119924-00-4; 1,3-$C_6H_4(COMn(CO)_5)_2$, 17477-05-3; 1,3,5-$C_6H_3(COMn(CO)_5)_3$, 122622-76-8; 1,4-$C_6H_4Fp_2$, 119945-86-7; 1,3,5-$C_6H_3Fp_3$, 119924-01-5; 1,4-$C_6H_4(Mn(CO)_5)_2$, 17477-07-5; 1,3,5-$C_6H_3(Mn(CO)_5)_3$, 122622-77-9; 1,4-$C_6F_4(Fp')_2$, 122622-78-0; 1,4-$C_6F_4(Fp)_2$, 37366-22-6; 1,4-$C_6F_4H(Mn(CO)_5)$, 122622-79-1; 1,4-$C_6Cl_4(COFp)H$, 122622-80-4; 1,4-$C_6Cl_4(Mn(CO)_5)H$, 122622-81-5; PPh_3, 603-35-0; 1,4-$Mn(CO)_5(C_6H_4I)$, 18701-89-8; 1,4-$C_6H_4(Mn(CO)_4(PPh_3))_2$, 122622-84-8; 1,3-$C_6H_4(Mn(CO)_5)(Mn(CO)_3(dppe))$, 122622-85-9; 1,3-$C_6H_4(Mn(CO)_4)_2(\mu$-dppen), 122622-82-6; 1,3-$C_6H_4(Mn(CO)_4(PPh_3))_2$, 122622-86-0; 1,3,5-$C_6H_3(COCl)_3$, 4422-95-1; 1,4-$C_6H_4(COFp)_2$, 119923-98-7; 1,3-$C_6H_4(COCl)_2$, 99-63-8; 1,4-$C_6H_4(COCl)_2$, 100-20-9; 1,2-$C_6H_4(COCl)_2$, 88-95-9; 1,4-$C_6H_4(COMn(CO)_5)_2$, 17477-08-6; $NaMn(CO)_5$, 13859-41-1; 1,3-$C_6H_4Fp_2$, 119970-49-9; 1,3-$C_6H_4(Mn(CO)_5)_2$, 17477-06-4; 1,4-$C_6F_4Br_2$, 344-03-6; Fp′I, 32628-97-0; FpI, 12078-28-3; $Mn(CO)_5Br$, 14516-54-2; 1,4-$C_6F_4(Mn(CO)_5)_2$, 122622-83-7; 1,4-$C_6Cl_4(COCl)_2$, 99651-72-6; 1,4-$C_6H_4Br_2$, 106-37-6; Br_2, 7726-95-6; I_2, 7553-56-2; 1,4-$C_6H_4I_2$, 624-38-4; $Mn(CO)_5I$, 14879-42-6.

Arene-Bridged Polymetallic Clusters: σ,π Complexes of $CpFe(CO)_2$ or $Cp'Fe(CO)_2$ and $Cr(CO)_3$, $Mo(CO)_3$, or $W(CO)_3$[1]

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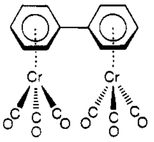
Received April 6, 1989

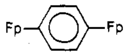
The synthesis of the complexes (η^6-1,3-$C_6H_4Fp_2$)$Cr(CO)_3$ (Fp = (η^5-C_5H_5)$Fe(CO)_2$), (η^6-1,4-$C_6H_4Fp_2$)$M(CO)_3$ (M = Cr, Mo, or W), (η^6-1,3,5-$C_6H_3Fp_3$)$M(CO)_3$ (M = Cr or Mo), (η^6-1,4-$C_6H_4Fp'_2$)$Cr(CO)_3$ (Fp′ = (η^5-C_5H_4Me)$Fe(CO)_2$), and (η^6-1,3,5-$C_6H_3Fp'_3$)$Cr(CO)_3$ is described. These clusters are prepared by the reaction of the parent phenylene-bridged complexes $C_6H_{6-n}Fp_n$ (where n = 2 or 3) with the appropriate metal hexacarbonyl in refluxing Bu_2O. These new materials have been fully characterized by conventional spectroscopic techniques and are shown to contain Fe–arene σ bonds and Cr–, Mo–, or W–arene π bonds. This results in a substantial transfer of electron density from the iron-containing fragments to the $M(CO)_3$ centers. The nature of the metal–arene and metal–metal interactions in these complexes is discussed, and evidence is presented for dimetalloquinone character in the Fe–arene–Fe linkage in (η^6-1,4-$C_6H_4Fp_2$)$Cr(CO)_3$.

Introduction

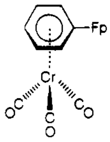
Organic ligands having delocalized π systems can act as electronic bridges between adjacent metal centers. For this reason, complexes containing such linkages have been extensively investigated over the last several years. Most of the ligands used in these studies contain an aromatic core; however, relatively few contain direct metal to arene-carbon bonds.[2] In those species that do possess metal–carbon bonds, the arene may be π bound to both metal centers as in **1**,[3] it may be σ bound to both metal centers[4] as in **2a**,[1,2] or it may have both σ and π interactions[6,7] as in **3d**.[1b,5] Such complexes are ideal models for studying the factors controlling the degree and nature of the electronic interactions in phenylene-bridged polymers. We have shown that the metal centers in σ-bound complexes such as **2a** do indeed interact and that they transfer



1



2a



3d

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(1) (a) Organometallic Complexes with Electronic Bridges. 3. For part 2 see ref 2b. (b) Presented in part at the Third Chemical Congress of North America, Toronto, Canada, June 1988, INOR 87.

(2) See, for example: (a) Hunter, A. D. *Organometallics* **1989**, *8*, 1118. (b) Hunter, A. D.; Szigety, A. B. *Organometallics*, preceding paper in this issue.

(3) For examples of complexes of the type $Ar_2(M(CO)_3)_2$ (where Ar_2 = $(C_6H_5)_2$, $C_6H_3(C_6H_5)_3$, $C_2H_2(C_6H_5)_2$, $(C_6H_4)_2$, etc.) and leading references on their ferrocene analogues and other related species, see: (a) Van Order, N.; Geiger, W. E.; Bitterwolf, T. E.; Rheingold, A. L. *J. Am. Chem. Soc.* **1987**, *109*, 5680. (b) Rieke, R. D.; Milligan, S. N.; Schulte, L. D. *Organometallics* **1987**, *6*, 699. (c) Reike, R. D.; Tucker, I.; Milligan, S. N.; Wright, D. R.; Willeford, B. R.; Randonovich, L. J.; Eyring, M. W. *Organometallics* **1982**, *1*, 938. (d) Pettijohn, T. M.; Lagowski, J. J. *J. Organomet. Chem.* **1988**, *356*, 67. (e) Kalchhauser, H.; Schlogl, K.; Weissensteiner, W.; Werner, A. *J. Chem. Soc., Perkin Trans. 1* **1983**, 1723. (f) Herrmann, W. A.; Andrejewski, D. *Chem. Ber.* **1986**, *119*, 878. (g) Bitterwolf, T. E. *J. Organomet. Chem.* **1983**, *252*, 305. (h) Ceccon, A.; Gambaro, A.; Venzo, A.; Lucchini, V.; Bitterwolf, T. E.; Shade, J. *J. Organomet. Chem.* **1988**, *349*, 315. (i) Corradini, P.; Allegra, G. *J. Am. Chem. Soc.* **1960**, *82*, 2075. (j) Boutonnet, J. C.; Rose-Munch, F.; Rose, E.; Precigoux, G. *J. Organomet. Chem.* **1985**, *284*, C25. (k) Mailvaganam, B.; McCarry, B. E.; Sayer, B. G.; Perrier, R. E.; Faggiani, R.; McGlinchey, M. J. *J. Organomet. Chem.* **1987**, *335*, 213. (l) Nesmeyanov, A. N.; Krivykh, V. V.; Kaganovich, V. S.; Rybinskaya, M. I. *J. Organomet. Chem.* **1975**, *102*, 185. (m) Ceccon, A.; Gambaro, A.; Romanin, M.; Venzo, A. *J. Organomet. Chem.* **1982**, *239*, 345. (n) Helvenston, M. C.; Lynch, T. J. *J. Organomet. Chem.* **1989**, *359*, C50. (o) Elschenbroich, C.; Schneider, J.; Massa, W.; Baum, G.; Mellinghoff, H. *J. Organomet. Chem.* **1988**, *355*, 163. (p) Chatt, J.; Guy, R. G.; Watson, H. R. *J. Chem. Soc.* **1961**, 2332. (q) Cowan, D. O.; LeVanda, C.; Park, J.; Kaufman, F. *Acc. Chem. Res.* **1973**, *6*, 1. (r) Lacoste, M.; Astruc, D.; Garland, M. T.; Varret, F. *Organometallics* **1988**, *7*, 2253.

(4) For examples of complexes of the type $Ar(ML_n)_2$ (where Ar = C_6H_4, C_6F_4, C_3N_3F, etc.), see: (a) Buchwald, S. L.; Lucas, E. A.; Dewan, J. C. *J. Am. Chem. Soc.* **1987**, *109*, 4396. (b) Nesmeyanov, A. N.; Anisimov, K. N.; Kolobova, N. E. *Dokl. Akad. Nauk SSSR* **1967**, *175*, 358 (Engl. transl., 627). (c) Nesmeyanov, A. N.; Anisimov, K. N.; Kolobova, N. E. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1963**, 1348 (Engl. transl., 1225). (d) Cohen, S. C. *J. Chem. Soc., Dalton Trans.* **1973**, 553. (e) Cohen, S. C. *Org. Mass Spectrom.* **1972**, *6*, 1283. (f) Cohen, S. C. *J. Organomet. Chem.* **1971**, *30*, C15. (e) Bruce, M. I. *J. Organomet. Chem.* **1970**, *21*, 415. (f) Artamkina, G. A.; Mil'chenko, A. Y.; Beletskaya, I. P.; Reutov, O. A. *J. Organomet. Chem.* **1987**, *321*, 371. (g) King, R. B.; Epstein, L. M.; Golwling, E. W. *J. Inorg. Nucl. Chem.* **1970**, *32*, 441. (h) Green, M.; Taunton-Rigby, A.; Stone, F. G. A. *J. Chem. Soc. A* **1968**, 2762. (i) King, R. B. *Inorg. Chem.* **1963**, *2*, 531.

(5) (a) Richter-Addo, G. B.; Hunter, A. D. *Inorg. Chem.*, submitted for publication. (b) Richter-Addo, G. B.; Hunter, A. D.; Wichrowska, N. *Can. J. Chem.*, submitted for publication.

(6) For complexes related to (η^6-aryl–ML_n)$M(CO)_3$, see: (a) Heppert, J. A.; Morgenstern, M. A.; Scherubel, D. M.; Takusagawa, F.; Shaker, M. R. *Organometallics* **1988**, *7*, 1715. (b) Heppert, J. A.; Thomas-Miller, M. E.; Swepston, P. N.; Extin, M. W. *J. Chem. Soc., Chem. Commun.* **1988**, 280. (c) Batsanov, A. S.; Struchkov, Y. T. *J. Organomet. Chem.* **1984**, *266*, 295. (d) Nametkin, N. S.; Tyurin, V. D.; Nekhaev, A. I.; Sobolev, Y. P.; Kondrat'eva, M. G.; Batsanov, A. S.; Struchkov, Y. T. *J. Organomet. Chem.* **1983**, *243*, 323. (e) Kolobova, N. E.; Goncharenko, L. V. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1979**, 900 (Engl. transl., 843). (f) Nesmeyanov, A. N.; Polovyanyuk, I. V.; Makarova, L. G. *Dokl. Akad. Nauk SSSR* **1976**, *230*, 1351 (Engl. transl., 650). (g) Argarwal, A.; McGlinchy, M. J.; Tan, T. S. *J. Organomet. Chem.* **1977**, *141*, 85.

(7) Analogous complexes of the general form (η^5-$C_5H_4(ML_n)$)$M(CO)_3$ have been reported, see for example: (a) Sizoi, V. F.; Nekrasov, Y. N.; Sukharev, L. I.; Leontyeva, L. I.; Eremin, S. A.; Kolobova, N. E.; Solodova, M. Y.; Valueva, Z. P. *J. Organomet. Chem.* **1980**, *202*, 83. (b) Franzreb, K. H.; Kreiter, C. G. *J. Organomet. Chem.* **1983**, *246*, 189.

0276-7333/89/2308-2679$01.50/0

Table I. Analytical, Mass Spectral, and Infrared Data for the Complexes

	anal. data					
	C		H		low-resolution mass spectral data P$^+$, m/z[b]	
complex[a]	calcd	found	calcd	found		infrared data ν_{CO} (CH_2Cl_2, cm^{-1})[c]
(1,4-$C_6H_4Fp_2$)Cr(CO)$_3$·$^1/_4$$CH_2Cl_2$ (**3a**)	47.55	47.62	2.49	2.53	566[d]	2030 (s), 1981 (s), 1937 (s), 1854 (s, br)
(1,4-$C_6H_4Fp'_2$)Cr(CO)$_3$·$^1/_4$$CH_2Cl_2$ (**4a**)	49.29	49.56	3.03	3.09	594	2025 (s), 1975 (s), 1934 (s), 1849 (s, br)
(1,4-$C_6H_4Fp_2$)Mo(CO)$_3$·$^1/_2$$CH_2Cl_2$ (**5a**)	43.26	42.87	2.32	2.14	610[d]	2030 (m), 1980 (m), 1936 (m), 1850 (m, br)
(1,4-$C_6H_4Fp_2$)W(CO)$_3$ (**6a**)					698[e]	2032 (m), 1981 (m), 1935 (m), 1848 (m, br)
(1,3-$C_6H_4Fp_2$)Cr(CO)$_3$ (**3b**)	48.80	48.48	2.49	2.58	566[d]	2033 (s), 2030 (sh), 1979 (s), 1935 (s), 1853 (s, br)
(1,3-$C_6H_4Fp_2$)Mo(CO)$_3$ (**5b**)					610[e]	2031 (s), 1981 (s), 1936 (s), 1852 (s, br)
(1,3,5-$C_6H_3Fp_3$)Cr(CO)$_3$·CH_2Cl_2 (**3c**)	45.03	45.32	2.44	2.46	742[f]	2031 (s), 2022 (s), 1979 (s), 1919 (s), 1836 (s, br)
(1,3,5-$C_6H_3Fp'_3$)Cr(CO)$_3$ (**4c**)	46.99	47.21	3.02	3.16	784	2027 (s), 2016 (sh), 1973 (s), 1919 (s), 1835 (s, br)
(1,3,5-$C_6H_3Fp_3$)Mo(CO)$_3$·CH_2Cl_2 (**5c**)	42.75	42.75	2.31	2.12	786[f]	2030 (s), 2026 (sh), 1980 (s), 1922 (s), 1836 (s, br)

[a] Where Fp = (η^5-C_5H_5)Fe(CO)$_2$ and Fp′ = (η^5-C_5H_4Me)Fe(CO)$_2$. [b] Probe temperature 150–280 °C. Assignments involve the following naturally occurring isotopes (i.e., ^{56}Fe, ^{52}Cr, ^{96}Mo, ^{184}W). All ions displayed peak patterns attributable to the expected isotopomers of the nonsolvated species, see text. [c] Abbreviations: w (weak), m (medium), s (strong), sh (shoulder), v (very), br (broad). [d] Peak assignments confirmed by high-resolution mass spectra. [e] These complexes were characterized spectroscopically but were not obtained in an analytically pure form, see text. [f] No parent ion observed in low-resolution mass spectrum. Parent ion observed in positive ion, Xe atom, fast atom bombardment mass spectrum (often as P$^+$ + H).

Table II. ^{1}H and ^{13}C NMR Data for the Complexes (δ in ppm; $(CD_3)_2SO$)

			^{13}C NMR[b] ($^1J_{CH}$, Hz)				
	^{1}H NMR[b]			arene			
complex[a]	Cp^*	C_6H_{6-n}	Cp^*	Fe–C	H–C	Fe–CO	M–CO
(1,4-$C_6H_4Fp_2$)Cr(CO)$_3$ (**3a**)	5.17 (s, 10 H)	5.32 (s, 4 H)	86.80 (181.6)	117.93	112.03 (173.2)	215.34	237.66
(1,4-$C_6H_4Fp_2'$)Cr(CO)$_3$ (**4a**)	5.04 (s, 4 H)	5.36 (s, 4 H)	106.81 (CMe)	122.36	111.74	215.45	237.3
	4.96 (s, 4 H)		84.91 (CH)				
	1.66 (s, 6 H)		84.82 (CH)				
			12.86 (CH$_3$)				
(1,3-$C_6H_4Fp_2$)Cr(CO)$_3$ (**3b**)[c]	5.10 (s, 10 H)	5.76 (s, 1 H)	87.15 (181.7)	126.62	127.22 (C2, 171.2)	215.76	237.09
		5.36 (d, 2 H, J = 6 Hz)			106.63 (C4/C6, 171.4)	215.60	
		5.26 (t, 1 H)			98.77 (C5, 170.2)		
(1,3,5-$C_6H_3Fp_3$)Cr(CO)$_3$ (**3c**)[f]	5.18[d]	5.18[d]	86.90 (181.2)	130.06	121.41 (171.2)[e]	215.74	237.61
(1,3,5-$C_6H_3Fp'_3$)Cr(CO)$_3$ (**4c**)	5.00 (s, 12 H)	5.23 (s, 3 H)	104.46 (CMe)	132.47	121.86	215.91	237.61
	1.80 (s, 9 H)		85.81 (CH)				
			85.05 (CH)				
			12.99 (CH$_3$)				
(1,3,5-$C_6H_3Fp_3$)Mo(CO)$_3$ (**5c**)[f]	5.20 (s, 15 H)	5.58 (s, 3 H)	86.51 (181.5)	136.16	124.53 (171.7)[g]	215.16	226.09

[a] Where Fp = (η^5-C_5H_5)Fe(CO)$_2$ and Fp′ = (η^5-C_5H_4Me)Fe(CO)$_2$; where Cp^* = η^5-C_5H_5 for Fp and η^5-C_5H_4Me for Fp′; M = Cr or Mo. [b] ^{1}H NMR were measured at 300.135 MHz, and ^{13}C NMR were measured at 75.469 MHz unless otherwise specified. [c] ^{1}H NMR run in $(CD_3)_2CO$. [d] Signals accidentally degenerate in $(CD_3)_2SO$; in CD_2Cl_2, δ 4.96 (s, 15 H, C_5H_5), 4.84 (s, 3 H, C_6H_3) ppm. [e] $^4J_{CH}$ = 7.7 Hz. [f] Signals due to CH_2Cl_2 of solvation are observed at δ 5.76 ppm in the ^{1}H NMR. [g] $^4J_{CH}$ = 7.5 Hz.

significant electron density to the arene ring.[1,2] The formation of a π complex of this electron-rich arene might be expected to significantly perturb any such interaction. In addition, a heterometallic σ,π interaction might be expected to occur. We have already communicated that our initial studies in this area confirm the existence of such electron transfer.[1a,2b] In this paper, we would like to report the complete results of these studies. In particular, the synthesis of a series of such σ,π complexes (η^6-$C_6H_{6-n}Fp^*_n$)M(CO)$_3$ (where n = 2, 3; Fp^* = Fp or Fp′; Fp = (η^5-C_5H_5)Fe(CO)$_2$; Fp′ = (η^5-C_5H_4Me)Fe(CO)$_2$; M = Cr, Mo, or W) is presented. The spectroscopic, structural and chemical properties of the arene bridges in these species is discussed as is the nature of the metal–metal interactions.

Experimental Section

Unless otherwise noted, all reactions and subsequent manipulation were performed under anaerobic and anhydrous conditions by using conventional techniques for the manipulation of air-sensitive compounds as described in detail previously.[2] The chemicals used were of reagent grade or comparable purity and where necessary were purified before use and had their purity ascertained by elemental analyses and/or other suitable methods.[8,9] Solvents used were dried, deaerated by standard procedures, and stored under N_2 or Ar.[2,8,9] In particular, Bu_2O was distilled from CaH_2. Unless specified otherwise, the chemical reactions described below were effected at ambient temperatures.

Infrared spectra were recorded on a Pye Unicam PU9522 infrared spectrophotometer calibrated with the 1601 cm^{-1} band of polystyrene. Nuclear magnetic resonance spectra were recorded on a Bruker WH-300 spectrometer with reference to the deuterium signal of the solvent employed. The ^{1}H and ^{13}C chemical shifts are reported in parts per million downfield from external Me_4Si with the assistance of the staff of the departmental NMR laboratory.[2] The low- and high-resolution and fast atom bombardment, FAB, mass spectra were recorded as previously described by the staff of the departmental mass-spectral laboratory.[2]

The analytical, mass spectral, IR, and NMR data for the complexes synthesized during this work are collected in Tables I and II. Synthetic procedures and yields are recorded below.

Caution! When overheated, these reactions (especially those of Mo(CO)$_6$) may produce a pyrophoric black solid and so appropriate precautions must be taken. In addition, the metal hexacarbonyls are volatile and toxic and should therefore be handled with care.

Preparation of the Complexes (η^6-$C_6H_{6-n}Fp^*_n$)Cr(CO)$_3$ (Fp^* = Fp, Fp′; n = 2, 3). All these reactions were performed in a similar manner. The procedure for (η^6-1,4-$C_6H_4Fp_2$)Cr(CO)$_3$ is described in detail as a representative example.

To a 300-mL, three-necked, round-bottomed flask equipped with a gas inlet and an air-cooled condenser[10,11] topped with a

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(8) Shriver, D. F.; Drezdzon, M. A. *The Manipulation of Air-Sensitive Compounds*, 2nd ed.; John Wiley and Sons: New York, 1986.

(9) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*, 2nd ed.; Pergamon: New York, 1980.

(10) It is dangerous to use a liquid-cooled condenser for high-boiling solvents such as Bu_2O (bp 142 °C) since an accidental breakage of the condenser could result in spillage of the cooling liquid into the reaction liquid. This may result in the formation of a super-heated solution and may consequently explode. Such liquids are readily condensed by an air-cooled condenser, and, in fact, in the apparatus the solvent vapors seldom rise more that 2–5 cm up the condenser.

gas inlet and bubbler was added a 2.5-cm Teflon-coated magnetic stir bar. This apparatus was charged under dinitrogen with $1,4\text{-}C_6H_4(COFp)_2$ (0.50 g, 1.02 mmol),[1,2] excess $Cr(CO)_6$ (1.00 g, 4.54 mmol), and Bu_2O[12] (80 mL). Around the flask was placed a loosely fitting 500-mL heating mantle; the reaction mixture was then heated to a gentle reflux.[11] The progress of the reaction was monitored by occasionally allowing the reaction to cool to room temperature and recording the IR spectrum of the supernatant solution. Over the course of the reaction carbonyl bands at $\approx$2015 and 1960 cm^{-1} were observed to first increase in intensity and then to decrease (the very strong band due to $Cr(CO)_6$ is observed at 1980 cm^{-1}). The heating was continued until the new carbonyl bands at 2015 and 1960 cm^{-1} (due to the decarbonylated Fp phenylene[1,2]) had disappeared or any carbonyl bands due to Fp_2 (especially that at 1790 cm^{-1}) started to increase in intensity (12–16 h). The final suspension was cooled to ambient temperature, and the resultant solids were collected on a sintered-glass frit in air. Large lumps of unreacted $Cr(CO)_6$ were removed by hand, and the remaining yellow solid was washed with hexanes (200 mL, undried, wash solvent grade), and then any remaining $Cr(CO)_6$ was removed by sublimation (from a flask warmed to $\approx$40 °C to a cold water cooled cold finger, 0.05 Torr). Fractional crystallization of the remaining solid (CH_2Cl_2, 50 mL, hexanes 100 mL, −35 °C) gives the desired product $(\eta^6\text{-}1,4\text{-}C_6H_4Fp_2)Cr(CO)_3\cdot{}^1/_4CH_2Cl_2$ (**3a**) as an analytically pure microcrystalline pale orange solid in 45% yield (0.26 g, 0.46 mmol).

The related complexes $(\eta^6\text{-}1,3\text{-}C_6H_4Fp_2)Cr(CO)_3$ (**3b**), $(\eta^6\text{-}1,3,5\text{-}C_6H_3Fp_3)Cr(CO)_3\cdot CH_2Cl_2$ (**3c**), $(\eta^6\text{-}1,4\text{-}C_6H_4Fp'_2)Cr(CO)_3\cdot{}^1/_4CH_2Cl_2$ (**4a**), and $(\eta^6\text{-}1,3,5\text{-}C_6H_3Fp'_3)Cr(CO)_3$ (**4c**) are prepared in a similar fashion from their parent acyl complexes.[2] They were isolated in 35%, 15%, 42%, and 39% nonoptimized yields, respectively, after generally shorter reaction times. From the synthesis of **3b** and **3c** were isolated traces of $(\eta^6\text{-}C_6H_5Fp)Cr(CO)_3$ (**3d**, ν_{CO} (CH_2Cl_2) 2030, 1980, 1951, and 1868 cm^{-1}; low-resolution mass-spectrum, P^+, m/z 390),[5b] and from the synthesis of **3c** both **3b** and **3d** were obtained and identified by comparison with authentic samples.

Preparation of the Complexes $(\eta^6\text{-}C_6H_{4-n}Fp_n)Mo(CO)_3$ (n = 2, 3). All of these reactions were performed in a similar manner. The procedure for $(\eta^6\text{-}1,4\text{-}C_6H_4Fp_2)Mo(CO)_3$ is described in detail as a representative example.

This reaction was carried out in the same reaction vessel as that described above. It was charged under dinitrogen with $1,4\text{-}C_6H_4(COFp)_2$ (0.25 g, 0.51 mmol), excess $Mo(CO)_6$ (1.00 g, 3.79 mmol) and Bu_2O (50 mL). The resulting stirred suspension was heated at a *gentle* reflux with IR monitoring of the course of the reaction. As before, the reaction was stopped upon the disappearance of the uncomplexed phenylene carbonyl bands from the IR spectrum of the supernatant solution ($\approx$5 h), and the mixture was then cooled to ambient temperature. The supernatant was removed by cannulation, the residue was taken to dryness in vacuo, and then the excess $Mo(CO)_6$ was removed by sublimation (from a flask warmed to $\approx$50 °C to a cold water cooled cold finger, 0.05 Torr) to give a brown solid. This residue was then crystallized from CH_2Cl_2 (50 mL) and hexanes (40 mL) at −35 °C to give the desired product $(\eta^6\text{-}1,4\text{-}C_6H_4Fp_2)Mo(CO)_3\cdot{}^1/_2CH_2Cl_2$ (**5a**) as analytically pure yellow feathery crystals in 48% (0.15 g, 0.25 mmol) isolated yield.

The related complex $(\eta^6\text{-}1,3,5\text{-}C_6H_3Fp_3)Mo(CO)_3\cdot CH_2Cl_2$ (**5c**) was produced in a similar fashion in 27% isolated yield. From this reaction was isolated a small quantity of $(\eta^6\text{-}1,3\text{-}C_6H_4Fp_2)Mo(CO)_3$ (**5b**, Table I), and in both of these reactions $(\eta^6\text{-}C_6H_5Fp)Mo(CO)_3$ (**5d**) was detected spectroscopically (IR ν_{CO} (CH_2Cl_2) $\approx$ 2032, 1984, 1954, and 1866 cm^{-1}; low-resolution mass spectrum, P^+, m/z 434), but it was not isolated in an analytically pure form.

Preparation of $(\eta^6\text{-}1,4\text{-}C_6H_4Fp_2)W(CO)_3$. This reaction was carried out in the same fashion as that used to prepare the analogous Cr and Mo complexes. Thus, an excess of $W(CO)_6$ (1.00 g, 2.84 mmol) was refluxed in Bu_2O (50 mL) with $1,4\text{-}C_6H_4(COFp)_2$ (1.00 g, 2.06 mmol) for 5 h and then taken to dryness in vacuo. The IR spectra of this solid indicated that it contained a complex mixture of products. This mixture was partially separated by chromatography on Florisil and by fractional crystallization. The more soluble fractions were shown to contain $1,4\text{-}C_6H_4Fp_2$,[2b] C_6H_5Fp, and Fp_2 by comparison to authentic samples. In addition to a number of products that were not identified, the least soluble fractions contained the desired complex $(\eta^6\text{-}1,4\text{-}C_6H_4Fp_2)W(CO)_3$ (**6a**) as well as $(\eta^6\text{-}C_6H_5Fp)W(CO)_3$ (**6d**, $\nu_{CO}(CH_2Cl_2) \approx$ 2030, 1985, 1955, and 1865 cm^{-1}; low-resolution mass-spectrum, P^+, m/z 522). These products were not obtained in an analytically pure state and were not characterized further.

Attempted Synthesis of $(\eta^6\text{-}1,4\text{-}C_6F_4Fp'_2)Cr(CO)_3$. To $1,4\text{-}C_6F_4Fp'_2$ (0.14 g, 0.26 mmol) and excess $Cr(CO)_6$ (1.0 g, 4.5 mmol) was added Bu_2O (50 mL), and then the resulting mixture was refluxed for a total of 25 h. The IR spectra of the supernatants and solids separated from this reaction mixture showed no carbonyl bands below 1940 cm^{-1} attributable to $Cr(CO)_3$ adducts and were not investigated further.

Pyrolysis of $(\eta^6\text{-}1,3\text{-}C_6H_4Fp_2)Cr(CO)_3$. To a flask containing $(\eta^6\text{-}1,3\text{-}C_6H_4Fp_2)Cr(CO)_3$ (0.10 g, 0.18 mmol) was added Bu_2O (40 mL), and the resulting suspension was stirred at a vigorous reflux for 24 h. Upon cooling to −40 °C, yellow crystals precipitated from solution and were collected by filtration to give recovered starting material, **3b**, in 70% yield. The complex $(\eta^6\text{-}C_6H_5Fp)Cr(CO)_3$ was the main ($\approx$ 90% of the total by IR) organometallic species found in the filtrate. In addition, smaller quantities of $1,3\text{-}C_6H_4Fp_2$ (**2b**) and C_6H_5Fp (**2d**) were identified as being present by their characteristic IR and mass spectra.[2a]

Results and Discussion

Transition-metal complexes containing π-bound arene rings have been extensively investigated because of both fundamental interest in the nature of their metal–arene interactions and their utility in organic synthesis.[13,14] The $(\eta^6\text{-arene})M(CO)_3$ complexes of the group six metals have been the most widely studied of such species because they are relatively air and thermally stable, they are reactive toward a wide variety of organic reagents (especially nucleophiles), and they are easily prepared for most arenes.[13–15] They are most often synthesized by the direct thermal reaction of the arene with either the metal hexacarbonyl or one of its solvates, i.e. eq 1 and 2 (where M

$$M(CO)_6 + \text{arene} \xrightarrow{\Delta} (\text{arene})M(CO)_3 + 3CO \quad (1)$$

$$M(CO)_3(\text{solv})_3 + \text{arene} \xrightarrow{\Delta} (\text{arene})M(CO)_3 \quad (2)$$

= Cr, Mo, or W; solv = THF, CH_3CN, C_7H_8, etc.). The first method is the route of choice in the cases where the products are relatively thermally stable, and one reagent can be used in excess. The second reaction is generally

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(11) With this apparatus having a straight-tube air-cooled condenser, the volatile $Cr(CO)_6$ tends to condense at the same level as the solvent and is therefore generally washed back into the reaction flask. Any $Cr(CO)_6$ that does stay in the condenser is readily reintroduced into the flask by either tapping the condenser with a pencil or placing a glass rod down the condenser (about every 12–24 h). To avoid extensive decomposition due to local overheating, care must be taken to ensure that the level of the solvent remains above that of the heating mantle. In addition, the suspension should be stirred at slow speed to avoid splashing the solid components in the reaction mixture onto the sides of the flask.

(12) The Bu_2O used in these reactions must not be distilled from $Na[Ph_2CO]$, since this procedure introduces traces of benzene into the solvent[8,9] which result in the formation of $(\eta^6\text{-}C_6H_6)Cr(CO)_3$.

(13) (a) Collman, J. P.; Hegedus, L. S.; Norton, J. K.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987. (b) Davies, S. G. *Organotransition Metal Chemistry: Applications to Organic Synthesis*; Pergamon: New York, 1982. (c) Silverthorn, W. E. *Adv. Organomet. Chem.* **1975**, *13*, 47. (d) Senoff, C. V. *Coord. Chem. Rev.* **1980**, *32*, 111.

(14) (a) Sneeden, R. P. A. *Organochromium Compounds*; Academic: New York, 1975. (b) Davis, R.; Kane-Maguire, L. A. P. *Comprehensive Organometallic Chemistry*; Wilkinson, G., Ed.; Pergamon: Oxford, England, 1982; Vol. 3, p 975. (c) Davis, R.; Kane-Maguire, L. A. P. *Comprehensive Organometallic Chemistry*; Wilkinson, G., Ed.; Pergamon: Oxford, England, 1982; Vol. 3, p 1204. (d) Davis, R.; Kane-Maguire, L. A. P. *Comprehensive Organometallic Chemistry*; Wilkinson, G., Ed.; Pergamon: Oxford, England, 1982; Vol. 3, p 1356.

(15) The most common exceptions are electron-poor arenes such as $C_6H_3F_3$ and $C_6H_3(CO_2Me)_3$ and those with oxidizing substituents such as NO_2 or COCl.[14]

preferred for more thermally sensitive species.[14] The properties of these arene complexes have been systematically investigated by a wide variety of means including IR[16] and NMR[16–18] spectroscopies, electrochemistry,[3a–c,19] and X-ray crystallography.[14,20] However, the exact nature of the metal–arene bond in these complexes is still somewhat controversial and has been the subject of numerous experimental[16–20] and theoretical[14,20e,21] studies.

Our interest in (η^6-arene)M(CO)$_3$ complexes stems from our investigations into the synthesis of organometallic polymers and, in particular, our efforts to elucidate the fundamental nature of the metal–ligand–metal bridging interactions that form the pathway for electrical conductivity in such species. Interest in such arene-bridged complexes (vide supra), has been growing in recent years, but most detailed studies have focused on complexes in which both metals are π-bound to the arenes.[3] Our primary interest is in σ-bridged species;[2] however, we are also interested in complexes with both σ and π metal–arene bonds since such species are excellent probes into the nature of the σ interactions. In addition, these σ,π linkages are of interest in themselves both from a fundamental viewpoint and because eventual organometallic polymers might be functionalized with π-bound M(CO)$_3$ groups to modify their photochemical and electronic properties. At the start of our study,[1b] a number of complexes containing a single metal group σ-bound to the arene ring of a Cr(CO)$_3$ complex were known.[6c–g] However, no detailed spectroscopic characterization of the metal–arene–Cr interaction had been presented, and, to the best of our knowledge, no complexes with more than one transition metal[22] σ bound to the arene or with Mo(CO)$_3$ or W(CO)$_3$ groups had been reported.[6] We therefore undertook a systematic study of the synthesis and spectroscopic properties of such species in an effort to elucidate the degree and nature of the σ,π and σ,σ metal–metal interactions in these species.

Synthesis of the σ,π Cluster Complexes. Phenylene-bridged complexes in which a benzene ring is σ-bound to two or three Fp groups (Fp = (η^5-C$_5$H$_5$)Fe(CO)$_2$) are readily prepared by heating the appropriate acyl precursors in refluxing Bu$_2$O, i.e. eq 3 (where n = 2 or 3), and may

$$C_6H_{6-n}(COFp)_n \xrightarrow[Bu_2O]{\Delta} C_6H_{6-n}Fp_n \tag{3}$$

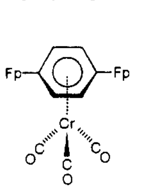
be isolated in 30–70% yields.[2] The arene ligands in these complexes are both electron rich and sterically crowded but retain their ability to form π complexes with 12-electron organometallic fragments.[2a,23,24] Thus, the reaction of these complexes with Cr(CO)$_6$ proceeds as desired, i.e. eq 4, to give the σ,π complexes. However, owing to the

$$C_6H_{6-n}Fp_n + Cr(CO)_6 \xrightarrow[Bu_2O]{\Delta} (\eta^6\text{-}C_6H_{6-n}Fp_n)Cr(CO)_3 \tag{4}$$

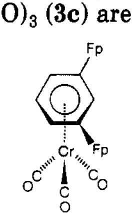
relative solubilities and stabilities of the complexed and uncomplexed phenylene products (vide infra), reactions 3 and 4 are best carried out concurrently. Thus, the acyls are decarbonylated in the presence of an excess of Cr(CO)$_6$, e.g. eq 5, to give the η^6-arene complexes in 15–45% isolated

$$1,4\text{-}C_6H_4(COFp)_2 + \text{excess } Cr(CO)_6 \xrightarrow[Bu_2O]{\Delta} (\eta^6\text{-}1,4\text{-}C_6H_4Fp_2)Cr(CO)_3 \tag{5}$$

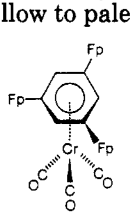
yields. These novel diamagnetic complexes (η^6-1,4-C$_6$H$_4$Fp$_2$)Cr(CO)$_3$ (**3a**), (η^6-1,3-C$_6$H$_4$Fp$_2$)Cr(CO)$_3$ (**3b**), and (η^6-1,3,5-C$_6$H$_3$Fp$_3$)Cr(CO)$_3$ (**3c**) are yellow to pale orange crystalline solids that are sufficiently air stable to be



3a



3b



3c

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(16) (a) Neuse, E. W. *J. Organomet. Chem.* **1975**, *99*, 287. (b) Bitterwolf, T. E. *Polyhedron* **1988**, *7*, 1377. (c) Bitterwolf, T. E. *Polyhedron* **1988**, *7*, 409. (d) van Meurs, F.; Baas, J. M. A.; Van Bekkum, H. *J. Organomet. Chem.* **1977**, *129*, 347. (e) Muller, J. *J. Organomet. Chem.* **1969**, *18*, 321. (f) van Meurs, F.; Baas, J. M. A. *J. Organomet. Chem.* **1976**, *113*, 353. (g) Levitt, L. S.; Levitt, B. W. *J. Inorg. Nucl. Chem.* **1976**, *38*, 1907. (h) Klopman, G.; Noack, K. *Inorg. Chem.* **1968**, *7*, 579.

(17) Rehder, D. *Multinuclear NMR*; Mason, J., Ed.; Plenum: New York, 1987; Chapter 19.

(18) (a) Mann, B. E.; Taylor, B. F. *^{13}C NMR Data for Organometallic Compounds*; Academic: New York, 1981. (b) Bodner, G. M.; Todd, L. J. *Inorg. Chem.* **1974**, *13*, 360. (c) Fedorov, L. A.; Petrovskii, P. V.; Fedin, E. I.; Panosyan, G. A.; Tsoi, A. A.; Baranetskaya, N. K.; Setkina, V. N. *J. Organomet. Chem.* **1979**, *182*, 499. (d) Cozak, D.; Butler, I. S.; Hickey, J. P.; Todd, L. J. *J. Magn. Reson.* **1979**, *33*, 149. (e) Tirouflet, J.; Besancon, J.; Mabon, F.; Martin, M. L. *Org. Magn. Reson.* **1976**, *8*, 444. (f) Fletcher, J. L.; McGlinchey, M. J. *Can. J. Chem.* **1975**, *53*, 1525. (g) van Meurs, F.; van der Toorn, J. M.; van Bekkum, H. *J. Organomet. Chem.* **1976**, *113*, 341. (h) Dyall, L. K. *Aust. J. Chem.* **1964**, *17*, 419. (i) Roques, B. P. *J. Organomet. Chem.* **1977**, *136*, 33. (j) Mann, B. E. *J. Chem. Soc., Dalton Trans.* **1973**, 2013. (k) Brown, D. A.; Chester, J. P.; Fitzpatrick, N. J.; King, I. J. *Inorg. Chem.* **1977**, *16*, 2497. (l) Mann, B. E. *Adv. Organomet. Chem.* **1974**, *12*, 135. (m) Price, J. T.; Sorensen, T. S. *Can. J. Chem.* **1968**, *46*, 516. (n) Jackson, W. R.; Pincombe, C. F.; Rae, I. D.; Thapebinkarn, S. *Aust. J. Chem.* **1975**, *28*, 1535. (o) Brown, D. A.; Chester, J. P.; Fitzpatrick, N. J.; King, I. J. *Inorg. Chem.* **1977**, *16*, 2497.

(19) (a) Connelly, N. G.; Geiger, W. E. *Adv. Organomet. Chem.* **1984**, *23*, 1. (b) Geiger, W. E.; Connelly, N. G. *Adv. Organomet. Chem.* **1985**, *24*, 87. (c) Rourke, F.; Crayston, J. A. *J. Chem. Soc., Chem. Commun.* **1988**, 1264. (d) Zoski, C. G.; Sweigart, D. A.; Stone, N. J.; Rieger, P. H.; Mocellin, E.; Mann, T. F.; Mann, D. R.; Gosser, D. K.; Doeff, M. M.; Bond, A. M. *J. Am. Chem. Soc.* **1988**, *110*, 2109. (e) Bullick, J. P.; Boyd, D. C.; Mann, K. R. *Inorg. Chem.* **1987**, *26*, 3084. (f) Rieke, R. D.; Henry, W. P.; Arney, J. S. *Inorg. Chem.* **1987**, *26*, 420. (g) Stone, N. J.; Sweigart, D. A.; Bond, A. M. *Organometallics* **1986**, *5*, 2553. (h) Doxsee, K. M.; Grubbs, R. H.; Anson, F. C. *J. Am. Chem. Soc.* **1984**, *106*, 7819. (i) Ikeshoji, T.; Parker, V. D. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 1112. (j) Degrand, C.; Radecki-Sudre, A.; Besancon, J. *Organometallics* **1982**, *1*, 1311. (k) Ceccon, A.; Gentiloni, M.; Romanin, A.; Venzo, A. *J. Organomet. Chem.* **1977**, *127*, 315. (l) Lloyd, M. K.; McCleverty, J. A.; Connor, J. A.; Jones, E. M. *J. Chem. Soc., Dalton Trans.* **1973**, 1768. (m) Gubin, S. P.; Khandkarova, V. S. *J. Organomet. Chem.* **1970**, *22*, 449.

(20) For example, there is controversy over the existence of C–C bond length alternation in the species, see for example: (a) Wang, Y.; Angermund, K.; Goddard, R.; Kruger, C. *J. Am. Chem. Soc.* **1987**, *109*, 587. (b) Byers, B. P.; Hall, M. B. *Inorg. Chem.* **1987**, *26*, 2168. (c) Koshland, D. E.; Myers, S. E.; Chesick, J. P. *Acta Crystallogr., Sect. B* **1977**, *33*, 2013. (d) Rees, B.; Coppens, P. *J. Organomet. Chem.* **1972**, *42*, C102. (e) Rogers, R. D.; Atwood, J. L.; Albright, T. A.; Lee, W. A.; Rausch, M. D. *Organometallics* **1984**, *3*, 263. (f) Carter, O. L.; McPhail, A. T., Sim, G. A. *J. Chem. Soc. A* **1967**, 1619.

(21) (a) Albright, T. A.; Hofmann, P.; Hoffmann, R. *J. Am. Chem. Soc.* **1977**, *99*, 7546. (b) Modelli, A.; Distefano, G.; Guerra, M.; Jones, D. *J. Am. Chem. Soc.* **1987**, *109*, 4440. (c) Byers, B. P.; Hall, M. B. *Organometallics* **1987**, *6*, 2319. (d) Rooney, D.; Chaiken, J.; Driscoll, D. *Inorg. Chem.* **1987**, *26*, 3939. (e) Semmelhack, M. F.; Garcia, J. L.; Cortes, D.; Farina, R.; Hong, R.; Carpenter, B. K. *Organometallics* **1983**, *2*, 467. (f) Albright, T. A.; Hofmann, P.; Hoffmann, R.; Lillya, C. P.; Dobosh, P. A. *J. Am. Chem. Soc.* **1983**, *105*, 3396. (g) Muetterties, E. L.; Bleeke, J. R.; Wucherer, E. J.; Albright, T. A. *Chem. Rev.* **1982**, *82*, 499. (h) Albright, T. A. *Acc. Chem. Res.* **1982**, *15*, 149. (i) Elian, M.; Chen, M. M. L.; Mingos, D. M. P.; Hoffmann, R. *Inorg. Chem.* 1976, *15*, 1148.

(22) Complexes with two main-group metals on the arene have been reported, see: Wright, M. E. *Organometallics* **1989**, *8*, 407 and references cited therein.

(23) For examples of other electron-rich arene complexes of Cr(CO)$_3$, see: (a) Schollkopf, K.; Stezowski, J. J.; Effenberger, F. *Organometallics* **1985**, *4*, 922. (b) Saillard, J. Y.; Grandjean, D.; Le Maux, P.; Jaouen, G. *Nouv. J. Chim.* **1981**, *5*, 153. (c) Gommans, L. H. P.; Main, L.; Nicholson, B. K.; Robinson, W. T.; Rae, A. D. *J. Organomet. Chem.* **1988**, *346*, 385. (d) McFarlane, W.; Grim, S. O. *J. Organomet. Chem.* **1966**, *5*, 147. (e) Davidson, G.; Riley, E. M. *Spectrochim. Acta, Part A* **1971**, *27*, 1649.

(24) The only complexes to experience a similar steric crowding are those with three or more Bu^t or Ph groups on the arene, see: (a) van Meurs, F.; van der Toorn, J. M.; van Bekkum, H. *J. Organomet. Chem.* **1976**, *113*, 341. (b) Jackson, W. R.; Pincombe, C. F.; Rae, I. D.; Thapebinkarn, S. *Aust. J. Chem.* **1975**, *28*, 1535. (c) Deberitz, J.; Noth, H. *J. Organomet. Chem.* **1973**, *55*, 153. (d) Mailvaganam, B.; McCarry, B. E.; Sayer, B. G.; Perrier, R. E.; Faggiani, R.; McGlinchey, M. J. *J. Organomet. Chem.* 1987, *335*, 213.

handled in air, even as solutions, for short periods of time without the occurrence of noticeable decomposition. They are much less soluble in common organic solvents than are their phenylene precursors and are almost totally insoluble in solvents such as Bu_2O or hexanes at ambient temperature. Since the desired products are the least soluble components of reaction 5 and are air stable, they may be conveniently collected by filtration of the final reaction mixtures in air. The analytical and spectral data for these complexes (Tables I and II) confirm the proposed formulations as σ,π clusters with three-legged piano-stool geometries. Of particular utility in determining the molecularity of these species and the other π complexes reported in this paper were the mass spectra in which were observed the expected parent ions. The description of many of the isolated materials as CH_2Cl_2 solvates was initially suggested by the analytical data and was subsequently confirmed by the observation of the expected CH_2Cl_2 signals in the ^1H and ^{13}C NMR spectra of these materials and the direct observation of the solvent of crystallization in the X-ray structure of **3a**.[2a] These solvate molecules do not appear to be strongly bound into the solid lattices since they are slowly lost after removal of the CH_2Cl_2/hexanes solvent either under a dinitrogen atmosphere or in vacuo. Nevertheless, they do seem to impart greater crystallinity to the complexes and desolvation of the solids generally results in the initially shiny crystals losing their lustrous appearance and sometimes their shape.[25] The related methylcyclopentadienyl complexes $(\eta^6\text{-}1,4\text{-}C_6H_4Fp'_2)Cr(CO)_3$ (**4a**) and $(\eta^6\text{-}1,3,5\text{-}C_6H_3Fp'_3)Cr(CO)_3$ (**4c**) (where Fp′ = $(\eta^5\text{-}C_5H_4Me)Fe(CO)_2)$ were prepared in an identical fashion. Their physical and spectroscopic properties (Tables I and II) are similar to those of the related cyclopentadienyl species. Most notably, the Fp′ complexes exhibit the increases in solubilities and decreases in carbonyl stretching frequencies (of about 3–6 cm^{-1} for **4a** vs **3a** due to the somewhat more electron-rich metal centers) that one would expect.

The phenylene-bridged complexes are also able to π bond to the $Mo(CO)_3$ fragment. Thus, when the acyl complexes are decarbonylated in the presence of an excess $Mo(CO)_6$, e.g. eq 6, the desired complexes $(\eta^6\text{-}1,4\text{-}C_6H_4Fp_2)Mo(CO)_3$ (**5a**) and $(\eta^6\text{-}1,3,5\text{-}C_6H_3Fp_3)Mo(CO)_3$ (**5c**) are isolated in 48 and 27% yields, respectively.

$$1,4\text{-}C_6H_4(COFp)_2 + \text{excess } Mo(CO)_6 \xrightarrow[Bu_2O]{\Delta} (\eta^6\text{-}1,4\text{-}C_6H_4Fp_2)Mo(CO)_3 \quad (6)$$

These reactions are often accompanied by extensive decomposition that gives rise to a black pyrophoric solid, but this does not appear to greatly affect the isolated yields by comparison with those observed for similar $Cr(CO)_3$ derivatives. As expected, the pale orange crystalline products of these reactions are more air and thermally sensitive than are their Cr analogues.[14c] The solids may be handled in air for short periods of time, but the solutions must be handled under an inert atmosphere. The trisubstituted species **5c** may be stored at ambient temperature for months with no noticeable decomposition, but the 1,4-complex **5a** undergoes noticeable thermal decomposition over this time period. Their analytical and spectroscopic properties (Tables I and II) are broadly similar to those of their Cr analogues (vide infra) and confirm that they also possess three legged piano stool structures with the $Mo(CO)_3$ group π-bonded to the arene ring.

An attempt was made to prepare the analogous W complex $(\eta^6\text{-}1,4\text{-}C_6H_4Fp_2)W(CO)_3$ (**6a**) using the same method that had previously proven successful for the Mo and Cr complexes, i.e. eq 7. However, IR monitoring of this reaction indicated that it was slower than that of Cr and Mo and that it gave a more complicated mixture of products.

$$1,4\text{-}C_6H_4(COFp)_2 + \text{excess } W(CO)_6 \xrightarrow[Bu_2O]{\Delta} (\eta^6\text{-}1,4\text{-}C_6H_4Fp_2)W(CO)_3 \quad (7)$$

This result was not unexpected,[14d] but it does result in the desired product **6a** being isolated in low yield. It was never obtained in an analytically pure state; however, its IR and mass spectra (Table I) suggest that is has the same piano-stool structure as do its lower molecular-weight congeners.

In each of the reactions where σ,π clusters were synthesized (i.e. eq 5–7), a number of additional organometallic products were observed in the IR, NMR, and mass spectra of various fractions of the final reaction mixtures. Some of these have not yet been fully purified and identified but the major byproducts could all be readily characterized by comparison of their characteristic properties to those of authentic samples. These byproducts included species soluble in nonpolar solvents (e.g. the ubiquitous Fp_2 dimer and various Fp phenylenes) and those soluble only in polar solvents (those with $M(CO)_3$ groups π-bound to the arene but containing less than the expected number of Fp groups). For example, in the synthesis of **3c**, complexes containing zero to three Fp groups, with or without a $Cr(CO)_3$ group, were detected, i.e., eq 8, and account for the low yields of desired products isolated from many of these reactions.

$$\begin{aligned}&1,3,5\text{-}C_6H_3(COFp)_3 + \text{excess } Cr(CO)_6 \xrightarrow{\Delta,\ Bu_2O}\\ &(\eta^6\text{-}1,3,5\text{-}C_6H_3Fp_3)Cr(CO)_3 + (\eta^6\text{-}1,3\text{-}C_6H_4Fp_2)Cr(CO)_3\\ &+ (\eta^6\text{-}C_6H_5Fp)Cr(CO)_3 + (\eta^6\text{-}C_6H_6)Cr(CO)_3 +\\ &1,3,5\text{-}C_6H_3Fp_3 + 1,3\text{-}C_6H_4Fp_2 + C_6H_5Fp + Fp_2 \quad (8)\end{aligned}$$

Independent experiments have shown that the Fp–phenylene π complexes are much more stable toward cleavage of the Fe–arene bonds under these conditions, i.e. eq 9, than are their uncomplexed analogues, i.e. eq 10.[2]

$$\begin{aligned}&(\eta^6\text{-}1,3\text{-}C_6H_4Fp_2)Cr(CO)_3 \xrightarrow{\Delta,\ 24\text{ h},\ Bu_2O}\\ &(\eta^6\text{-}1,3\text{-}C_6H_4Fp_2)Cr(CO)_3\ (\approx 70\%) +\\ &(\eta^6\text{-}C_6H_5Fp)Cr(CO)_3\ (\approx 25\%) + 1,3\text{-}C_6H_4Fp_2 +\\ &C_6H_5Fp + Fp_2 \quad (9)\end{aligned}$$

$$1,3\text{-}C_6H_4Fp_2 \xrightarrow[24\text{ h}]{\Delta,\ Bu_2O} Fp_2 + C_6H_6 \quad (10)$$

Thus, even after 24 h in refluxing Bu_2O, the starting material **3b** may be recovered in excellent yield, whereas the uncomplexed phenylene complexes are much more thermally sensitive and undergo complete iron–aryl bond cleavage under these conditions to give benzene and Fp_2. Therefore, the origin of the lower molecular weight π complexes in these syntheses (i.e. eq 5–8) appears to be predominantly thermal degradation of the uncomplexed-phenylene reagents that may then be π complexed by "$M(CO)_3$" to give the ultimate products.[26] The extent of the byproduct formation is greatest for the 1,3,5-substituted complexes and least for the 1,4-substituted species, as would be expected if the decomposition was sterically controlled. In addition,

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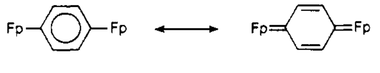
[25] Similar CH_2Cl_2 solvates are observed in many related $(\eta^6\text{-}Ar\text{-}(ML_n)_m)M(CO)_3$ complexes where the presence of CH_2Cl_2 has been confirmed by Cl elemental analysis, ^1H and ^{13}C NMR spectroscopies: Hunter, A. D.; McLernon, J. L., unpublished observations.

[26] The $M(CO)_3$ groups on the lower molecularity complexes probably arise from the excess $M(CO)_6$ present; however, direct arene exchange, especially in reaction 9, cannot be entirely ruled out.[14]

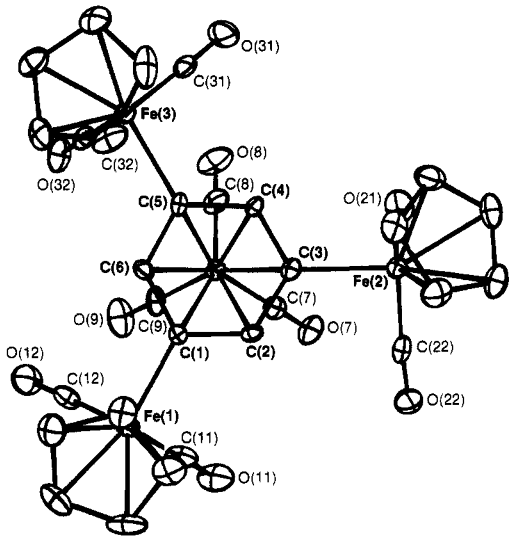
these decomposition reactions are least prevalent for Mo and most prevalent for W as would be expected on the basis of the ease of metal π-complex formation. Finally, it is tempting to suggest that the decreased rate of thermal Fe–arene bond cleavage observed upon π complexation is a result of the net transfer of electron density from iron to the group six metal and perhaps due to an increase in the Fe–arene bond order (vide infra).

Spectroscopic and Structural Characterization of the Complexes and the Nature of the Metal–Arene and Metal–Metal Interactions. The η^1 metal–arene bond in Fp-aryl complexes is primarily σ bonding in character, but, also contains a significant π component. The Fp group in these species is acting as both a σ and π donor,[2b,27,28] and when two of these groups are bonded to the same arene in a 1,4 fashion, a synergic metal–arene–metal interaction may occur giving the complex significant dimetalloquinone resonance character, i.e., **2a**.[2b,5a]

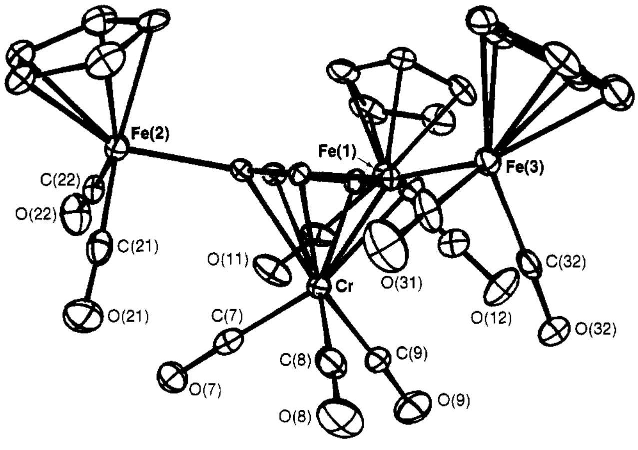


Similarly, when two $Cr(CO)_3$ groups are π-bound to biphenyl or a related ligand, the metal centers also may interact strongly (i.e. in 1 (vide supra)).[3] However, to the best of our knowledge, we are the first to have prepared members of a new class of complexes[1b,2a] in which two or three organometallic fragments are bound to (η^6-arene)M(CO)$_3$ groups by direct transition-metal–arene bonds (examples of complexes in which one metal is σ bound to the (η^6-arene)M(CO)$_3$ group (e.g. (η^6-C_6H_5(ML$_n$))Cr(CO)$_3$) have been reported[2a,5b,6]). The interaction between non-transition-metal arene substituents is transmitted through both the σ- and π-bonding frameworks. The magnitude of this σ and π transmission is affected differentially upon coordination of the arene to $Cr(CO)_3$.[14,29-31] We therefore felt that such complexes would be ideal models for trying to determine the relative components of the metal–arene–metal interactions in species such as **2a**. In particular, we were interested in seeing if the 1,4-dimetalloquinone interaction would be attenuated and if there were any direct σ,π metal–arene–metal interactions.[2a]

We recently reported the single-crystal X-ray crystal structure of the CH_2Cl_2 solvate of **3c**, (η^6-1,3,5-$C_6H_3Fp_3$)-



1a



1b

Figure 1. ORTEP plots of the molecular structure of (η^6-1,3,5-$C_6H_3Fp_3$)Cr(CO)$_3$·CH_2Cl_2. View **1a** is approximately down the axis joining the Cr atom and the centroid of the arene ring. View **1b** is in the plane containing the arene carbons.

Table III. Selected Bond Distances (Å) for (η^6-1,3,5-$C_6H_3Fp_3$)Cr(CO)$_3$•CH_2Cl_2

Fe(1)–C(1)	1.993 (8)	Fe(1)–C(11)	1.73 (1)	C(11)–O(11)	1.14 (1)
Fe(2)–C(3)	2.033 (8)	Fe(1)–C(12)	1.76 (1)	C(12)–O(12)	1.15 (1)
Fe(3)–C(5)	2.005 (8)	Fe(2)–C(21)	1.77 (1)	C(21)–O(21)	1.16 (1)
Cr–C(1)	2.282 (8)	Fe(2)–C(22)	1.74 (1)	C(22)–O(22)	1.17 (1)
Cr–C(2)	2.252 (8)	Fe(3)–C(31)	1.706 (9)	C(31)–O(31)	1.17 (1)
Cr–C(3)	2.261 (8)	Fe(3)–C(32)	1.734 (9)	C(32)–O(32)	1.16 (1)
Cr–C(4)	2.237 (8)	Cr–C(7)	1.814 (9)	C(7)–O(7)	1.18 (1)
Cr–C(5)	2.300 (8)	Cr–C(8)	1.81 (1)	C(8)–O(8)	1.15 (1)
Cr–C(6)	2.227 (8)	Cr–C(9)	1.82 (1)	C(9)–O(9)	1.17 (1)
C(1)–C(2)	1.42 (1)	C(3)–C(4)	1.40 (1)	C(5)–C(6)	1.41 (1)
C(2)–C(3)	1.42 (1)	C(4)–C(5)	1.44 (1)	C(1)–C(6)	1.40 (1)
Fe–C(Cp)	2.10 (av)	C(Cp)–C(Cp)	1.39 (av)		

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(27) For good leading reference on the nature of the Fp–aryl bond, see: (a) Butler, I. R.; Lindsell, W. E.; Thomas, M. J. K. *J. Organomet. Chem.* **1984**, *262*, 59. (b) Gansow, O. A.; Schexnayder, D. A.; Kimura, B. Y. *J. Am. Chem. Soc.* **1972**, *94*, 3406. (c) Stewart, R. P., Jr.; Isbrandt, L. R.; Benedict, J. J.; Palmer, J. G. *J. Am. Chem. Soc.* **1976**, *98*, 3215. (d) Jacobson, S. E.; Wojcicki, A. *J. Am. Chem. Soc.* **1973**, *95*, 6962. (e) Stewart, R. P.; Treichel, P. M. *J. Am. Chem. Soc.* **1970**, *92*, 2710. (f) Bolton, E. S.; Knox, G. R.; Robertson, C. G. *J. Chem. Soc., Chem. Commun.* **1969**, 664. (g) Nesmeyanov, A. N.; Leshcheva, I. F.; Polovyanyuk, I. V.; Ustynyuk, Y. A. *J. Organomet. Chem.* **1972**, *37*, 159. (h) Casey, C. P.; Konings, M. S.; Gohdes, M. A.; Meszaros, M. W. *Organometallics* **1988**, *7*, 2103. (i) Nesmeyanov, A. N.; Chapovskii, Y. A.; Denisovich, L. I.; Lokshin, B. V.; Polovyanyuk, I. V. *Dokl. Akad. Nauk SSSR* **1967**, *174*, 1342 (*Engl. transl.*, 576). (j) Denisovich, L. I.; Polovyanyuk, I. V.; Lokshin, B. V.; Gubin, S. P. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1971**, 1964 (Engl. transl., 1851). (k) Nesmeyanov, A. N.; Makarova, L. G.; Polovyanyuk, I. V. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1972**, 607 (Engl. transl., 567).

(28) Molecular orbital calculations on a number of metal–aryl complexes have emphasized the importance of the ring orientation, see for example: (a) Schilling, B. E. R.; Hoffmann, R.; Lichtenberger, D. L. *J. Am. Chem. Soc.* **1979**, *101*, 585. (b) Seeman, J. I.; Davies, S. G. *J. Am. Chem. Soc.* **1985**, *107*, 6522. (c) Green, J. C.; Jackson, S. E. *J. Chem. Soc., Dalton Trans.* **1976**, 1698. (d) Crocco, G. L.; Gladysz, J. A. *J. Am. Chem. Soc.* **1988**, *110*, 6110.

(29) (a) Levy, G. C.; Lichter, R. L.; Nelson, G. L. *Carbon-13 Nuclear Magnetic Resonance Spectroscopy*; John Wiley and Sons: New York, 1980. (b) Stothers, J. B. *Carbon-13 NMR Spectroscopy*; Academic: New York, 1972. (c) Mann, B. E. *Adv. Organomet. Chem.* **1974**, *12*, 135. (d) Ernst, L.; Wray, V.; Chertkov, V. A.; Sergeyev, N. M. *J. Magn. Reson.* **1977**, *25*, 123. (e) Nelson, G. L.; Levy, G. C.; Cargioli, J. D. *J. Am. Chem. Soc.* **1972**, *94*, 3089. (f) Ewing, D. F. *Org. Magn. Reson.* **1979**, *12*, 499. (g) Katritzky, A. R.; Topsom, R. D. *Angew. Chem., Int. Ed.* **1970**, *9*, 87. (h) Nelson, G. L.; Williams, E. A. *Prog. Phys. Org. Chem.* **1976**, *12*, 229.

(30) (a) Bromilow, J.; Brownlee, R. T. C.; Craik, D. J.; Sadek, M.; Taft, R. W. *J. Org. Chem.* **1980**, *45*, 2429. (b) Hugel, H. M.; Kelly, D. P.; Spear, R. J.; Bromilow, J.; Brownlee, R. T. C.; Craik, D. J. *Aust. J. Chem.* **1979**, *32*, 1511. (c) Brownlee, R. T. C.; Sadek, M. *Aust. J. Chem.* **1981**, *34*, 1593. (d) Bromilow, J.; Brownlee, R. T. C.; Topsom, R. D.; Taft, R. W. *J. Am. Chem. Soc.* **1976**, *98*, 2020.

(31) Substituent effects transmitted through the σ-framework are attenuated by complexation onto a $Cr(CO)_3$ center, see: (a) Dossor, P. J.; Eaborn, C.; Walton, D. R. M. *J. Organomet. Chem.* **1974**, *71*, 207. (b) Wu, A.; Biehl, E. R.; Reeves, P. C. *J. Chem. Soc., Perkin Trans. 2* **1972**, 449. (c) Senoff, C. V. *Coord. Chem. Rev.* **1980**, *32*, 111 and references cited therein.

Table IV. Selected Bond Angles (deg) for (η^6-1,3,5-$C_6H_3Fp_3$)$Cr(CO)_3 \cdot CH_2Cl_2$

Fe(1)-C(1)-C(2)	120.1 (6)	Fe(2)-C(3)-C(2)	122.5 (6)	Fe(3)-C(5)-C(4)	121.9 (6)
Fe(1)-C(1)-C(6)	122.5 (6)	Fe(2)-C(3)-C(4)	119.2 (6)	Fe(3)-C(5)-C(6)	120.4 (6)
C(2)-C(1)-C(6)	117.2 (7)	C(1)-C(2)-C(3)	122.7 (7)	C(2)-C(3)-C(4)	118.0 (7)
C(3)-C(4)-C(5)	121.4 (7)	C(4)-C(5)-C(6)	117.6 (7)	C(1)-C(6)-C(5)	122.7 (7)
C(1)-Fe(1)-C(11)	90.3 (4)	C(3)-Fe(2)-C(21)	92.5 (4)	C(5)-Fe(3)-C(31)	94.5 (4)
C(1)-Fe(1)-C(12)	92.1 (4)	C(3)-Fe(2)-C(22)	93.5 (4)	C(5)-Fe(3)-C(32)	87.0 (4)
Fe(1)-C(1)-Cr	135.9 (4)	Fe(2)-C(3)-Cr	133.9 (4)	Fe(3)-C(5)-Cr	138.2 (4)
C(11)-Fe(1)-C(12)	94.5 (5)	C(21)-Fe(2)-C(22)	92.8 (4)	C(31)-Fe(3)-C(32)	92.9 (4)
Fe(1)-C(11)-O(11)	176.9 (9)	Fe(2)-C(21)-O(21)	176.8 (8)	Fe(3)-C(31)-O(31)	177.2 (8)
Fe(1)-C(12)-O(12)	176.3 (9)	Fe(2)-C(22)-O(22)	176.9 (8)	Fe(3)-C(32)-O(32)	178.5 (8)
C(7)-Cr-C(8)	89.5 (4)	C(8)-Cr-C(9)	84.4 (4)	C(7)-Cr-C(9)	87.7 (4)
Cr-C(7)-O(7)	178.9 (8)	Cr-C(8)-O(8)	178.4 (9)	Cr-C(9)-O(9)	177.1 (8)

$Cr(CO)_3 \cdot CH_2Cl_2$.[2a,32] As expected on the basis of its spectroscopic properties, this sterically crowded molecule has three Fp groups σ-bound to the benzene ring in the 1-, 3-, and 5-positions and has a $Cr(CO)_3$ group π-bound to the benzene center (Figure 1). The structure of the Fp and arene–$Cr(CO)_3$ fragments are similar to those of their monometallic analogues with normal Fe–Cp, Fe–CO, and Cr–CO linkages (Tables III and IV).[14,20,23,27] The most notable features are the Fe–arene bond lengths, the nonplanarity of the arene ligand, the arrangement of the Cr carbonyls with respect to the arene substituents, and the interaction between the Fe and Cr carbonyl groups. These features are all related to the nature of the metal–arene–metal interactions and are discussed in detail below.[2a]

The Fe–arene bond lengths in the complex (1.993 (8)–2.033 (8), 2.015 (av) Å, Tables III and IV) are in the range typically reported for related complexes reported as having multiple-bond character but *formal* Fe–C(sp^2) single bonds (1.94–2.03 Å)[33-36] and are close to those reported for cationic Fp–carbene complexes (1.91–2.00 Å) having *formal* Fe–C(sp^2) double bonds.[37] This suggests partial double-bond character to the Fe–arene bonds in the complexes[27a,h,35a,36b] and is also consistent with the ^{13}C NMR data (vide infra). Any double-bond character between the arene ring and its substituents would be expected to result in dramatic changes to the structure of the complex. In valence bond terms, this would result in an increased contribution from a zwitterionic resonance form (e.g. for (η^6-$C_6H_5(NR_2)$)$Cr(CO)_3$).[23b]

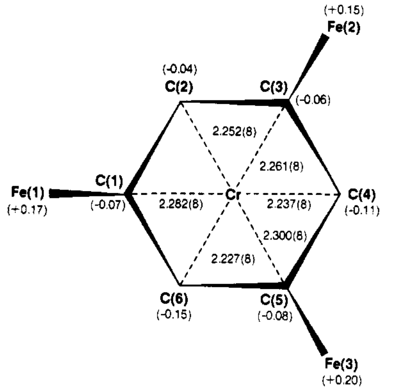
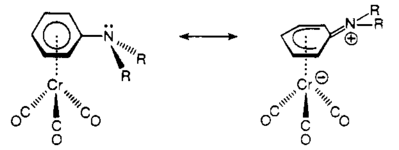


Figure 2. Least-squares plane of **3c** which includes the atoms C(1) to C(6) and Fe(1) to Fe(3). Atomic distances out of the plane are given in parentheses (Å), and Cr–arene distances (in Å, esds in parentheses) are given beside the dashed lines which represent the Cr–C bonds.[39]



Such a contribution would result in a number of potentially observable structural changes; in particular, an increase in the planarity of the NR_2 substituents and a decrease in the planarity of the arene ring. This, in turn, would result in a shift of the substituted arene carbon and the functional group away from the $Cr(CO)_3$ group and thus would result in an increase in this Cr to arene carbon bond distance. Such changes have been observed previously (e.g. where R = Et, above[23b])[14,38] and with 1,3,5 trisubstitution would be expected to give rise to a chair conformation for the arene (a prediction that has been confirmed for (η^6-1,3,5-$C_6H_3(NR_2)_3$)$Cr(CO)_3$ (**7c**) complexes).[23a] The crystal structure of **3a** shows strong evidence of a similar resonance contribution to its bonding. Inspection of the data for the least-squares plane which includes the arene carbons and the iron atoms (Figure 2)[39] indicates that this complex adopts a crown-like geometry

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(32) X-ray data on **3c**·CH_2Cl_2: the solution of this structure has been described in detail in ref 2a and in its supplementary material, briefly: Orange crystals of (η^6-1,3,5-$C_6H_3Fp_3$)$Cr(CO)_3 \cdot CH_2Cl_2$ were grown from CH_2Cl_2/hexanes at −35 °C and are orthorhombic: space group *Pbca* (No. 61); a = 19.546 (3) Å, b = 19.652 (4) Å, c = 16.624 (3) Å; V = 6385.5 $Å^3$; Z = 8; μ = 18.810 cm^{-1}. Data in the range $1.0 \leq 2\theta \leq 50.0°$ were collected at 22 °C by using Mo Kα radiation on an Enraf-Nonius CAD4 diffractometer. The structure was solved by direct methods and subsequent difference Fourier syntheses and refined by full-matrix least-squares techniques. Final R = 0.044 and R_w = 0.051 for 2267 observed reflections (h, k, l) [$F_o^2 \geq 3\sigma(F_o)^2$] and 415 variables.

(33) The X-ray crystal structures of simple Fp aryls have not been reported;[27a] however, numerous studies of related Fe–C(sp^2) interactions have been published.[34-36]

(34) For structures of CpFe(CO)L aryls, see: (a) Andrianov, V. G.; Sergeeva, G. N.; Struchkov, Y. T.; Anisimov, K. N.; Kolobova, N. E.; Beschastnov, A. S. *Zh. Strukt. Khim.* **1970**, *11*, 168 (Engl. transl., 163). (b) Lehmkuhl, H.; Mehler, G.; Benn, R.; Rufinska, A.; Schroth, G.; Kruger, C.; Raabe, E. *Chem. Ber.* **1987**, *120*, 1987. (c) Semion, V. A.; Struchkov, Y. T. *Zh. Strukt. Khim.* **1969**, *10*, 88 (Engl. transl., 80).

(35) For structures of Fp–R (where R is sp^2-hybridized), see: (a) Churchill, M. R.; Wormald, J. *Inorg. Chem.* **1969**, *8*, 1936. (b) Ferede, R.; Noble, M.; Cordes, A. W.; Allison, N. T.; Lay, J., Jr. *J. Organomet. Chem.* **1988**, *339*, 1. (c) Bruce, M. I.; Liddell, M. J.; Snow, M. R.; Tiekink, E. R. T. *J. Organomet. Chem.* **1988**, *354*, 103. (d) Dahl, L. F.; Doedens, R. J.; Huble, W.; Nielsen, J. *J. Am. Chem. Soc.* **1966**, *88*, 446. (e) Kolobova, N. E.; Rozantseva, T. V.; Struchkov, Y. T.; Batsanov, A. S.; Bakhmutov, V. I. *J. Organomet. Chem.* **1985**, *292*, 247. (f) Bruce, M. I.; Liddell, M. J.; Snow, M. R.; Tiekink, E. R. T. *Organometallics* **1988**, *7*, 343.

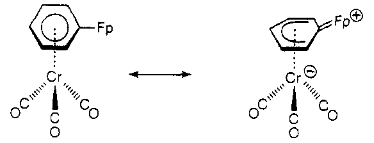
(36) For structures of Fp–Ar (where the aryl is π-bound to a 12-electron metal center) and related species, see: (a) ref 6a,b and 27h. (b) Batsanov, A. S.; Struchkov, Yu. T. *J. Organomet. Chem.* **1984**, *266*, 295. (c) Nametkin, N. S.; Tyurin, V. D.; Nekhaev, A. I.; Sobolev, Y. P.; Kondrat'eva, M. G.; Batsanov, A. S.; Struchkov, Y. T. *J. Organomet. Chem.* **1983**, *243*, 323.

(37) O'Connor, E. J.; Helquist, P. *J. Am. Chem. Soc.* **1982**, *104*, 1869 and references cited therein.

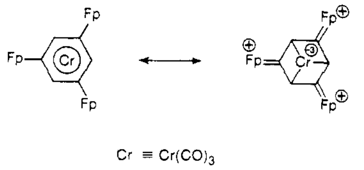
(38) This bending of substituents away from the $Cr(CO)_3$ group may involve the rehybridization of the arene carbons to give them greater sp^3 character and may be partly due to the steric interactions in this molecule.[21]

(39) The least-squares plane that includes the arene carbons and the iron atoms has the form: $0.1497x - 0.2161y - 0.9648z = -1.9675$ (where x, y, and z are the orthogonalized coordinates). The estimated standard deviations are 0.008 and 0.001 Å for the carbon and iron atoms, respectively.

(atomic displacements from the mean plane (C(H), −0.10 (av) Å, C(Fe), −0.07 (av) Å, and Fe, +0.17 (av) Å). Thus, the Fp groups are bent away from the arene plane (Figure 1b, by ≈0.25 Å), and the Cr–C bonds are longer to those arene carbons bearing Fp substituents (i.e. 2.261 (8)–2.300 (8), 2.28 (av) Å) than they are to those bearing H atoms (i.e. 2.227 (8)–2.252 (8), 2.24 (av) Å). Thus, in valence-bond terms, each individual Fp–arene interaction would have two resonance forms



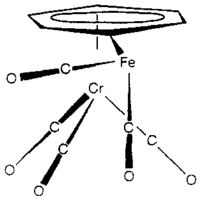
and the zwitterionic resonance form would makes a significant contribution to the overall bonding. For complexes with three π-donor substituents in the 1,3,5-positions (such as NR_2[23a] or Fp (Figure 2b)), such resonance interactions would, in the extreme case, lead to the observed crown geometries.



Cr ≡ $Cr(CO)_3$

The orientation of the Cr carbonyl ligands with respect to the arene substituents has been shown to be dependent on both the donor and steric properties of the substituent.[14,20,21] Like its NR_2 analogues, **7c**,[23a] **3c** adopts a structure in the solid state that is a compromise between these two requirements (Figure 1a). Thus, the carbonyls on Cr are arranged in close to a syn-eclipsed geometry below the Fp groups as would be expected for a π-donor substituent. However, the steric requirements of these bulky ligands cause a slight distortion toward a staggered arrangement.[21a,23a] The arene C–C bonds have normal values (1.40 (1)–1.44 (1), 1.415 (av) Å), and, in particular, no evidence for significant bond-length alternation is observed.[14,20]

The metal–carbonyl linkages of both the Fp (i.e. Fe–CO = 1.71 (1)–1.77 (1), 1.74 (av) Å, and C–O = 1.14 (1)–1.17 (1), 1.16 (av) Å) and $Cr(CO)_3$ (i.e. Cr–CO = 1.81 (1)–1.82 (1), 1.81 (av) Å, and C–O = 1.15 (1)–1.18 (1), 1.17 (av) Å) groups are normal. However, in both the molecular structure of **3c** and that of its mono-Fp analogue ($(\eta^6\text{-}1,4\text{-}C_6H_4ClFp)Cr(CO)_3$,[6a] the Fp-carbonyl ligands adopt the same unusual geometry with respect to the Cr carbonyls. Thus, one of the Fp carbonyls is nested between two of the Cr carbonyls to give and interlocking "molecular gear" arrangement.



Although this arrangement may be due to simple steric considerations, it is tempting to speculate that a van der Waals interaction between these adjacent carbonyls may account for the unusual stability of this conformation in the solid state (electronic considerations[28] suggest that an alternate structure with the pseudo mirror plane of the Fp group lying in the arene plane should be favored). Unfortunately, we have not, as yet, been able to ascertain the most stable conformation in solution (or the barrier to rotation about this Fe–C bond) so as to determine the origin of this effect.[40]

Four or five IR bands are observed in solution that may be attributed to the carbonyl ligands of our σ,π complexes (Table I).[41] These complexes all exhibit two bands below 1940 cm^{-1}, the lower energy band being broader. The positions of these bands are linearly dependent on the degree of Fp substitution around the ring (i.e. $(\eta^6\text{-}C_6H_{6-n}Fp_n)Cr(CO)_3$ where n = 1,[5b] 2, and 3), and they are all at lower frequencies than those of the parent $(\eta^6\text{-}C_6H_6)Cr(CO)_3$ complex (i.e. ν_{CO} (CH_2Cl_2) 1973 (s), 1893 (s, br) cm^{-1}) (vide infra). In addition, their intensities are independent of the degree of Fp substitution. Those bands having higher frequencies than 1970 cm^{-1} have band positions that are independent of the degree of arene substitution. They are also 15–20 cm^{-1} higher in energy than those of the uncomplexed Fp phenylenes (i.e. $C_6H_{6-n}Fp_n$, n = 1–3, ν_{CO} (CH_2Cl_2) ≈ 2015, 1960 cm^{-1}).[2] In addition, their intensities increase with increasing Fp substitution (i.e. they are weaker than those of $Cr(CO)_3$ for n = 1 and stronger than those of $Cr(CO)_3$ for n = 3). These facts conclusively indicate that the lower energy pair of bands are due to the $Cr(CO)_3$ fragment and that the higher energy bands are due to the Fp fragments.[2a,42] This data can be entirely explained without having to invoke vibrational mixing[2a,42] and is consistent with the assignments of other Fp and $Cr(CO)_3$ complexes.[16,23,27] We therefore believe that each set of carbonyl bands can be uniquely assigned to either the Fe or the Cr fragments and that any vibrational mixing between these Fe and Cr centers is negligible.

There is no splitting observed in the E symmetry IR bands of the $M(CO)_3$ complexes; however, they are considerably broader than are the A_1 bands (i.e. the widths at half-height of the A_1 and E bands of a saturated solution of **3b** in CH_2Cl_2 are 13 and 35 cm^{-1}, respectively).[14,16,23,41] More interestingly, the Fp symmetric stretching bands (at ≈2030 cm^{-1}, Table I) show no splitting for the 1,4-substituted complexes but are split by about 3 and 10 cm^{-1} for the 1,3 and 1,3,5 isomers, respectively.[43] Since the ^{13}C NMR data suggest a strong electronic interaction between the 1,4 Fp substituents that is absent between the 1,3 and 1,3,5 substituents (vide infra), we feel that the origin of this splitting is probably the steric interaction between meta substituents in these very crowded complexes.

The decrease observed in the Fp-carbonyl stretching frequencies upon π coordination of the Fp phenylenes to $Cr(CO)_3$ centers indicates that, as expected,[14,16] the $Cr(CO)_3$ group withdraws electron density from the arene and consequently from its Fp substituents. In fact, the relatively large magnitude of this change, 15–20 cm^{-1}, is somewhat surprising considering the known insensitivity of the carbonyl stretching frequencies of Fp aryls to changes in aryl substituents.[27b] [This change is the same as is observed when four H atoms on **2a** are formally replaced by F atoms to give $1,4\text{-}C_6F_4Fp_2$ (**2e**) (where ν_{CO} changes from 2014 and 1959 cm^{-1} to 2027 and 1981 cm^{-1}, respectively).[2b]] This implies that a substantial transfer

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[40] Variable-temperature ^1H and ^{13}C NMR and cyclic voltametric studies do show, however, that the conformation does change with temperature. Richter-Addo, G. B.; Hunter, A. D., unpublished observations.

[41] Cotton, F. A.; Kraihanzel, C. S. *J. Am. Chem. Soc.* **1962**, *84*, 4432.

[42] The previous report[6a] appears to have assigned the solid-state (KBr) IR spectra of some related complexes differently and thus concluded that vibrational mixing was necessary to explain the resultant anomalous carbonyl band shifts.

[43] The doublet observed in the ^{13}C NMR for the Fp carbonyls of **3b** is undoubtedly due to the diasteriotopic nature of these substituents (i.e. carbon atoms 1 and 3 on the arene are chiral in this complex).

of electron density from Fe to Cr is occurring. Such a hypothesis is confirmed by the changes observed in the carbonyl stretching frequencies of the $Cr(CO)_3$ groups compared to those of $(\eta^6\text{-}C_6H_6)Cr(CO)_3$ (vide supra). The addition of each Fp group to the benzene ring decreases the Cr–carbonyl stretching frequencies by 15–20 cm^{-1}. This change is as large as is observed for the very strong organic donor NMe_2 and indicates that the Fp group is among the strongest net electron donors known.[2a,14,16,23a] This suggestion of substantial electron transfer is confirmed by the ^{13}C NMR data of these complexes (Table II). Thus, the Fp carbonyls are shielded by about 2 ppm compared to the uncomplexed phenylenes (i.e. δ_{CO} of **2a** at 217.47 ppm in $(CD_3)_2SO$[2b]) while the Cr carbonyls are deshielded by 3–4 ppm compared to those in $(\eta^6\text{-}C_6H_6)Cr(CO)_3$ (i.e. δ_{CO} at 234.00 ppm in $(CD_3)_2SO$[5b]). These changes are in the direction that would be predicted (on the basis of the expected changes in the paramagnetic screening of the carbonyl) and confirm that electron density is transferred from Fe to Cr.[18c,27b]

The ^1H and ^{13}C NMR signals attributable to the cyclopentadienyl rings of our complexes are observed as siglets in the regions previously reported for those in related monometallic complexes[2a,6a,14,18] and, along with the carbonyl data discussed above, indicate that the Fp groups in these complexes retain their three-legged piano-stool geometries and that the two or three Fp fragments in these phenylene complexes are equivalent. The invariance of the IR and ^{13}C NMR data for Fp (both for Cp and CO (vide supra)) and its linear dependence on the degree of Fp substitution, *n*, for the $M(CO)_3$ groups (Tables I and II) unambiguously indicate that no electronic saturation of the arene's ability to accept and/or transfer electron density is taking place in these complexes. In addition, these data indicate that the congeneric Cr, Mo, and W complexes are, as expected,[14,16,18] experiencing very similar degrees of net electron transfer. In fact, the IR and ^{13}C NMR spectra for sets of congeneric complexes are similar with the chemical shifts of the $M(CO)_3$ groups showing the usual variations (i.e. the Mo carbonyls are shielded by about 11 ppm with respect to their Cr congeners).[14,18a,j]

The NMR spectral data for these novel phenylene bridges are listed in Tables I and II and may be compared with those of the related uncomplexed Fp–phenylene and $(arene)Cr(CO)_3$ species.[2,6a,14,18,23,27] The ^1H and ^{13}C NMR spectra of the phenylene bridges in these complexes are relatively simple due to the high symmetry of these molecules. They were initially assigned by analogy with the uncomplexed Fp phenylenes,[2] and these assignments were subsequently confirmed by using the peak multiplicities, chemical shifts, and homo- and heteronuclear coupling constants of the signals. In addition, the ^{13}C assignments were confirmed by consideration of the characteristic substituent effects of the pendant metal fragments (vide infra). The ^1H NMR signals of the phenylene groups occur in the regions previously reported for their monometallic analogues,[2a,5b,6a] and they are shielded by about 2 ppm compared to the uncomplexed Fp phenylenes (i.e. for **2a** in $(CD_3)_2SO$ $\delta(C_6H_4)$ in 6.95 ppm).[2] Both the ^1H and ^{13}C spectra display the singlets expected for the 1,4 and 1,3,5 isomers and the three multiplets (with the characteristic coupling patterns) expected for the less symmetric 1,3 species. The J_{CH} coupling constants are also in the region previously reported.[18]

Because they are directly related to the arene-carbon electron density and they may be used to elucidate the nature of arene–substituent bonding interactions, the ^{13}C NMR chemical shifts of the arene carbons are particularly useful[29] and this approach has been successfully extended to substituted $(arene)Cr(CO)_3$ complexes.[18] They are best understood in terms of the substituent effects of the Fp fragments on the ^{13}C chemical shifts of the arene carbons. It is known that, to a good first approximation, the effects of non-transition-metal substituents on the chemical shifts of arene carbons are linearly additive[29] and the ^{13}C NMR data available for polysubstituted $(arene)Cr(CO)_3$ complexes suggest that this holds true for them as well.[18] They have, therefore, been widely used to assign the ^{13}C NMR spectra of substituted arenes. In Table V are presented some representative values for the substituent constants of a variety of common functional groups in $(\eta^6\text{-}C_6H_5X)Cr(CO)_3$ complexes (where X = NMe_2, NH_2, OMe, F, Cl, Me, and CO_2Me) derived from the literature values for the chemical shifts of these species.[18b]

Table V. ^{13}C Substituent Effects for $(\eta^6\text{-}C_6H_5X)Cr(CO)_3$[a]

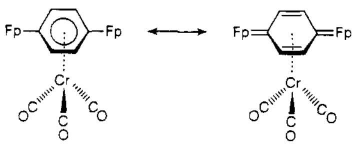
	substituent consts[b]					
X =	Δ_{ipso}	Δ_{ortho}	Δ_{meta}	Δ_{para}	Δ_π[b]	ref
NMe_2	42.2	−18.7	4.0	−10.3	−14.3	*c*
NH_2	37.9	−15.8	3.5	−9.7	−13.2	*c*
OMe	50.2	−14.8	2.2	−7.6	−9.8	*c*
F	52.7	−13.8	0.4	−6.5	−6.9	*c*
Cl	19.7	−1.8	0.3	−4.8	−5.1	*d*
Me	16.9	1.4	−0.1	−3.3	−3.2	*c*
CO_2Me	1.5	1.5	−3.3	1.9	5.2	*c*
Fp	30.0	16.0	2.0	−3.0	−5.0	*e*
Fp[f]	17.0	17.0	−1.0	−6.0	−5.0	*f*

[a] Where the values for the substituent constants, Δ, are quoted in ppm relative to $(\eta^6\text{-benzene})Cr(CO)_3$ (at 93.5 and 95.1 ppm in CH_2Cl_2 and $(CD_3)_2SO$, respectively) and positive shifts indicate deshielding. [b] The Δ_π values are the substituent chemical shifts, $\Delta = \delta_{arenecarbon} - \delta(C_6H_6)Cr(CO)_3$ and $\Delta_\pi = \Delta_{para} - \Delta_{meta}$. [c] Reference 18b in text (CH_2Cl_2). [d] Reference 18c in text (CH_2Cl_2). [e] This work, derived so as to give the most consistent set of values from the data for all the Fp–phenylene π complexes ($(CD_3)_2SO$). [f] Substituent constants for uncomplexed Fp phenylenes, ref 2b in text ($(CD_3)_2SO$).

Substituent constants are a measure of the effect that a substituent will have on the chemical shifts of the four types of arene carbon. The interpretation of the ipso and ortho values is, in general, quite complicated while those for the meta position show little systematic variation.[18,29a,b] The para values or, more precisely, the difference between the meta and para values ($\Delta_\pi = \Delta_p - \Delta_m$) can, however, be very readily interpreted in terms of the π-donor and -acceptor properties of the substituents. Substituents that are π donors have negative Δ_π values while π-electron-withdrawing groups have positive Δ_π values, and the magnitude of Δ_π is proportional to the degree of π donation or acceptance.[18,29] Coordination of an arene to $Cr(CO)_3$ has been shown to perturb the transmission of substituent effects through the σ framework.[14,18,31] However, no significant perturbations of the transmission of such effects through the π framework are generally observed.[18,31]

Analysis of our chemical shift data (Table II) allows us to conclude that our organometallic substituents also possess a set of linearly additive substituent constants. A consistent set of values (Table V) can be obtained that both predicts the observed chemical shifts to within an average error of less than 0.8 ppm (with the exception of the ipso carbon of $(\eta^6\text{-}1,4\text{-}C_6H_4Fp_2)Cr(CO)_3$ (vide infra)) and agrees with the values previously reported for Fp. The fact that our substituent effects are linearly additive for these complexes suggests that (as we previously proposed on the bases of the IR and NMR data for the Cp and CO groups (vide supra)) electronic saturation of the arene's π system is not occurring.[29] Inspection of the derived Δ_π values for Fp indicates that is is −5 ppm for both the complexed and uncomplexed phenylenes and thus that both are strong π donors to the arene ring. In fact, the magnitude of this π donation is similar to that for the more familiar organic π donor Cl. The net electron donation by each Fp group to $Cr(CO)_3$ is equivalent to that of an NMe_2 group (vide supra) while the π-donor ability of the Fp group is only equivalent to that of Cl (i.e. Δ_π = −5, −14.3, and −5.1 for Fp, NMe_2, and Cl, respectively, Table V). It therefore seems reasonable to suggest that this electron transfer from Fe to Cr is going primarily (by about 2 to 1) through the arene's σ rather than its π skeleton. This is not totally surprising since transition-metal substituents are less electronegative than is carbon and are therefore σ donors (in contrast to most organic π donors which are generally σ acceptors).[27e] Substituents such as Fp (and probably most other related 17-electron fragments[27e]) are therefore rather unique in being both good σ and π donors. This explains why the phenylene-bridged π complexes have such unusually electron-rich $M(CO)_3$ centers (vide supra). The chemical shift data for the arenes in **3c** and **5c** show the expected deshielding by Mo.[14c,18j]

The observed chemical shift of the ipso carbons of $(\eta^6\text{-}1,4\text{-}C_6H_4Fp_2)Cr(CO)_3$ are shielded by about 4.2 ppm *more* than would be predicted on the basis of linear additivity. This implies that when two Fp groups are arranged 1,4 to each other on the benzene ring the para substituent constant increases from its usual value of about −5 to about −9 ppm (i.e. π donation increases). This is the same effect that occurs in uncomplexed 1,4-phenylenes[2b] and indicates that the Fp centers in these complexes are involved in a Fe–arene–Fe conjugative interaction.[2b,29,30] No studies directly analogous to those on uncomplexed arenes which discuss ^{13}C NMR chemical shift evidence for such cross-ring interactions have been reported.[30] However, a similar π conjugation has been suggested for the complex $(\eta^6\text{-}1,4\text{-}C_6H_4(CHO)(NMe_2))Cr(CO)_3$, and we observe similar effects in other $(\eta^6\text{-}1,4\text{-}C_6H_4XY)Cr(CO)_3$ complexes.[5b] In valence bond terms, the dimetalloquinone resonance hybrid contribution to the bonding in the phenylene complexes is maintained upon π complexation, i.e.



As before,[2b] we cannot entirely rule out the possibility that the Fp group is sensitizing the ipso carbon to changes in total electron density and thus causing the anomalous chemical shift effects.[30] Nevertheless, preliminary electrochemical studies of some of these complexes support our proposal of quinoidal character to the metal–arene–metal interaction in the 1,4 species.[5a] However, confirmation of this must await crystallographic characterization of a number of such species and a detailed molecular orbital analysis of the bonding in these unusual phenylene-bridged π complexes.

Conclusions

These studies have shown that phenylene-bridged polymetallic clusters $(\eta^6\text{-}C_6H_{6-n}Fp_n)M(CO)_3$ (M = Cr, Mo, or W) may be readily prepared. This complexation increases the thermal stability of the Fe–arene bonds and results in a substantial transfer of electron density from the Fp groups to the $M(CO)_3$ centers. This transfer does not appear to be through any direct Fe–M interaction but rather occurs through the σ and π frameworks of the arene bridge. This complexation does not perturb the Fe–Fe π interactions, and thus the 1,4 complexes exhibit dimetalloquinone character. The characteristic chemistry of these linkages is now being explored as are the redox properties of the various metal–metal interactions.

Acknowledgment. We are grateful to the Natural Sciences and Engineering Research Council of Canada and the University of Alberta for support of this work.

Registry No. **3a**, 119924-02-6; **3b**, 119924-03-7; **3c**, 119924-05-9; **3d**, 62010-71-3; **4a**, 122722-10-5; **4c**, 122698-65-1; **5a**, 122698-62-8; **5b**, 122698-64-0; **5c**, 122698-66-2; **5d**, 122698-67-3; **6a**, 122698-63-9; **6d**, 122698-68-4; $1,4\text{-}C_6H_4(COFp)_2$, 119923-98-7; $1,3\text{-}C_6H_4(COFp)_2$, 119923-99-8; $1,3,5\text{-}C_6H_3(COFp)_3$, 119924-00-4; $1,4\text{-}C_6H_4(COFp')_2$, 122698-69-5; $1,3,5\text{-}C_6H_3(COFp')_3$, 122698-70-8.