$)$Cr(CO)_3$



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[3] Present addresses: Department of Chemistry, Youngstown State University, Youngstown, OH 44555 (for A.D.H); Molecular Structure Corp., 3200A Research Forest Dr., The Woodlands, TX 77381-4238 (for B.D.S.).

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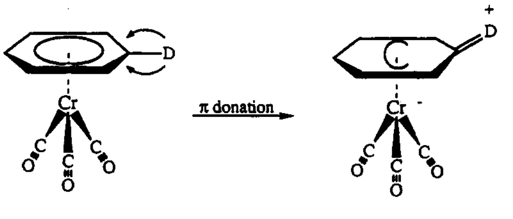
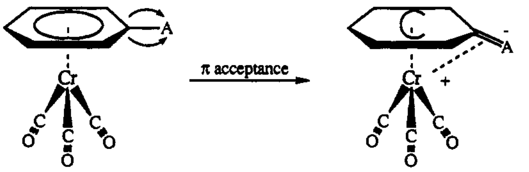
had a strongly crown shaped arene ligand) was observed. We tentatively proposed that these varied effects were due to a common cause, namely, π-donor interactions between the iron-containing substituents and the η^6-arene rings.[2,5a,c-e] Indeed, similar π-symmetry interactions were later demonstrated to be important for (η^6-arene)Cr(CO)$_3$ complexes having conventional main-group substituents.[8] Thus, π-donor substituents and the ipso carbon atoms to which they are attached in such complexes are observed to bend away from Cr(CO)$_3$, while π-acceptor substituents and their ipso carbon atoms bend toward it, i.e.[8]



(1)



(2)

(where D is a π-donor and A is a π-acceptor substituent). To test if this explanation for the observed arene nonplanarity was valid for (η^6-arene)Cr(CO)$_3$ complexes having transition-metal-containing substituents, we decided to compare predictions derived from this model for the structures of such heterometallic complexes to experimental results. In this paper, the complete results of these studies are presented, including new X-ray crystal structures of three such complexes, and it is shown that the structural distortions observed in such materials are due primarily to electronic rather than steric effects.

Experimental Section

Unless otherwise noted, all reactions and subsequent manipulations were performed under anaerobic and anhydrous conditions. Reagents and chemicals used were handled by conventional techniques which have been described in detail previously.[5,9] Infrared spectra were recorded as CH_2Cl_2 solutions on a Pye Unicam PU9522 infrared spectrometer and were calibrated with the 1601-cm^{-1} band of polystyrene. Nuclear magnetic resonance spectra were recorded as CD_2Cl_2 solutions on a Bruker WH-300 spectrometer with a deuterium solvent lock. The ^{1}H and ^{13}C NMR chemical shifts are reported in parts per million downfield from external Me_4Si. The other analytical and spectroscopic data were obtained as described previously.[5]

Preparation of (η^6-C_6H_5Fp′)Cr(CO)$_3$ (3; Fp′ = (η^5-C_5H_4Me)Fe(CO)$_2$). To an excess of sodium amalgam (~8 mmol of Na, 2 mL of Hg)[5b] was added THF (25 mL) and then Fp′$_2$ (0.40 g, 1.05 mmol).[10a] After the resulting solution was vigorously stirred for 40 min, the excess amalgam was drained through a side arm[10c] and the red solution was slowly filtered through Celite into a second flask containing a yellow solution of (η^6-C_6H_5F)Cr(CO)$_3$ (0.25 g, 1.08 mmol)[10d] in THF (15 mL) at ~-78 °C (dry ice/acetone). This solution was maintained at ~-78 °C for 5 h and then warmed to ambient temperature and stirred for a further 10 h. The solvent was then removed in vacuo, and the resulting solid was washed with hexanes (3 × 30 mL), leaving a yellow solid which was recrystallized from a minimum of CH_2Cl_2/hexanes. The yellow crystalline product, (η^6-C_6H_5Fp′)Cr(CO)$_3$ (3), was isolated in 57% yield (0.25 g, 0.62 mmol). Anal. Calcd for $C_{17}H_{12}O_5CrFe$: C, 50.53; H, 2.99. Found: C, 50.48; H, 3.09. IR (CH_2Cl_2): ν_{CO} 2029 (s), 1975 (s), 1952 (s), 1868 (s, br) cm^{-1}. Low-resolution mass spectrum: m/z 404 (P$^+$). ^{1}H NMR (CD_2Cl_2): 5.41 (2 H), 5.22 (3 H), 4.78 (2 H), 4.69 (2 H), 1.74 (3 H) ppm. ^{13}C NMR (CD_2Cl_2): 235.76 (Cr–CO), 215.09 (Fe–CO), 108.98 (C2/C6), 106.11 (Cp′, C-Me), 95.70 (C3/C5), 91.63 (C4), 85.3 (Cp′, 4 C-H), 13.31 (CH_3) ppm.

Preparation of (η^6-C_6H_5Fp‡)Cr(CO)$_3$ (4; Fp‡ = (η^5-indenyl)Fe(CO)$_2$). The yellow crystalline complex (η^6-C_6H_5Fp‡)Cr(CO)$_3$ was prepared in a manner similar to that described above (42% yield). It was not obtained in an entirely analytically pure form,[5c-e] but its spectroscopic data indicated that no other metal carbonyl products were present. Anal. Calcd for $C_{20}H_{12}O_5CrFe$: C, 54.58; H, 2.75. Found: C, 53.97; H, 2.86. IR (CH_2Cl_2): ν_{CO} 2029 (s), 1978 (s), 1952 (s), 1870 (s, br) cm^{-1}. Low-resolution mass spectrum: m/z 440 (P$^+$). ^{1}H NMR (CD_2Cl_2): 7.33 (indenyl, 2 H, m), 7.21 (indenyl, 2 H, m), 5.48 (indenyl, 2 H, m), 5.13 (5 H, m), 5.02 (indenyl, 1 H, m) ppm. ^{13}C NMR (CD_2Cl_2): 235.57 (Cr–CO), 215.04 (Fe–CO), 129.23 (indenyl, 2 C-H), 125.42 (indenyl, 2 C-H), 108.11 (C2/C6), 105.51 (indenyl, 2 C), 95.63 (C3/C5), 94.18 (indenyl, C-H), 91.48 (C4), 73.51 (indenyl, 2 C-H) ppm.

The preparation of (η^6-1,4-C_6H_4MeFp)Cr(CO)$_3$ (5; Fp = (η^5-C_5H_5)Fe(CO)$_2$) has been reported previously.[5d,11a]

X-ray Crystal Structure Determinations for the Title Complexes. Crystals of 3–5 suitable for X-ray examination were grown from CH_2Cl_2/hexanes and were mounted on glass fibers and optically centered in the X-ray beam on an Enraf-Nonius CAD4 automated diffractometer. Data collection and structure solution parameters are given in Table I. Data were corrected for Lorentz and polarization effects and also for absorption via the method of Walker and Stuart for 3 and 4[12] and via empirical ψ scans for 5.[13] Details of the usual procedures in our laboratories have been published elsewhere.[5f,13a] Structure solution proceeded in a routine fashion for all three compounds with use of the SDP structure solution package[12] for compounds 3 and 4 and SHELXS-86[13b] and SHELX-76[13b] for 5. All non-hydrogen atoms were treated with anisotropic displacement parameters, and all hydrogen atoms were geometrically generated and included in the model as "riding" on the attached atoms, with isotropic displacement parameters constrained to be 1.2 times those of the

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Table I. Summary of Crystal Data and Intensity Collection for the Complexes

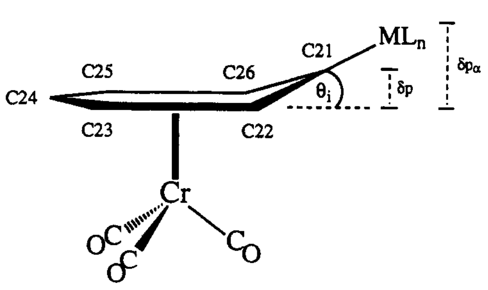
param	$(\eta^6\text{-}C_6H_5Fp')Cr(CO)_3$ (3)	$(\eta^6\text{-}C_6H_5Fp^{\ddagger})Cr(CO)_3$ (4)	$(\eta^6\text{-}1,4\text{-}C_6H_4MeFp)Cr(CO)_3$ (5)
formula	$C_{17}H_{12}O_5CrFe$	$C_{20}H_{12}O_5CrFe$	$C_{17}H_{12}O_5CrFe$
fw	404.13	440.16	404.13
cryst dimens, mm	0.5 × 0.9 × 0.9	0.32 × 0.43 × 0.48	0.15 × 0.21 × 0.52
space group	$P2_1/c$	$P2_1/n$	$P2_1/n$
cryst syst	monoclinic	monoclinic	monoclinic
a, Å	7.599 (2)	8.024 (1)	7.9042 (7)
b, Å	15.054 (4)	19.471 (4)	19.112 (2)
c, Å	14.448 (3)	11.780 (2)	10.8860 (8)
β, deg	99.90 (2)	104.88 (1)	90.981 (7)
V, Å^3	1628	1778	1644
Z	4	4	4
calcd density, g cm^{-3}	1.649	1.644	1.639
abs coeff, cm^{-1}	15.64	14.39	15.55
diffractometer	Enraf-Nonius CAD4	Enraf-Nonius CAD4	Enraf-Nonius CAD4
radiation	Mo Kα (λ = 0.7107 Å)	Mo Kα (λ = 0.7107 Å)	Mo Kα (λ = 0.7107 Å)
monochromator/filter	Zr filter	Zr filter	incident beam, graphite cryst
takeoff angle, deg	3.00	3.00	2.8
detector aperture, mm	3.00 horiz × 4.0 vert	3.00 horiz × 4.0 vert	3.00 + tan θ horiz × 4.0 vert
cryst-to-detector dist, mm	205	205	205
scan type	θ–2θ	θ–2θ	θ–2θ
scan width	0.80 + 0.347 tan θ	0.65 + 0.347 tan θ	0.80 + 0.35 tan θ
scan rate, deg min^{-1}	1.0–20.1	1.5–20.1	0.8–8.0
2θ range, deg	2–60	2–60	2–50
data collection index range	$h,k,\pm l$	$h,k,\pm l$	$h,k,\pm l$
no. of rflns	4729 total, averaged	5220 total, averaged	3051 total
no. of rflns used in refinement	3218 ($I > 3\sigma_I$)	2663 ($I > 3\sigma_I$)	2000 ($I > 3\sigma_I$)
observns/variables ratio	3218/218	2663/245	2000/218
agreement factor R_1, R_2, GOF	0.045, 0.061, 2.12	0.046, 0.059, 1.39	0.0317, 0.0329, 1.29
cor applied	empirical abs cor	empirical abs cor	ψ scans

attached atoms. Final fractional atomic coordinates and equivalent isotropic displacement parameters are given in Table II for compounds **3–5**. Selected bond lengths and angles for **3–5** are given in Tables III and IV, respectively. Tables of structure factors are available from the authors.

Analysis of Arene Planarity. To measure deviations in arene planarity and the bending of the α-substituent atoms away from $Cr(CO)_3$, we have chosen a set of standard parameters, δd, δp, δp_α, $\delta p_{\alpha'}$, and θ_i, which are similar to those we have used previously.[8a] The parameter δd is defined as the difference between the Cr–C_{ipso} bond length and the average of the other Cr–C(H) bond lengths (in Å), i.e.

$$\delta d = d_{Cr\text{-}C21} - d_{Cr\text{-}(C22\text{-}C26,\ \mathrm{average})} \quad (3)$$

The parameters δp and δp_α are defined as the distances (in Å) that the ipso carbon atom, C21, and the α-substituent atoms, Fe, respectively, are lifted out of the least-squares plane defined by the four ortho and meta carbon atoms (C22, C23, C25, and C26), i.e.



The parameter $\delta p_{\alpha'}$ is the value of δp_α corrected for the arene-substituent bond length, i.e.

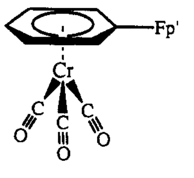
$$\delta p_{\alpha'} = \delta p_\alpha(1.301\ \text{Å}/d_{Fe\text{-}C21}) \quad (4)$$

(where 1.301 Å is the shortest $d_{C_{ipso}\text{-}X}$ distance we have measured) and is particularly useful for transition-metal substituents having C–X bond lengths in excess of 2 Å.[8a] The parameter θ_i is defined as the angle (in degrees) between the least-squares planes defined by the ipso and ortho carbon atoms of the arene (C21, C22, and C26) and the least-squares plane defined by the ortho and meta carbon atoms of the arene (C22, C23, C25, and C26) (see above). These five parameters are defined such that they have positive values when the substituents and their ipso carbon atoms are displaced away from the $Cr(CO)_3$ centers.

Electrochemical Analysis of the Products. The cyclic voltammetric experiments were carried out in CH_2Cl_2 (0.1 M $[n\text{-}Bu_4N]PF_6$ as support electrolyte) using a platinum-bead working electrode and a Ag/AgCl quasi-reference electrode as described in detail previously.[2,5d,e] The cyclic voltammograms of the complexes $(\eta^6\text{-}C_6H_5((\eta^5\text{-}C_5H_4Me)Fe(CO)_2))Cr(CO)_3$, $(\eta^6\text{-}C_6H_5((\eta^5\text{-indenyl})Fe(CO)_2))Cr(CO)_3$, and $(\eta^6\text{-}C_6H_5((\eta^5\text{-}C_5H_5)Fe(CO)_2))Cr(CO)_3$ showed chemically reversible oxidations similar to those reported previously for related complexes.[2,5d,e] Thus, the formal oxidation potentials were 0.54, 0.53, and 0.55 V (vs Ag/AgCl), respectively ($i_{p,c}/i_{p,a}$ = 0.98, 0.90, and 0.98, respectively). The complex $[Cp_2Co]PF_6$ was used as an internal standard after the completion of each set of experiments ($E°'$ = −0.95 V vs Ag/AgCl).

Results and Discussion

To elucidate the nature and origins of the distortions in arene planarity in transition-metal-substituted $(\eta^6\text{-arene})Cr(CO)_3$ complexes, we have characterized three representative examples by X-ray crystallography, i.e.



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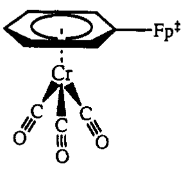

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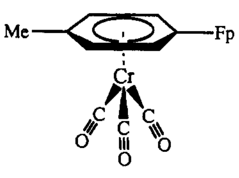

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(where Fp′ = $(\eta^5\text{-}C_5H_4Me)Fe(CO)_2$, Fp‡ = $(\eta^5\text{-indenyl})Fe(CO)_2$, and Fp = $(\eta^5\text{-}C_5H_5)Fe(CO)_2$). They were prepared by the *formal* nucleophilic substitution method we have described previously, e.g.[5d]

$$Na[Cp^{\ddagger}Fe(CO)_2] + (\eta^6\text{-}C_6H_5F)Cr(CO)_3 \xrightarrow[-78\ °C]{THF} (\eta^6\text{-}C_6H_5Fp^{\ddagger})Cr(CO)_3 + NaF \quad (5)$$

(where Cp‡ = η^5-indenyl). These yellow crystalline complexes display the expected high air and thermal stabilities, and their solution-phase IR and NMR data unambiguously establish that the organoiron substituents are σ-bonded to the arene ring with the $Cr(CO)_3$ group π-bonded to the

Table II. Positional and Equivalent Isotropic Gaussian Parameters for the Complexes[a]

atom	x	y	z	U_{eq}	atom	x	y	z	U_{eq}
$(\eta^6\text{-}C_6H_5((\eta^5\text{-}C_5H_4Me)Fe(CO)_2))Cr(CO)_3$[b]									
Fe	3228.5 (5)	1123.8 (3)	1264.9 (3)	3.96 (1)	C11	5108 (4)	1356 (3)	2512 (3)	7.1 (1)
Cr	−11.1 (6)	3209.7 (3)	683.3 (3)	3.95 (1)	C12	5976 (4)	1350 (3)	1718 (3)	7.1 (1)
O1	2819 (4)	1507 (2)	−722 (2)	7.8 (1)	C13	5721 (4)	533 (3)	1294 (3)	7.4 (1)
O2	−149 (3)	205 (2)	1147 (2)	7.42 (9)	C14	4707 (5)	6 (3)	1773 (3)	7.4 (1)
O3	376 (5)	3894 (2)	−1209 (2)	9.6 (1)	C15	4295 (5)	509 (3)	2538 (3)	7.9 (1)
O4	−1861 (4)	1654 (2)	−328 (2)	8.9 (1)	C16	5130 (7)	2081 (4)	3221 (3)	12.7 (2)
O5	−3473 (4)	4181 (2)	464 (2)	9.1 (1)	C21	2227 (3)	2325 (2)	1455 (2)	3.98 (8)
C1	2979 (4)	1354 (2)	61 (2)	5.07 (9)	C22	863 (4)	2455 (2)	2004 (2)	4.97 (9)
C2	1148 (4)	585 (2)	1176 (2)	4.87 (9)	C23	346 (5)	3315 (3)	2229 (2)	6.9 (1)
C3	235 (5)	3641 (2)	−475 (2)	5.7 (1)	C24	1115 (6)	4066 (3)	1892 (3)	7.1 (1)
C4	−1144 (4)	2251 (2)	73 (2)	5.6 (1)	C25	2389 (5)	3953 (2)	1333 (3)	6.4 (1)
C5	−2153 (5)	3793 (2)	553 (3)	5.5 (1)	C26	2934 (4)	3090 (2)	1106 (2)	5.08 (9)
$(\eta^6\text{-}C_6H_5((\eta^5\text{-indenyl})Fe(CO)_2))Cr(CO)_3$[b]									
Fe	1627.4 (8)	1152.2 (3)	2802.7 (5)	3.60 (2)	C13	1229 (7)	658 (3)	4277 (4)	6.7 (2)
Cr	2581.5 (8)	1780.0 (3)	−203.5 (5)	3.43 (2)	C14	2100 (8)	1260 (3)	4611 (4)	6.4 (2)
O1	−1383 (5)	549 (2)	1197 (4)	7.9 (2)	C15	3671 (7)	1236 (3)	4319 (4)	5.2 (2)
O2	388 (6)	2551 (2)	2429 (4)	7.9 (2)	C16	5199 (7)	276 (3)	3429 (4)	7.1 (2)
O3	1541 (6)	1597 (2)	−2796 (3)	8.3 (2)	C17	4965 (10)	−377 (3)	3015 (5)	11.2 (2)
O4	−1157 (4)	1983 (2)	−359 (4)	7.4 (1)	C18	3441 (12)	−738 (3)	2965 (6)	11.9 (4)
O5	2929 (5)	3274 (2)	−645 (5)	9.1 (2)	C19	2107 (10)	−468 (3)	3328 (6)	9.4 (3)
C1	−199 (6)	801 (2)	1804 (4)	4.8 (1)	C21	2950 (5)	1266 (2)	1602 (3)	3.4 (1)
C2	886 (6)	1999 (2)	2574 (4)	4.9 (1)	C22	4154 (5)	1800 (2)	1657 (4)	4.3 (1)
C3	1954 (6)	1664 (3)	−1786 (4)	5.3 (2)	C23	5271 (6)	1813 (3)	905 (4)	5.1 (1)
C4	293 (6)	1905 (2)	−280 (4)	4.6 (1)	C24	5178 (6)	1307 (3)	64 (4)	4.9 (1)
C5	2774 (6)	2698 (3)	−457 (5)	5.3 (2)	C25	3938 (6)	780 (2)	−42 (4)	4.7 (1)
C11	3845 (6)	576 (2)	3829 (3)	4.5 (1)	C26	2854 (6)	760 (2)	704 (3)	4.0 (1)
C12	2288 (7)	201 (3)	3782 (4)	5.4 (2)					
$(\eta^6\text{-}1,4\text{-}C_6H_4Me((\eta^5\text{-}C_5H_5)Fe(CO)_2))Cr(CO)_3$									
Fe	0.06735 (7)	0.84113 (3)	0.65394 (5)	0.041 (1)	C(11)	−0.0337 (6)	0.8707 (2)	0.4803 (4)	0.060 (8)
Cr	0.00490 (8)	0.63691 (3)	0.69263 (6)	0.038 (4)	C(12)	0.1389 (7)	0.8819 (3)	0.4847 (5)	0.075 (7)
O(1)	0.3860 (4)	0.7781 (2)	0.7327 (3)	0.080 (21)	C(13)	0.1754 (8)	0.9308 (3)	0.5785 (6)	0.092 (15)
O(2)	−0.0809 (5)	0.8441 (2)	0.8951 (3)	0.089 (21)	C(14)	0.0213 (9)	0.9477 (2)	0.6303 (5)	0.084 (44)
O(3)	0.3635 (4)	0.5888 (2)	0.6922 (3)	0.065 (17)	C(15)	−0.1065 (7)	0.9101 (2)	0.5709 (5)	0.067 (10)
O(4)	0.0590 (5)	0.6872 (2)	0.9499 (3)	0.089 (32)	C(21)	−0.0248 (5)	0.7469 (2)	0.6128 (3)	0.039 (2)
O(5)	−0.0830 (5)	0.4967 (2)	0.7905 (4)	0.101 (30)	C(22)	−0.1821 (5)	0.7218 (2)	0.6566 (4)	0.045 (7)
C(1)	0.2601 (6)	0.8028 (2)	0.7018 (4)	0.054 (4)	C(23)	−0.2523 (5)	0.6582 (2)	0.6163 (4)	0.052 (14)
C(2)	−0.0210 (6)	0.8410 (2)	0.8009 (4)	0.058 (5)	C(24)	−0.1690 (6)	0.6158 (2)	0.5317 (4)	0.055 (10)
C(3)	0.2251 (5)	0.6076 (2)	0.6921 (4)	0.045 (3)	C(25)	−0.0120 (6)	0.6388 (2)	0.4892 (4)	0.054 (12)
C(4)	0.0378 (5)	0.6687 (3)	0.8508 (4)	0.056 (10)	C(26)	0.0586 (5)	0.7031 (2)	0.5306 (4)	0.046 (3)
C(5)	−0.0495 (6)	0.5516 (3)	0.7548 (4)	0.063 (10)	C(27)	−0.2455 (7)	0.5477 (2)	0.4876 (5)	0.080 (23)

[a] Estimated standard deviations, in parentheses, refer to the last significant digit. U_{eq} is $^1/_3\sum_{i=1}^{3} r_i^2$, where r_i values are the root-mean-square amplitudes of displacement, in Å^2. [b] For complexes 3 and 4, x, y, and z are $\times 10^4$ and U_{eq} is $\times 10^2$.

Table III. Selected Bond Distances (Å)[a]

bond	3	4	5
Cr–C21	2.294 (2)	2.300 (3)	2.286 (4)
Cr–C22	2.222 (2)	2.231 (4)	2.225 (4)
Cr–C23	2.208 (2)	2.218 (4)	2.220 (4)
Cr–C24	2.221 (3)	2.225 (4)	2.244 (4)
Cr–C25	2.207 (2)	2.215 (4)	2.216 (4)
Cr–C26	2.223 (2)	2.240 (4)	2.218 (4)
Fe–C21	1.998 (2)	1.987 (4)	1.991 (4)
Fe–Cp[b]	2.100	2.123	2.095
Fe–Ce[c]	1.729	1.748	1.730
Cr–Ar[d]	1.732	1.741	1.736 (5)
Fe–C1	1.751 (2)	1.765 (5)	1.761 (5)
Fe–C2	1.762 (2)	1.751 (5)	1.756 (5)
Cr–C3	1.834 (3)	1.816 (4)	1.829 (4)
Cr–C4	1.828 (3)	1.831 (4)	1.840 (5)
Cr–C5	1.830 (3)	1.825 (5)	1.820 (5)
C1–O1	1.140 (3)	1.142 (5)	1.146 (5)
C2–O2	1.134 (3)	1.143 (5)	1.139 (5)
C3–O3	1.149 (3)	1.157 (5)	1.152 (5)
C4–O4	1.153 (3)	1.154 (5)	1.145 (5)
C5–O5	1.149 (3)	1.157 (5)	1.150 (5)

[a] Estimated standard deviations, in parentheses, refer to the last digit printed. [b] Fe–Cp is the average of the five Fe–(C11–C15) bond distances. [c] Fe–Ce is the distance from Fe to the centroid of the plane defined by C11–C15. [d] Cr–Ar is the distance from Cr to the centroid of the plane defined by C21–C26.

Table IV. Selected Bond Angles (Å)[a]

angle	3	4	5
Fe–C1–O1	180.0 (6)	176.7 (4)	179.7 (2)
Fe–C2–O2	176.5 (2)	179.3 (5)	176.7 (5)
Cr–C3–O3	178.6 (3)	179.2 (4)	179.6 (3)
Cr–C4–O4	178.7 (2)	178.3 (4)	178.7 (4)
Cr–C5–O5	178.0 (3)	177.7 (5)	177.9 (5)
C1–Fe–C2	94.3 (1)	94.1 (2)	94.9 (2)
C1–Fe–C21	88.8 (1)	94.2 (2)	90.1 (2)
C2–Fe–C21	93.9 (1)	90.4 (2)	93.1 (2)
C1–Fe–Ce	125.7 (2)	124.0 (2)	127.2 (2)
C2–Fe–Ce	123.7 (2)	125.6 (2)	123.6 (2)
Ce–Fe–C21	121.2 (2)	119.7 (2)	118.7 (2)
C3–Cr–C4	87.3 (1)	87.5 (2)	89.1 (2)
C3–Cr–C5	88.0 (1)	88.1 (2)	87.6 (2)
C4–Cr–C5	89.6 (1)	89.3 (2)	88.8 (2)

[a] Estimated standard deviations, in parentheses, refer to the last digit printed.

arene. Of particular interest are the IR and ^{13}C NMR signals attributable to the carbonyl ligands of each of the $(\eta^6\text{-}C_6H_5Fp^\#)Cr(CO)_3$ complexes (where Fp$^\#$ = Fp′ for 3, Fp‡ for 4, and Fp for 1[5d]) and $(\eta^6\text{-}1,4\text{-}C_6H_4MeFp)Cr(CO)_3$ (5), which are very sensitive to changes in electron richness at the metal centers[5b–d,g,8] and are extremely similar in magnitude (varying by less than 5 cm^{-1} and 0.3 ppm, respectively, among these derivatives). Similarly, the oxidation potentials of 1, 3, and 4 (0.55, 0.54, and 0.53 V, vs Ag/AgCl) are not significantly different from one another. These data unambiguously established that each of the

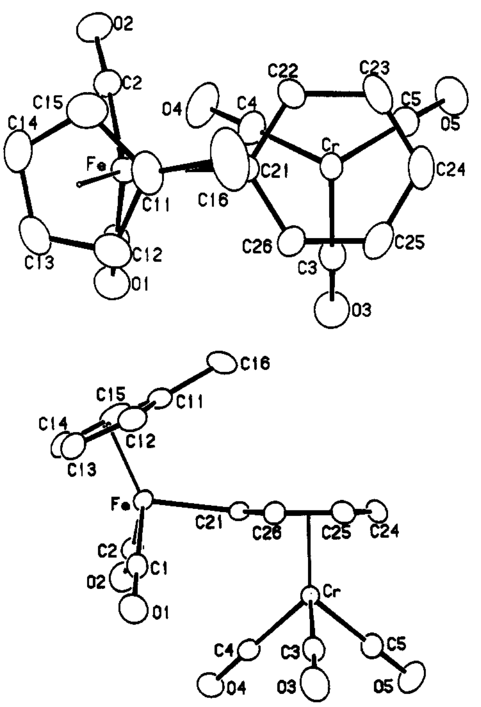


Figure 1. ORTEP plots for the complex (η^6-C_6H_5Fp')$Cr(CO)_3$ (3): (a, top) view perpendicular to the C21–C26 arene plane; (b, bottom) view in the C21–C26 plane and perpendicular to the Fe–C21 bond.

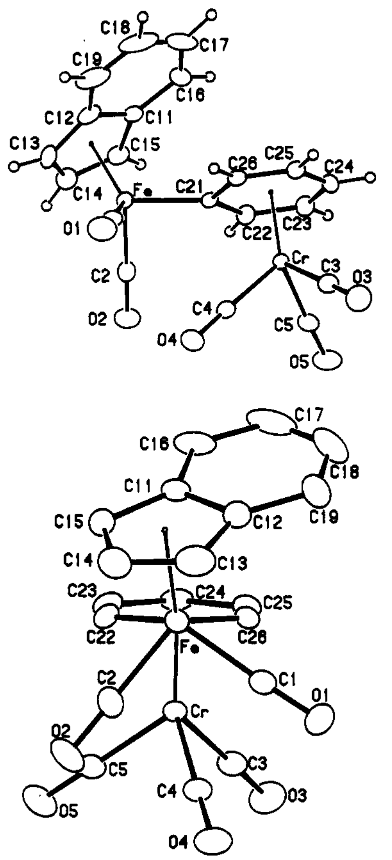


Figure 2. ORTEP plots for the complex (η^6-$C_6H_5Fp^{\ddagger}$)$Cr(CO)_3$ (4): (a, top) perspective view; (b, bottom) view down the Fe–C21 bond.

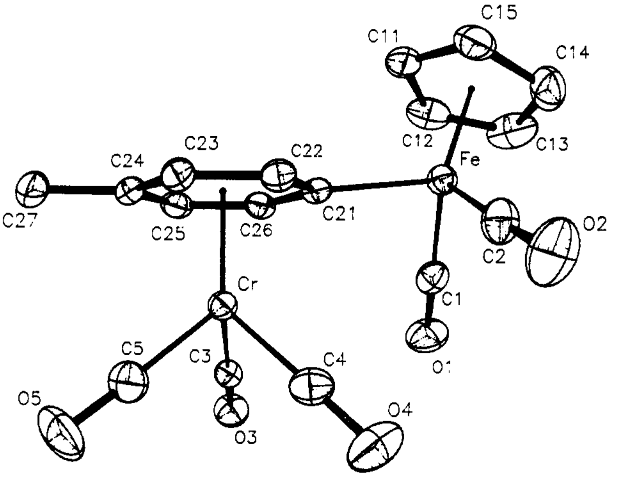
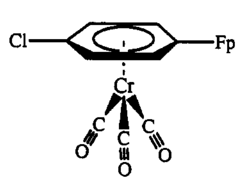


Figure 3. ORTEP plot for the complex (η^6-1,4-C_6H_4MeFp)$Cr(CO)_3$ (5).

three η^5 ligands, and thus the different $\mathrm{Fp}^{\#}$ fragments, are approximately electronically equivalent in these complexes in their abilities to transfer electron density through the arene to $Cr(CO)_3$.

The X-ray crystallographic analyses of the three complexes 3–5 were routine (Tables I–IV) and established the expected three-legged piano-stool structures about the Fe and Cr atoms (Figures 1–3). The various metal–carbonyl linkages are as expected for the (η^6-arene)$Cr(CO)_3$[8a] and $\mathrm{Fp}^{\ddagger}$–aryl[14,15] fragments displaying substantially shorter Fe–CO (i.e. 1.751–1.765, 1.758 (average) Å) than Cr–CO (i.e. 1.816–1.840, 1.827 (average) Å) bond lengths, as were observed for (η^6-1,4-C_6H_4ClFp)$Cr(CO)_3$ (6)[11a] and for (η^6-1,3,5-$C_6H_3Fp_3$)$Cr(CO)_3$ (7) i.e.[5a,c]



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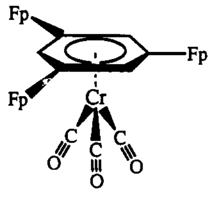

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This is consistent with the observed electron transfer from Fe to Cr, which makes the $Cr(CO)_3$ fragment relatively electron rich,[2,5a,c–e,8a] and with the contraction of the metals' covalent radius, as expected across the first transition series (i.e. r_{cov} is shorter for Fe than for Cr).[16] The Fe–Cp and Fe–Cp linkages of 3 and 5 are also normal,[5c,f,g,11a,14,15] having symmetric Fe–(η^5-cyclopentadienyl) linkages, as is the Fe–(η^5-indenyl) linkage of 4, which consists of three short (i.e. 2.076 (5), 2.098 (4), and 2.081 (5) Å) and two long (i.e. 2.187 (4) and 2.175 (4) Å) bonds.[17] The three Fe–aryl bonds in these complexes (i.e. 1.998 (3), 1.987 (4), and 1.991 (4) Å) are very similar in length to one another and to those of related complexes 6 and 7 (i.e. 1.990 (4), 1.993 (8) and

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(17) See, for example: Kakkar, A. K.; Jones, S. F.; Taylor, N. J.; Collins, S.; Marder, T. B. *J. Chem. Soc., Chem. Commun.* **1989**, 1454–1456 and references cited therein.

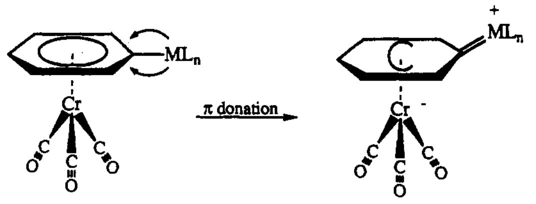
Table V. Structural and Substituent Parameters for the Substituted (η^6-arene)Cr(CO)$_3$ Complexes[a]

arene	ref[b]	δd	δp	δp_α	$\delta p_{\alpha'}$	θ_i
C_6H_5Fp' (3)	c	0.078	0.041	0.284	0.185	3.2
$C_6H_5Fp^‡$ (4)	c	0.074	0.032	0.308	0.202	2.4
1,4-C_6H_4MeFp (5)	c	0.061	0.026	0.223	0.146	2.0
1,4-C_6H_4ClFp (6)	11a	0.066	0.033	0.214	0.140	2.5
$C_6H_5(Mn(CO)_4(PPh_3)$ (8)	11d	0.106	0.034	0.234	0.145	2.5
1,2-$C_6H_4F(Cp_2TiCl)$ (9)	11c	0.134	0.041	0.492	0.289	3.0
1,4-$C_6H_4Me(Cp_2TiCl)$ (10)	11c	0.070	0.005	0.278	0.163	0.4
$C_6H_5(W(CO)_5^-)$ (11)	11b	0.10	0.023	0.062	0.036	1.6

[a] These parameters are defined in the text and are calculated from the reported X-ray crystallographic data for each complex. [b] Reference number in the text. [c] This work.

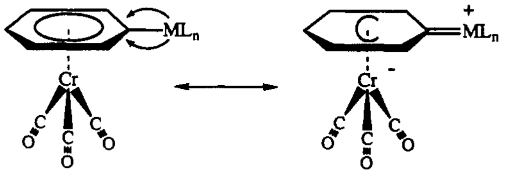
2.033 (8), 2.009 (8) Å, respectively) and those of other Fe–aryl derivatives having *formal* Fe–C(sp^2) single bonds.[5a,c,f,g,14,15] None of these complexes displayed any unusually short *inter*molecular contacts. However, the *intra*molecular steric interactions between the carbonyl ligands on the Fe and Cr centers apparently force a staggered or "molecular gear" arrangement (Figures 1–3),[5c,11a] in which one carbonyl ligand on Cr (i.e. C4O4) is in close contact with the two carbonyl ligands on Fe (i.e. C1O1 and C2O2), giving relatively short, but nonbonding, C4 and O4 to C1, O1, C2, and O2 contacts of 3.1–3.7 Å (cf. the sums of C–C, C–O, and O–O van der Waals radii are 3.4, 3.2, and 3.0 Å, respectively).[16] This *inter*metallic interaction may also account for the observed arene–Cr(CO)$_3$ conformations, which are different from those predicted for complexes having electron-releasing Fp substituents.[8a]

The most interesting features of the X-ray crystal structures of these complexes are the (η^6-arene)–Cr linkages. Inspection of the ORTEP plots of these complexes (Figures 1–3) and of the bond lengths (Table III) indicates that the iron-containing substituents and the ipso carbon atoms (i.e. C21) to which they are attached are bent substantially away from Cr. For each of the heterobimetallic complexes of iron and chromium, 3–6, the structural distortion parameters (Table V, defined in the Experimental Section) are in agreement with this bending and their positive values are similar to those of more familiar main-group substituents having similar π-donor character (i.e. NMe$_2$, OMe, F, etc.), which also bend away from Cr(CO)$_3$.[8a,18] In fact, the other (η^6-arene)Cr(CO)$_3$ complexes which have been crystallographically characterized and which have transition-metal atoms σ-bonded to the arene (i.e. (η^6-$C_6H_5(Mn(CO)_4(PPh_3))$)Cr(CO)$_3$ (8), (η^6-1,2-$C_6H_4F(TiCp_2Cl)$)Cr(CO)$_3$ (9), (η^6-1,4-$C_6H_4Me(TiCp_2Cl)$)-Cr(CO)$_3$ (10), [NEt$_4$][(η^6-$C_6H_5(W(CO)_5)$)Cr(CO)$_3$] (11))[11a-d] all display similar distortions (Table V), as would be expected on the basis of the π-donor character of transition-metal substituents. Similarly, (η^6-1,3,5-$C_6H_3Fp_3$)Cr-(CO)$_3$ (7) has the predicted crown-shaped arene ring.[2,5b-g,8,18] In particular, it is worth emphasizing that the observed magnitudes of the structural distortions in these organometallic derivatives display the same dependence on substituent π-donor character, $\Delta\pi$, as they do for main-group substituents.[5,8,18-21] Thus, the origin of this bending can be ascribed to primarily electronic rather than steric factors, i.e.

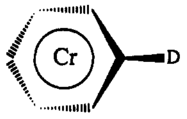


(6)

In valence bond terms, these structural distortions can be explained by an increased contribution from the zwitterionic resonance form, i.e.



to the electronic structures of these species. It therefore does not seem necessary to invoke steric interactions to explain these distortions. Interestingly, in complexes 3–5 the aromatic atoms in the para positions are also significantly bent away from Cr(CO)$_3$, and the arenes show secondary structural distortions away from planarity, i.e.



as was observed for (η^6-arene)Cr(CO)$_3$ complexes having main-group π-donor substituents.[8a] Although this elementary valence bond rationale appears to be useful in explaining the structures of these complexes, a more satisfactory and quantitative explanation for this and the other structural distortions discussed above must await detailed molecular orbital calculations.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada (J.L., A.D.H., R.M., and B.D.S.), the National Science Foundation (S.B. and J.A.), and the University of North Texas (S.B.) for their financial support. We also thank Dr. Simon Lotz and Dr. Joseph Heppert for providing preprints and/or copies of the supplementary material for their work.

Registry No. 3, 142781-52-0; 4, 142781-53-1; 5, 114636-16-7; Fp'$_2$, 32028-30-1; (η^6-C_6H_5F)Cr(CO)$_3$, 12082-05-2.

Supplementary Material Available: Text giving complete descriptions of the X-ray crystal structure determinations for 3 and 4, tables of anisotropic Gaussian parameters, bond lengths, bond angles, hydrogen atom coordinates and Gaussian parameters, and least-squares planes for 3–5, and tables of torsional angles, root-mean-square amplitudes of vibration, and selected bonded and nonbonded distances for 3 and 4 (39 pages). Ordering information is given on any current masthead page.

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(18) The derivations of δd and $\Delta\pi$ values for the organic substituents have been reported previously (i.e. for X = NEt$_2$, NH$_2$, OMe, Me, SiMe$_3$, C(O)Me, and CO$_2$Me).[8]

(19) For references to the π-donor nature of transition-metal–arene interactions, see ref 5 and, for example: (a) Stewart, R. P.; Treichel, P. M. *J. Am. Chem. Soc.* **1970**, *92*, 2710–2718. (b) Bolton, E. S.; Knox, G. R.; Robertson, C. G. *J. Chem. Soc., Chem. Commun.* **1969**, 664. (c) Nesmeyanov, A. N.; Leshcheva, I. F.; Polovyanyuk, I. V.; Ustynyuk, Y. A. *J. Organomet. Chem.* **1972**, *37*, 159–165. (d) Butler, I. R.; Lindsell, W. E. *J. Organomet. Chem.* **1984**, *262*, 59–68. (e) Schilling, B. E. R.; Hoffmann, R.; Lichtenberger, D. L. *J. Am. Chem. Soc.* **1979**, *101*, 585–591.

(20) From the ^{13}C NMR data for the Fp', Fp‡ (Table I), and Fp derivatives (η^6-$C_6H_5Fp^\#$)Cr(CO)$_3$, the π-donor parameter, $\Delta\pi$, is measured as −4.07, −4.15, and −4.16 ppm, respectively.

(21) For the W(CO)$_5$-substituted complex 11, a relatively small distortion of the arene away from planarity (compared to that found in complexes 3–10) is observed and is consistent with the reported tungsten–aryl single bond.[11b]