Biphenyl-, Terphenyl-, Naphthalene-, and Anthracene-Bridged Bi- and Trimetallic Complexes of Iron and Chromium[1-3]

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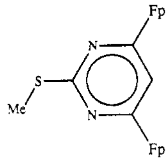
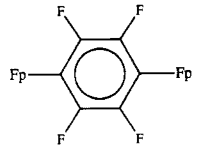
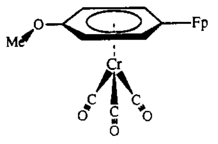
The reactions between 2 equiv of NaFp (where Fp = (η^5-C_5H_5)Fe(CO)$_2$) and each of six bifunctional acid chloride derivatives of biphenyl, terphenyl, naphthalene, or anthracene produce six new bimetallic acyl-bridged complexes of iron (e.g., 4,4'-$C_{12}H_8(COFp)_2$, 4,4''-$C_{18}H_{12}(COFp)_2$, 1,4-$C_{10}H_6(COFp)_2$, 2,6-$C_{10}H_6(COFp)_2$, 2,7-$C_{10}H_6(COFp)_2$, and 9,10-$C_{14}H_8(COFp)_2$). Attempts to thermally decarbonylate these materials were successful in three cases, producing new bimetallic complexes having polyaromatic bridging groups (e.g., 4,4'-$C_{12}H_8Fp_2$, 2,6-$C_{10}H_6Fp_2$, and 2,7-$C_{10}H_6Fp_2$). The monometallic analogues of these complexes (e.g., 1,4-C_6H_4PhFp, 1-$C_{10}H_7$Fp, and 2-$C_{10}H_7$Fp) were thermally decarbonylated from their acyls similarly. Three of the acyl complexes were heated in the presence of an excess of $Cr(CO)_6$, producing new heterometallic complexes (e.g., (η^6-1,4-C_6H_4PhFp)$Cr(CO)_3$, (η^6-4,4'-$C_{12}H_8Fp_2$)$Cr(CO)_3$, and (η^6-2,6-$C_{10}H_6Fp_2$)$Cr(CO)_3$). Each of these complexes was completely characterized by conventional analytical and spectroscopic means which established that the bifunctional aryl- and acyl-bridged complexes were bonded to the Fp fragments by Fe–C σ bonds and that the $Cr(CO)_3$ fragments were π bonded to one arene ring in each of the heterometallic complexes. In addition, cyclic voltammetric studies (in CH_2Cl_2, [n-Bu_4N]PF_6, Pt bead electrode) were carried out on representative examples. These studies confirm that the complexes display the expected transfer of electron density from Fe to Cr and indicate that the $Cr(CO)_3$ fragment in (η^6-1,4-C_6H_4PhFp)$Cr(CO)_3$ preferentially coordinates to the more electron-rich, but also more sterically crowded, arene ring bearing the Fp substituent.

Introduction

Recently, we have reported the syntheses of polymetallic complexes having two or more transition-metal fragments bonded to aromatic[4a-e] and heteroaromatic[2,4f] bridging groups, e.g.







(where Fp = (η^5-C_5H_5)Fe(CO)$_2$). The primary goal of these studies has been to model the intermetallic linkages in related one-dimensional organometallic polymers. In particular, we are attempting to use these discrete model complexes to elucidate how the magnitudes of the long-range metal–metal interactions in the related polymeric species would be expected to vary as a function of the structure of the aromatic bridging group. This should allow us to rationally design new materials having maximized conjugation down the polymer backbone and hence having optimal *intra*chain electrical conductivity.[2,4b,c] One approach to increasing the magnitude of such intermetallic conjugation is to replace the benzene bridging groups pictured above by more extensively conjugated aromatic bridging groups such as biphenyl, terphenyl, naphthalene, and anthracene since this will decrease the energies of their π^* orbitals and hence increase their overlap with the metal centered d orbitals. In this paper, we report the preparation and characterization of a series of such polymetallic arene-bridged model complexes of Fe and Cr, we compare their properties to the benzene-bridged species, and we comment on the magnitudes of their metal–metal interactions.

Experimental Section

Unless otherwise noted, all reactions and subsequent manipulations were performed under anaerobic and anhydrous conditions. General procedures routinely employed in these laboratories have been described in detail previously.[2b,f,5] 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.[6] Solvents used were dried and deaerated by standard procedures and stored under N_2 or Ar.[4b,c,f,5,6] In particular, Bu_2O was distilled over CaH_2. Unless specified otherwise, the chemical reactions described below were effected at ambient temperatures. The Fp_2 and FpI (where Fp = CpFe(CO)$_2$) used in these syntheses were prepared and purified by standard procedures.[7] Infrared spectra were recorded on a Pye Unicam PU9522 infrared spectrophotometer calibrated with the 1601-cm^{-1} band of polystyrene. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker WH-300 spectrometer with reference to the deuterium signal of the $(CD_3)_2SO$ solvent. The ^{1}H and ^{13}C NMR chemical shifts are reported in parts per million downfield from external Me_4Si. These spectra were recorded with the assistance of the staff of the departmental NMR laboratory while the low-resolution and fast atom bombardment (FAB) mass spectra were recorded by the staff of the

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

complex[a]	yield (%)	anal. data C calcd	anal. data C found	anal. data H calcd	anal. data H found	low-resolution mass spectral data P$^+$, m/z[b]	infrared data: ν_{CO} (CH_2Cl_2, cm^{-1})[c]
1,4-$C_6H_4Ph(COFp)$	44	67.07	66.71	3.94	4.20	330[d]	2024 (s), 1964 (s), 1617 (m)
1-$C_{10}H_7(COFp)$	26	65.09	64.64	3.64	3.76	304[d]	2021 (s), 1968 (s), 1606 (m, br)
2-$C_{10}H_7(COFp)$	90	65.09	65.25	3.64	3.98	304[d]	2024 (s), 1968 (s), 1611 (m, br)
4,4′-$C_{12}H_8(COFp)_2\cdot{}^1/_2CH_2Cl_2$[e,f]	86	56.62	56.82	3.17	2.91	562[g]	2021 (s), 1964 (s), 1613 (m), 1591 (m, sh)
4,4″-$C_{18}H_{12}(COFp)_2$	60	63.98	63.39	3.47	3.37	582[i]	2017 (m), 1963 (m), 1609 (w), 1591 (w)
1,4-$C_{10}H_6(COFp)_2\cdot{}^1/_2CH_2Cl_2$[f,h]	18	45.80	44.56	3.01	2.96	536[g]	2016 (m), 1965 (m)[j]
2,6-$C_{10}H_6(COFp)_2$[h]	85	58.25	57.83	3.01	3.03	536[g]	2022 (m), 1965 (m), 1604 (w)
2,7-$C_{10}H_6(COFp)_2$[h]	50	58.25	57.79	3.01	3.14	508[d]	2024 (s), 1968 (s), 1609 (w)
9,10-$C_{14}H_8(COFp)_2$	51	59.83	59.60	3.23	3.26	*k*	2020 (w), 1967 (w)[l]
1,4-C_6H_4PhFp	40	69.12	68.60	4.27	4.39	330	2018 (s), 1964 (s)
1-$C_{10}H_7Fp$	31	67.14	66.79	3.98	4.05	304	2016 (s), 1964 (s)
2-$C_{10}H_7Fp$	50	67.14	67.18	3.98	4.19	304	2016 (s), 1964 (s)
4,4′-$C_{12}H_8Fp_2\cdot{}^1/_4CH_2Cl_2$[f]	52	59.79	59.77	3.54	3.77	506	2016 (s), 1961 (s)
2,6-$C_{10}H_6Fp_2\cdot{}^1/_4CH_2Cl_2$[f]	45	58.10	58.69	3.32	3.39	480	2016 (s), 1962 (s)
2,7-$C_{10}H_6Fp_2\cdot{}^1/_2CH_2Cl_2$[f,h]	81	55.25	54.69	3.22	4.23	480	2016 (s), 1962 (s)
(η^6-1,4-$C_6H_4PhFp)Cr(CO)_3$	7	56.68	56.62	3.03	3.08	466	2033 (s), 1982 (s), 1951 (s), 1872 (s, br)
(η^6-4,4′-$C_{12}H_8Fp_2)Cr(CO)_3$	48	54.24	54.50	2.83	3.12	642	2029 (sh), 2016 (s), 1979 (m), 1964 (s), 1948 (m), 1868 (m, br)
(η^6-2,6-$C_{10}H_6Fp_2)Cr(CO)_3$	24	52.64	52.84	2.62	2.86	616	2025 (m), 2018 (m), 1976 (m), 1968 (m, sh), 1939 (m), 1856 (m, br)

[a] Where Fp = (η^5-C_5H_5)$Fe(CO)_2$ and where C_{10}-, C_{12}-, C_{14}- and C_{18}-containing species are naphthalene, biphenyl, anthracene, and terphenyl derivatives, respectively. [b] Probe temperature 150–280 °C. Assignments involve the most abundant naturally occurring isotopes (i.e., ^{56}Fe and ^{52}Cr). 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] No parent ion observed in the low-resolution mass spectrum, heaviest ion observed as P$^+$ − CO. [e] Chlorine anal.: calcd, 5.86; found, 5.55. [f] These complexes were obtained as CH_2Cl_2 solvates having variable CH_2Cl_2 contents; see text. The presence of CH_2Cl_2 was confirmed by NMR; see Table II. [g] 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). [h] These complexes were characterized spectroscopically but were not obtained in an analytically pure form; see text. [i] No parent ion observed in the low-resolution mass spectrum, heaviest ion observed as P$^+$ − 2CO. [j] IR recorded in THF. [k] No mass spectral signals due to the product were observed when low-resolution mass spectra were recorded under the usual conditions. [l] IR recorded as a Nujol mull.

departmental mass spectral laboratory.[4b,f]

Synthetic procedures for the complexes prepared in this work are described below, and their nonoptimized yields and analytical, mass spectral, IR, and NMR data are recorded in Tables I and II.

Preparation of the Acyl-Bridged Complexes. All these reactions were performed in a similar manner. The procedure for 9,10-$C_{14}H_8(COFp)_2$ is described in detail as a representative example.

An excess of solid sodium amalgam[7c] (100 g, 100 mmol of Na) was liquified by the addition of mercury (≈10 mL), and then THF (120 mL) and Fp_2[7a] (4.00 g, 11.3 mmol) were added. The resultant dark red solution was stirred vigorously for 1 h to produce a solution containing NaFp. Excess amalgam was drained from the reaction through a sidearm on the reaction flask. The solution was then filtered through Celite (2 × 3 cm) supported on a medium-porosity frit to remove any finely divided amalgam (2 × 20 mL of THF wash). The resulting orange-red solution of NaFp was cooled to ≈−78 °C using a dry ice/acetone bath, and then 9,10-$C_{14}H_8(COCl)_2$ (2.69 g, 8.89 mmol) was added. This stirred solution was allowed to warm slowly to room temperature (≈1 h) and then taken to dryness in vacuo. The resulting solid was then recrystallized from CH_2Cl_2/heptane and dried in vacuo to give the desired product, 9,10-$C_{14}H_8(COFp)_2$, in 51% yield (2.52 g, 4.48 mmol) as a tan powder.

The other eight acyl products (Table I) were prepared similarly from the respective acid chlorides. Some of the products were purified by washing the dried reaction product successively with Et_2O,[8] H_2O, Et_2O[8] and hexanes[8] in air and by recrystallizing the resulting tan solids from CH_2Cl_2/hexanes.

Preparation of the Aryl-Bridged Complexes. All these reactions were performed in a similar manner. The procedure for 2,7-$C_{10}Fp_2$ is described in detail as a representative example.

A suspension of 2,7-$C_{10}H_6(COFp)_2$ (0.50 g, 0.93 mmol) in Bu_2O (100 mL) was stirred slowly (to avoid splashing the diacyl on the sides of the flask) and was heated at a gentle reflux (note: care must be taken to avoid local overheating of the solution).[9] The progress of this reaction was monitored by occasionally allowing the reaction to cool to ambient temperature and recording the IR spectrum of the supernatant solution. Over the course of the reaction, the initially colorless solution became yellow and new carbonyl bands at 2018 and 1966 cm^{-1} grew in intensity. The reaction was stopped upon appearance of Fp_2 bands (most noticeably that at 1790 cm^{-1}) or when no further increase in product IR bands was observed (≈12.5 h). The supernatant solution was then taken to dryness in vacuo, the resulting tan solid was washed with Et_2O (50 mL), and the combined washings were again taken to dryness in vacuo. Recrystallization of the solid from CH_2Cl_2 gave an 81% yield of an analytically pure brown powder which was identified as a dichloromethane solvate of the desired product, 2,7-$C_{10}H_6Fp_2\cdot{}^1/_2CH_2Cl_2$ (0.40 g, 0.75 mmol).

The other aryl derivatives (1,4-C_6H_4PhFp, 1-$C_{10}H_7Fp$, 2-$C_{10}H_7Fp$, 4,4′-$C_{12}H_8Fp_2\cdot{}^1/_4CH_2Cl_2$, 2,6-$C_{10}H_6Fp2\cdot{}^1/_4CH_2Cl_2$) were prepared similarly with Fp_2, often being observed as a byproduct by IR spectroscopy. In these cases, the solids obtained from the Et_2O extracts were crystallized from CH_2Cl_2/hexanes. In the cases of the four naphthalene derivatives, naphthalene was identified (initially by its characteristic odor and later by comparison of its ^1H and ^{13}C NMR spectra to those of an authentic sample) as the organic byproduct. Alternatively, these transformations could be carried out in refluxing Bu_2O/toluene (50:50). The decarbonylation of 4,4″-$C_{18}H_{12}(COFp)_2$ was attempted in both Bu_2O and Bu_2O/toluene (60:40), and IR bands attributable to the desired product, 4,4″-$C_{18}H_{12}Fp_2$, were observed (ν_{CO} (Bu_2O) 2017, 1965 cm^{-1}). However, this complex was not obtained in an analytically pure state. Repeated attempts to decarbonylate 9,10-$C_{14}H_8(COFp)_2$ in both Bu_2O and Bu_2O/toluene (50:50) were not entirely successful, producing mixtures of the desired product, 9,10-$C_{14}H_8Fp_2$, and the acyl starting material.

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(8) Wash solvent grade.

(9) It is dangerous to use a water-cooled condenser for high-boiling solvents such as Bu_2O (bp 142 °C) since 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 superheated solution, and consequently, an explosion may result. Such solvents are readily condensed by an air-cooled condenser, and in fact, in the apparatus the solvent vapors seldom rise more than 2–5 cm up the condenser.

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

complex[a]	^{1}H NMR[b]		^{13}C NMR[b]					
				arene				
	η^5-C_5H_5	C_6H_{6-n}	η^5-C_5H_5	X—C	H—C	acyl C=O	Fe—CO	Cr—CO
1,4-$C_6H_4Ph(COFp)$	5.19 (s, 5 H)	7.7 (m, 4 H)	87.01	148.87 (C4)	129.00 (C3′/C5′)	252.58	214.95	
		7.35–7.6 (m, 5 H)		141.70	127.92 (C4′)			
				139.17	126.79			
					126.51			
					126.31			
2-$C_{10}H_7(COFp)$	5.24 (s, 5 H)	8.16 (m, 1 H)	86.95	147.80 (C2)	129.46	253.05	214.83	
		8.04 (s, 1 H)		133.42	127.40			
		7.91 (m, 2 H)		132.18	127.32 (2C)			
		7.56 (m, 3 H)			126.69			
					126.42			
					122.40			
4,4′-$C_{12}H_8(COFp)_2$[c]	5.20 (s, 10 H)	7.77 (d, 4 H, *J* = 8)	87.04	149.27 (C4/C4′)	126.52	252.90	214.89	
		7.57 (d, 4 H)		140.63 (C1/C1′)	126.43			
4,4″-$C_{18}H_{12}(COFp)_2$	5.23 (s, 10 H)	7.85 (s, 4 H)	87.04	148.98 (C4/C4″)	127.46 (C2′/C3′/C5′/C6′)	252.65	214.96	
		7.79 (d, 4 H, *J* = 8)		140.96 (C1/C1″)	126.58 126.25			
		7.58 (d, 4 H)		138.61 (C1′/C4′)				
2,6-$C_{10}H_6(COFp)_2$	5.26 (s, 10 H)	8.15 (d, 2 H, *J* = 8)	87.09	149 (C2/C6)	129.38	*d*	214.86	
		8.01 (s, 2 H)		132.88 (C9/C10)	125.99			
		7.58 (d, 2 H)			122.90			
2,7-$C_{10}H_6(COFp)_2$	5.26 (s, 10 H)	8.18 (s, 2 H)	87.04	148.48 (C2/C7)	127.39	253.37	214.82	
		7.92 (d, 2 H, *J* = 8)		133.81	127.23			
		7.63 (d, 2 H)		131.60	124.28			
9,10-$C_{14}H_8(COFp)_2$	5.05 (s, 10 H)	7.96 (m, 4 H)	88.21	*d*	125.78	*d*	214.46	
		7.55 (m, 4 H)			124.91			
1,4-C_6H_4PhFp	5.16 (s, 5 H)	7.56 (d, 2 H, *J* = 7)	86.59	146.16 (C4)	145.02 (C3/C5)		216.90	
		7.49 (d, 2 H, *J* = 7)		140.65 (C1′)	128.72 (C3′/C5′)			
		7.40 (t, 2 H, *J* = 7)		134.66 (C1)	126.50 (C4′)			
		7.27 (t, 1 H, *J* = 7)			126.04 (C2′/C6′)			
		7.21 (d, 2 H, *J* = 7)			125.23 (C2/C6)			
1-$C_{10}H_7Fp$	5.20 (s, 5 H)	8.14 (dd, 1 H, *J* = 8, 1)	86.93	147.70 (C1)	143.93		216.77	
		7.80 (dd, 1 H, *J* = 7, 1)		143.85	133.27			
		7.72 (dd, 1 H, *J* = 8, 1)		134.11	128.62			
		7.45 (m, 2 H)			124.79			
		7.38 (ddd, 1 H, *J* = 8, 7, 1)			124.34			
		7.11 (dd, 1 H, *J* = 8, 7)			124.09			
					123.58			
2-$C_{10}H_7Fp$	5.18 (s, 5 H)	7.89 (s, 1 H)	86.67	144.77 (C2)	142.76		216.87	
		7.69 (d, 1 H, *J* = 8)		133.42	142.39			
		7.56 (m, 2 H)		130.29	127.14			
		7.43 (d, 1 H, *J* = 8)			125.35			
		7.34 (ddd, 1 H, *J* = 8, 7, 1)			125.03			
		7.26 (ddd, 1 H, *J* = 8, 6, 1)			124.70			
					123.54			
4,4′-$C_{12}H_8Fp_2$[c]	5.14 (s, 10 H)	7.43 (d, 4 H, *J* = 8)	86.55	143.93 (C4/C4′)	144.85 (C3/C5/C3′/C5′)		216.98	
		7.14 (d, 4 H)		135.16 (C1/C1′)	124.95 (C2/C6/C2′/C6′)			
2,6-$C_{10}H_6Fp_2$[c]	5.15 (s, 10 H)	7.67 (s, 2 H)	86.59	139.29 (C2/C6)	141.85		217.09	
		7.38 (d, 2 H, *J* = 8)		131.52 (C9/C10)	141.83			
		7.15 (d, 2 H)			123.08 (C4/C8)			
2,7-$C_{10}H_6Fp_2$	5.22 (s, 10 H)	7.64 (s, 2 H)	86.58	142.30 (C2/C7)	140.55		217.06	
		7.35 (m, 4 H)		134.37	140.32			
				127.62	124.48 (C4/C5)			
(η^6-4-$C_{12}H_{13}Fp$)$Cr(CO)_3$	5.22 (s, 5 H)	7.57 (d, 2 H, *J* = 7)	86.92	136.25 (C1′)	128.65 (C4′)		215.11	235.66
		7.41 (m, 3 H)		123.70 (C4)	128.65 (C3′/C5′)			
		5.99 (d, 2 H, *J* = 7)		107.78 (C1)	126.42 (C2′/C6′)			
		5.75 (d, 2 H, *J* = 7)			109.87 (C3/C5)			
					94.99 (C2/C6)			

Table II (Continued)

	^{1}H NMR^b		^{13}C NMR^b					
				arene				
complex^a	η^5-C_5H_5	C_6H_{6-n}	η^5-C_5H_5	X—*C*	H—*C*	acyl *C*=O	Fe—*C*O	Cr—*C*O
(η^6-4,4′-$C_{12}H_8Fp_2$)Cr(CO)$_3$	5.19 (s, 5 H)	7.41 (d, 2 H, *J* = 8)	86.84	149.16 (C4′)	144.60 (C3′/C5′)		216.75 (*C*O4′) 215.10 (*C*O4)	235.92
	5.13 (s, 5 H)	7.11 (d, 2 H, *J* = 8)	86.61	130.40 (C1′)	124.70 (C2′/C6′)			
		5.89 (d, 2 H, *J* = 7)		119.35 (C4)	109.96 (C3/C5)			
		5.71 (d, 2 H, *J* = 7)		109.42 (C1)	94.57 (C2/C6)			
(η^6-2,6-$C_{10}H_6Fp_2$)Cr(CO)$_3$^{e}	4.88	7.54	86.57	*d*	144.52 (C5 or C7)		*d*	236.11
		7.44	86.39		141.79 (C7 or C5)			
		7.02			125.27 (C8)			
		6.21			110.00 (C1 or C3)			
		5.82			109.88 (C3 or C1)			
		5.68			90.06 (C4)			

^{a} Where Fp = (η^5-C_5H_5)Fe(CO)$_2$. Also, where C_{10}-, C_{12}-, C_{14}-, and C_{18}-containing species are naphthalene, biphenyl, anthracene, and terphenyl derivatives, respectively. ^{b} ^{1}H NMR were measured at 300.135 MHz, and ^{13}C NMR were measured at 75.469 MHz unless otherwise specified. *J* in hertz. ^{c} Signals due to CH_2Cl_2 of solvation are observed in $(CD_3)_2SO$ at 5.76 ppm in the ^{1}H NMR and at 54.87 ppm in the ^{13}C NMR. ^{d} The expected signal(s) were not observed in the NMR spectrum recorded under the usual conditions. ^{e} NMR spectra were recorded in CD_2Cl_2. The ^{1}H NMR signals were broadened, and no coupling information is therefore available.

Reaction of 9,10-$C_{14}H_8Li_2$ with FpI and FpCl. To a suspension of 9,10-$C_{14}H_8Br_2$ (1.00 g, 2.98 mmol) in Et_2O (50 mL) was added 2 equiv of *n*-BuLi (2.5 M solution in hexanes, 3.5 mL, 9.02 mmol). After being stirred for 0.5 h, the solution was cooled to −78 °C and then FpI (1.85 g, 6.1 mmol)[7b] was added to the resultant suspension. This mixture was kept at −78 °C for 1 h and then allowed to warm to room temperature over a period of 1 h, producing a red solution displaying strong IR bands characteristic of Fp_2 and two new IR bands (at ≈2016 and 1967 cm^{-1} in Et_2O) in the region previously observed for other Fp–aryl complexes. However, this product was not successfully isolated from solution. If this reaction is performed with FlCl used in place of FpI, a similar result is observed.

Preparation of the (η^6-Arene)Cr(CO)$_3$ Complexes. All these reactions were performed in a similar manner. The procedure for (η^6-4,4′-$C_{12}H_8Fp_2$)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[9,10] and topped with a gas inlet and bubbler was added a 2.5-cm Teflon-coated magnetic stir bar. This apparatus was charged under dinitrogen with 4,4′-$C_{12}H_8(COFp)_2$ (1.12 g, 1.99 mmol), and then Cr(CO)$_6$ (0.44 g, 2.01 mmol) and Bu_2O (75 mL) were added. Around the flask was placed a loosely fitting 500-mL heating mantle. The reaction mixture was then heated to a gentle reflux.[4c] 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 ≈2019(s) and 1967 (sh) cm^{-1} (attributable to 4,4′-$C_{12}H_8Fp_2$) were observed first to increase and then to decrease in intensity (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 2019 and 1967 cm^{-1} had disappeared or carbonyl bands due to Fp_2 (especially that at 1790 cm^{-1}) started to increase in intensity (10.5 h of heating in total). 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 manually, the remaining yellow solid was washed with Et_2O[8] (≈50 mL), and then any remaining Cr(CO)$_6$ was removed by sublimation (from a flask warmed to ≈40 °C to a cold-water-cooled cold finger, 0.05 Torr). Fractional crystallization of the remaining solid (CH_2Cl_2, 60 mL; hexanes, 90 mL; −35 °C) gave the desired product, (η^6-4,4′-$C_{12}H_8Fp_2$)Cr(CO)$_3$, as an analytically pure microcrystalline pale orange solid in 48% yield (0.61 g, 0.95 mmol).

The related complexes, (η^6-1,4-C_6H_4PhFp)Cr(CO)$_3$ and (η^6-2,6-$C_{10}H_6Fp_2$)Cr(CO)$_3$, are prepared in a similar fashion from their parent acyl complexes.

Electrochemical Analysis of the Products. The electrochemical analyses were carried out using the equipment and experimental methods described in detail previously.[2,4e] Thus, the working electrode was a small (≈1-mm diameter) Pt bead sealed in soft glass, an aqueous SCE reference electrode was used, the support electrolyte was [*n*-Bu_4N]PF_6, and the solvent (dichloromethane, Spectrograde, BDH) was dried over alumina (5 g, ICN Biomedical, neutral, W200 Super 1) before use. The solutions employed during cyclic voltammetry were typically (5–7) × 10^{-4} M in organometallic complex and 0.1 M in [*n*-Bu_4N]PF_6, and these experiments were carried out ambient temperatures (≈23 ± 2 °C). The formal oxidation potential, $E^{\circ\prime}$, for reversible couples is defined as the average of the anodic ($E_{p,a}$) and cathodic ($E_{p,c}$) peak potentials. The separation of the cathodic and anodic potentials ΔE is defined by $|E_{p,c} - E_{p,a}|$, and the cathodic to anodic peak current ratio is defined by $i_{p,c}/i_{p,a}$.[11a] The oxidation of ferrocene is reported to be highly reversible in many solvents[11b] and was used as an internal reference (under our experimental conditions, $E^{\circ\prime}$ = +0.47 V vs SCE, $i_{p,c}/i_{p,a}$ = 1.0, ΔE = 60–70 mV, 0.1 V s^{-1}).[11c] The ratio $i_{p,c}/i_{p,a}$ was used to establish chemical reversibility for the complexes studied, and the electrochemical reversibility was established by comparison of the scan rate dependence of ΔE of the analyte to that of ferrocene recorded under identical conditions. The oxidation waves were established to be 1 electron in nature by comparison of the anodic–cathodic peak potential separations and peak currents at a variety of scan rates

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(10) 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.

(11) (a) Nicholson, R. S. *Anal. Chem.* **1966**, *38*, 1406. (b) Holloway, J. D. L.; Geiger, W. E. *J. Am. Chem. Soc.* **1979**, *101*, 2038–2044. (c) Gagne, R. R.; Koval, C. A.; Lisensky, G. C. *Inorg. Chem.* **1980**, *19*, 2854–2855.

(0.1–10.0 Vs^{-1}) to those of ferrocene recorded under identical conditions.[11c]

Three complexes displayed chemically reversible oxidation behavior: (η^6-1,4-C_6H_4PhFp)$Cr(CO)_3$ ($E^{\circ\prime}$ = 0.65 V vs SCE, $i_{p,c}/i_{p,a}$ = 0.95, ΔE = 75 mV, 0.4 V s^{-1}), (η^6-4,4′-$C_{12}H_8Fp_2$)$Cr(CO)_3$ ($E^{\circ\prime}$ = 0.59 V vs SCE, $i_{p,c}/i_{p,a}$ = 0.96, ΔE = 75 mV, 0.1 V s^{-1}), and (η^6-2,6-$C_{10}H_6Fp_2$)$Cr(CO)_3$ ($E^{\circ\prime}$ = 0.46 V vs SCE, $i_{p,c}/i_{p,a}$ = 1.0, ΔE = 122 mV, 0.1 V s^{-1}). Under the same electrochemical conditions, two related biphenyl complexes without Fp substituents displayed similar reversible oxidation behavior: (η^6-$C_{12}H_{10}$)$Cr(CO)_3$[12] ($E^{\circ\prime}$ = 0.88 V vs SCE, $i_{p,c}/i_{p,a}$ = 0.97, ΔE = 81 mV, 0.1 V s^{-1}) and (μ_2-η^6,η^6-$C_{12}H_{10}$)$(Cr(CO)_3)_2$[12] ($E^{\circ\prime}$ = 0.91 V vs SCE, $i_{p,c}/i_{p,a}$ = 1.0, ΔE = 106 mV, 0.1 V s^{-1}). Five representative aryl- and acyl-bridged complexes displayed only chemically irreversible oxidation behavior at the scan rates (0.1–10.0 V s^{-1}) employed: 4,4′-$C_{12}H_8Fp_2$ ($E_{p,a}$ = 1.05, 0.1 V s^{-1}), 2,6-$C_{10}H_6Fp_2$ ($E_{p,a}$ = 1.06, 0.1 V s^{-1}), 1,4-$C_{10}H_6(COFp)_2$ ($E_{p,a}$ = 1.14, 1.0 V s^{-1}), 4,4′-$C_{18}H_{12}(COFp)_2$ ($E_{p,a}$ = 1.08, 1.0 V s^{-1}), and 9,10-$C_{14}H_8(COFp)_2$ ($E_{p,a}$ = 1.03, 1.0 V s^{-1}).

Results and Discussion

New bimetallic acyl-bridged complexes of iron having biphenyl, terphenyl, naphthyl, and anthracenyl cores (Table I) were prepared by the reaction of 2 equiv of NaFp (where Fp = (η^5-C_5H_5)$Fe(CO)_2$) and the requisite bifunctional acid chloride, e.g.

$$2NaFp + 4,4'\text{-}C_{12}H_8(COCl)_2 \xrightarrow[THF]{-78\ ^\circ C} 4,4'\text{-}C_{12}H_8(COFp)_2 + 2NaCl \quad (1)$$

(where $C_{12}H_8$ is the biphenyl bridge) in yields of 18–86% (Table I).[4b,13] The related monometallic acyl derivatives (Table I) of biphenyl and naphthalene were prepared analogously in 26–90% yields.[13] Each of these yellow to tan acyl complexes are very air and moisture stable, and they were therefore worked up in air. Spectroscopic monitoring of the course of these syntheses suggests that each proceeds in qualitatively similar yields. Thus, the low isolated yields found in some cases are due primarily to losses in workup. However, Fp_2 was occasionally formed in significant yield in these reactions due to competitive electron-transfer reactions.[4b] All of these acyl complexes of Fp are diamagnetic solids having the expected analytical and spectroscopic properties.[4b] In addition, their ^1H and ^{13}C NMR spectra (Table II) unambiguously establish that no rearrangement of geometry about the aromatic groups occurs. Unfortunately, many of these complexes display the tendency we have described earlier[4a–d,f] for related complexes to form CH_2Cl_2 solvates[14] upon crystallization from solvent systems containing CH_2Cl_2. These solvates are generally nonstoichiometric, and the occluded CH_2Cl_2 may often be removed by placing the samples under vacuum for extended periods. As this CH_2Cl_2 is removed, the analytical and NMR data change in the expected fashion (e.g., for 4,4′-$C_{12}H_8(COFp)_2$ the CH_2Cl_2 content shows a steady decrease from one CH_2Cl_2 of solvation through 0.5 CH_2Cl_2 toward no occluded CH_2Cl_2).

We have previously demonstrated that bi- and trimetallic acyl derivatives of benzene (e.g., 1,4-$C_6H_4(COFp)_2$ and 1,3,5-$C_6H_3(COFp)_3$) can be thermally decarbonylated in refluxing butyl ether.[4a–c] We were therefore not surprised that the three monometallic acyls and three of the six bimetallic acyls described above could be decarbonylated in an analogous fashion, e.g.

$$2\text{-}C_{10}H_7(COFp) \xrightarrow[Bu_2O/toluene]{\Delta} 2\text{-}C_{10}H_7Fp + CO\uparrow \quad (2)$$

$$2,7\text{-}C_{10}H_6(COFp)_2 \xrightarrow[Bu_2O]{\Delta} 2,7\text{-}C_{10}H_6Fp_2 + 2CO\uparrow \quad (3)$$

in yields of 31–81%.[13] The primary synthetic limitation to these reactions is that the desired organometallic products thermally decompose at temperatures only slightly above those required (≈120–140 °C) to carry out the thermal decarbonylations. Thus, any localized overheating of the walls of the reaction flask or overly long heating of the reaction mixture results in the decomposition of the desired products, e.g.

$$2,6\text{-}C_{10}H_6Fp_2 \xrightarrow[Bu_2O]{\Delta} C_{10}H_8 + Fp_2 \quad (4)$$

lowering the isolated yields and complicating the workup procedure. In a number of cases, the use of a mixed Bu_2O/toluene (50:50) solvent mixture for carrying out these transformations was found to give increased yields of product. This is probably due to the fact that some of the acyl starting materials have much higher solubilities of toluene than they do in Bu_2O. In addition, the boiling point of the mixed solvent is lower than that of pure Bu_2O which reduces the thermal decomposition of the desired products. Unfortunately, the boiling point of pure toluene is too low to effect the thermal decarbonylation reactions at a useful rate, and it therefore cannot be used as the sole solvent to carry out these decarbonylations. We were not successful in using thermal decarbonylation to prepare 4,4″-$C_{18}H_{12}Fp_2$, 1,4-$C_{10}H_6Fp_2$, or 9,10-$C_{14}H_8Fp_2$ although the first of these derivatives was observed spectroscopically. In the case of the decarbonylation of 9,10-$C_{14}H_8(COFp)_2$, this reaction probably failed because of the extremely low solubility of this acyl-bridged species. We therefore attempted to use metathesis to prepare one of these bimetallic derivatives, e.g.

$$9,10\text{-}C_{14}H_8Li_2 + 2FpI \xrightarrow{-78\ ^\circ C} 9,10\text{-}C_{14}H_8Fp_2 + Fp_2 \quad (5)$$

as this route has previously been used successfully to prepare monometallic Fp–aryl complexes. However, as with the analogous electron-rich benzene derivatives, electron transfer, to give Fp_2 rather than the desired products, appears to be the predominant reaction pathway, and no synthetically useful yields of the bimetallic product were obtained.[4b] All of the new bimetallic arene-bridged derivatives are yellow to tan solids displaying high thermal and oxidative stabilities and unexceptional[4b] analytical and mass spectral behavior (Table I).

The IR and ^1H and ^{13}C NMR spectra of the Fp substituents of these complexes are unexceptional[4a,b] and unambiguously confirm that in each complex the Fp substituents are equivalent.[15,16] Interestingly, the carbonyl ligands of these polyaromatic derivatives display no de-

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(12) These complexes were prepared by the literature procedures, see: (a) Top, S.; Jaouen, G. *J. Organomet. Chem.* **1979**, *182*, 381–392. (b) Rieke, R. D.; Milligan, S. N.; Schulte, L. D. *Organometallics* **1987**, *6*, 699–705. (c) Hull, J. W., Jr.: Gladfelter, W. L. *Organometallics* **1982**, *1*, 264–274. (d) Coletta, F.; Gambara, A.; Rigatti, G.; Venzo, A. *Spectrosc. Lett.* **1977**, *10*, 971–977.

(13) Generally, no attempt was made to optimize the yields of the organometallic products from these reactions.

(14) The CH_2Cl_2 of solvation may be detected in each case by ^1H and ^{13}C NMR spectroscopy (e.g., by the appearance of signals at 5.76 and 54.87 ppm, respectively, in $(CD_3)_2SO$), by elemental analysis (e.g., for 4,4′-$C_{12}H_8(COFp)_2\cdot{}^1/_2CH_2Cl_2$ chlorine analysis (calcd, 5.86; found, 5.55), and even by X-ray crystallography in one related case.[4a,c]

(15) Thus, $\nu_{CO} \approx$ 2020 and 1966 cm^{-1} for the acyl complexes and 2016 and 1962 for the aryl complexes; (^{13}C) $\delta \approx$ 215 and 217 ppm for the carbonyl ligands of the acyl and aryl complexes, respectively; and for the cyclopentadienyl ligands (^1H) δ = 5.05–5.26 ppm and (^{13}C) δ = 86.55–88.21 ppm.

(16) In solution, no evidence is observed for vibronic coupling of the IR bands attributable to the Fp and/or $Cr(CO)_3$ fragments in these complexes.[4a,c–e]

pendence of their IR stretching frequencies or their ^{13}C NMR chemical shifts on the number of conjugated aromatic rings in the bridging group, the substitution geometries about the aromatic core, or the number of Fp groups around the aromatic rings. A similar insensitivity was observed for the benzene-bridged complexes and is probably a reflection of the fact that the Fp–aryl linkage in each complex is predominantly σ bonding in nature and that in Fp–X complexes these parameters are only weakly dependent upon the nature of the X group σ bonded to Fp.[4b,c,f,17]

We have demonstrated previously that when organometallic substituents are σ bonded to benzene rings, the electron density of both their σ and π frameworks is significantly increased.[4b,c,f] This makes such arene-bridged complexes excellent ligands for 12-electron organometallic fragments such as $Cr(CO)_3$.[4a,c–e] Thus, we were not surprised that the polyaromatic derivatives of iron (i.e., 1,4-C_6H_4PhFp, 4,4′-$C_{12}H_8Fp_2$, and 2,6-$C_{10}H_6Fp_2$) react with $Cr(CO)_6$ under conditions similar to those used for their phenylene-bridged analogues. Thus, we find that the polyaromatic π complexes are prepared in greatest overall isolated yields when the $Cr(CO)_3$ complexation

$$4,4'\text{-}C_{12}H_8Fp_2 + Cr(CO)_6 \xrightarrow[Bu_2O]{\Delta} (\eta^6\text{-}4,4'\text{-}C_{12}H_8Fp_2)Cr(CO)_3 + 3CO\uparrow \tag{6}$$

and thermal decarbonylation

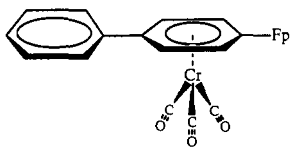
$$4,4'\text{-}C_{12}H_8(COFp)_2 \xrightarrow[Bu_2O]{\Delta} 4,4'\text{-}C_{12}H_8Fp_2 + 2CO\uparrow \tag{7}$$

reactions are carried out concomitantly.

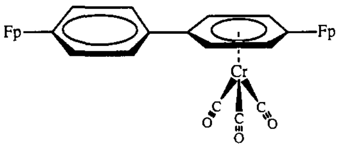
$$4,4'\text{-}C_{12}H_8(COFp)_2 + Cr(CO)_6 \xrightarrow[Bu_2O]{\Delta} (\eta^6\text{-}4,4'\text{-}C_{12}H_8Fp_2)Cr(CO)_3 + 5CO\uparrow \tag{8}$$

In no case was any evidence observed for the formation of π-bonded aroyl complexes (e.g., $(\eta^6\text{-}4,4'\text{-}C_{12}H_8(COFp)_2)Cr(CO)_3$).[4c] The superiority of the one-step synthesis is probably a reflection of the fact that the Fe–aryl σ bonds in complexes of this class are more stable toward thermal degradation when the arene is π complexed to $Cr(CO)_3$ than in the absence of this group.[4c] Using the one-step procedure (i.e., eq 8), the desired heterometallic species, $(\eta^6\text{-}1,4\text{-}C_6H_4PhFp)Cr(CO)_3$, $(\eta^6\text{-}4,4'\text{-}C_{12}H_8Fp_2)Cr(CO)_3$, and $(\eta^6\text{-}2,6\text{-}C_{10}H_6Fp_2)Cr(CO)_3$, were obtained in 7–48% yields[13] as yellow-orange to orange-red crystalline solids. As expected,[4a,c–e] the two biphenyl complexes of $Cr(CO)_3$ display excellent thermal, solvent, and air stabilities while the naphthalene derivative has somewhat lower stabilities, particularly in solution.[18]

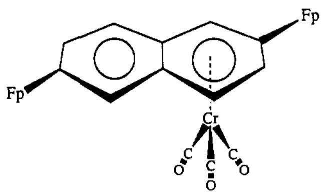
The IR and ^{13}C NMR spectra for the carbonyl ligands of each of the Fp-substituted $(\eta^6\text{-arene})Cr(CO)_3$ complexes are more complex than they are for the analogous complexes without the π-bonded $Cr(CO)_3$ groups (Tables I and II). Thus, specific IR bands and ^{13}C NMR resonances attributable to the $Cr(CO)_3$ fragments and the two types of Fp substituents[19] are readily distinguishable for each complex.[16] From these spectroscopic data, it is clear that the complex $(\eta^6\text{-}1,4\text{-}C_6H_4PhFp)Cr(CO)_3$ has the $Cr(CO)_3$ group π bonded to the more electron-rich, but also much more stericially crowded, benzene ring which is σ bonded to Fp, i.e.



rather than to the less sterically congested, but relatively electron-poor, benzene ring. Indeed, no spectroscopic evidence for the presence of the second isomer, in which the $Cr(CO)_3$ group is bonded to the other aryl ring, is observed. This selectivity is consistent with the structures proposed for other $(\eta^6\text{-}1,4\text{-}C_6H_4PhX)Cr(CO)_3$ complexes having strongly π-donating substituents (e.g., NH_2)[20] and confirms that the arene ring to which Fp is bonded is very electron rich. Similarly, the IR and ^{13}C NMR data for the heterotrimetallic complexes, $(\eta^6\text{-}4,4'\text{-}C_{12}H_8Fp_2)Cr(CO)_3$ and $(\eta^6\text{-}2,6\text{-}C_{10}H_6Fp_2)Cr(CO)_3$[16] (Tables I and II), clearly indicate that each of these complexes have two different Fp substituents, one of which is relatively electron poor and is σ bonded to the aromatic ring which is π complexed to $Cr(CO)_3$ and the other of which is relatively electron rich and is σ bonded to the other aromatic ring. For the 1,4-biphenyl-bridged complex, i.e.



the electron-poor Fp substituent is that which is closest to $Cr(CO)_3$ as it is for the 2,6-naphthalene-bridged complex.[21]



At ambient temperatures, the $Cr(CO)_3$ groups of each of the three heterometallic complexes give rise to single resonances in the ^{13}C NMR and to a pair of carbonyl bands[22] in the IR, suggesting free rotation about the Cr–arene bond. The relative positions of these bands are determined by the relative electron richness of the various $Cr(CO)_3$ centers, with the lowest carbonyl stretching frequencies and the highest ^{13}C NMR carbonyl chemical shifts[23] being expected for the most electron-rich $Cr(CO)_3$

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(17) (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.

(18) For example, weakly nucleophilic $(CD_3)_2SO$ will decompose substituted $(\eta^6\text{-naphthalene})Cr(CO)_3$ complexes (liberating the free arene), but the analogous substituted $(\eta^6\text{-benzene})Cr(CO)_3$ or $(\eta^6\text{-biphenyl})Cr(CO)_3$ derivatives are inert to $(CD_3)_2SO$ under the same conditions.

(19) Those Fp substituents on rings *not* π bonded to $Cr(CO)_3$ displayed IR and ^{13}C NMR signals in the same regions as reported previously for Fp-aryl complexes[4b,15] while those Fp substituents on rings which are π bonded to $Cr(CO)_3$ have bands analogous to those in the $(\eta^6\text{-aryl-Fp})Cr(CO)_3$ complexes (i.e., 2030–1980 cm^{-1} in the IR and 214.77–215.76 ppm in the ^{13}C NMR).[4c,e]

(20) The ratio of isomeric products observed for $(\eta^6\text{-}1,4\text{-}C_{12}H_9NH_2)Cr(CO)_3$ is 93:7 favoring complexation at the more electron-rich disubstituted benzene ring; see: (a) Silverthorn, W. E. *Adv. Organomet. Chem.* **1975**, *13*, 80. (b) Solladié-Cavallo, A. *Polyhedron* **1985**, *4*, 924. (c) Lumbroso, H.; Liegeois, C.; Brown, D. A.; Fitzpatrick, N, J. *J. Organomet. Chem.* **1979**, *165*, 341–351.

(21) For $(\eta^6\text{-}2,6\text{-}C_{10}H_6Fp_2)Cr(CO)_3$, the ^{13}C NMR chemical shifts for the resonances due to the iron carbonyls were not unambiguously determined due to the low signal to noise ratio in the spectrum and the fact that this complex decomposed relatively rapidly in solution.[18]

(22) (a) Cotton, F. A.; Kraihanzel, C. S. *J. Am. Chem. Soc.* **1962**, *84*, 4432. (b) Neuse, E. W. *J. Organomet. Chem.* **1975**, *99*, 287–295. (b) Rawlings, J.; Mahaffy, C. A. L. *Spectrosc. Lett.* **1988**, *21*, 597–606.

center. For the heterometallic complexes, these two measures are in accord and they agree with the cyclic voltammetric results; see below. They indicate that the $Cr(CO)_3$ center of $(\eta^6\text{-}2,6\text{-}C_{10}H_6Fp_2)Cr(CO)_3$ is more electron rich than is that in $(\eta^6\text{-}4,4'\text{-}C_{12}H_8Fp_2)Cr(CO)_3$ which is, in turn, more electron rich than is that in $(\eta^6\text{-}1,4\text{-}C_6H_4PhFp)Cr(CO)_3$. In addition, these two biphenyl derivatives are more electron rich than are the parent complex $(\eta^6\text{-}C_{12}H_{10})Cr(CO)_3$ while the naphthalene derivative is more electron rich than is $(\eta^6\text{-}C_{10}H_8)Cr(CO)_3$.[24] Clearly, the Fp substituents are transferring substantial electron density to the chromium centers in these complexes as they do in the analogous benzene complexes (e.g., $(\eta^6\text{-}1,4\text{-}C_6H_4XFp)Cr(CO)_3$ and $(\eta^6\text{-}1,4\text{-}C_6H_4Fp_2)Cr(CO)_3$).[4c,e]

The ^1H and ^{13}C NMR spectra of the aromatic rings in all of these complexes are relatively simple, as would be expected for such highly symmetric molecules, and they display the expected peak multiplicities and intensities. The ^{13}C NMR resonances of the aromatic carbon atoms were assigned by comparison to the NMR spectra of the related materials without Fp groups (i.e., $C_{12}H_{10}$, $C_{18}H_{14}$, $C_{10}H_8$, $C_{14}H_{10}$, $(\eta^6\text{-}C_{12}H_{10})Cr(CO)_3$, and $(\eta^6,\eta^6\text{-}C_{12}H_{10})(Cr(CO)_3)_2$),[26] by consideration of the peak intensities and chemical shifts, and by the use of the characteristic substituent effects of the Fp and $Cr(CO)_3$ groups.[27] These data indicate that the effects of the Fp groups on the ^{13}C NMR chemical shifts in these polyaromatic complexes are similar to that for Fp substituents in the related benzene derivatives.[4b,c,e,27-30] The NMR data for these complexes unambiguously confirm that $(\eta^6\text{-}1,4\text{-}C_6H_4PhFp)Cr(CO)_3$ has the structure described above and that the other two heterometallic complexes have their $Cr(CO)_3$ groups bonded to only one of the two aromatic rings in each complex. Interestingly, no evidence for haptotropic rearrangement was observed in the biphenyl- and naphthalene-bridged complexes under the conditions employed.

To try and compare the relative efficiencies of the polyaromatic and $\mu\text{-}C_6X_4$ bridging groups at establishing electronic communication between adjacent metal centers as a function of the degree of conjugation of the bridging aryl group,[31] representative examples of the three classes of new bi- and trimetallic complexes prepared in this study had their oxidative behavior characterized by cyclic voltammetry (CH_2Cl_2, $[n\text{-}Bu_4N]PF_6$, Pt bead electrode). The bimetallic arene- and acyl-bridged complexes (i.e., $4,4'\text{-}C_{12}H_8Fp_2$, $2,6\text{-}C_{10}H_6Fp_2$, $1,4\text{-}C_{10}H_6(COFp)_2$, $4,4'\text{-}C_{18}H_{12}(COFp)_2$, and $9,10\text{-}C_{14}H_8(COFp)$) displayed only chemically irreversible behavior at the scan rates employed (0.1–10.0 V s^{-1}), e.g.

$$1,4\text{-}C_{10}H_6(COFp)_2 \xrightarrow{-e^-} \text{decomposition} \qquad (9)$$

$$2,6\text{-}C_{10}H_6Fp_2 \xrightarrow{-e^-} \text{decomposition} \qquad (10)$$

(where $E_{p,a}$ = 1.05 (0.1 V s^{-1}), 1.06 (0.1 V s^{-1}), 1.14 (1.0 V s^{-1}), 1.08 (1.0 V s^{-1}), and 1.03 (1.0 V s^{-1}), respectively). We have observed similar behavior for the related phenylene-bridged complexes (e.g., $C_6H_4Fp_2$), and it is characteristic of the most closely related monometallic Fp–aryl and Fp–acyl complexes.[2,32] This behavior is unfortunate since it means that we cannot evaluate the magnitudes of the metal–metal interactions in these species and so we cannot predict the efficacy with which these polyaromatic bridging groups will establish conjugation down the polymer backbones in organometallic polymers having analogous linkages.

The three heterometallic complexes, on the other hand, displayed chemically reversible oxidative behavior

$$(\eta^6\text{-}4,4'\text{-}C_{12}H_8Fp_2)Cr(CO)_3 \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} [(\eta^6\text{-}4,4'\text{-}C_{12}H_8Fp_2)Cr(CO)_3]^{\bullet+} \qquad (11)$$

at formal oxidation potentials ($E^{\circ\prime}$) of 0.65 V vs SCE for $(\eta^6\text{-}1,4\text{-}C_6H_4PhFp)Cr(CO)_3$, 0.59 V vs SCE for $(\eta^6\text{-}4,4'\text{-}C_{12}H_8Fp_2)Cr(CO)_3$, and 0.46 V vs SCE for $(\eta^6\text{-}2,6\text{-}C_{10}H_6Fp_2)Cr(CO)_3$. These potentials are similar to those of other electron-rich $(\eta^6\text{-arene})Cr(CO)_3$ complexes such as $(\eta^6\text{-}1,4\text{-}C_6H_4XFp)Cr(CO)_3$ (where X = H, Me, etc.),[4d,e] $(\eta^6\text{-}1,4\text{-}C_6H_4Fp_2)Cr(CO)_3$,[4d] and $(\eta^6\text{-}C_6H_5(NR_2))Cr(CO)_3$[33,34]

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(24) Using authentic samples,[12] we have measured ν_{CO} (CH_2Cl_2), $\delta(^{13}CO)$ ($(CD_3)_2SO$), and $E^{\circ\prime}$ (CH_2Cl_2) for $(\eta^6\text{-}C_6H_5Ph)Cr(CO)_3$ as 1970 and 1895 cm^{-1}, 233.83 ppm, and 0.88 V, respectively.[25] Similarly, for $(\mu_2\text{-}\eta^6,\eta^6\text{-}C_{12}H_{10})(Cr(CO)_3)_2$ these values are 1969 and 1903 cm^{-1}, 233.17 ppm, and 0.91 V, respectively. For $(\eta^6\text{-}C_{10}H_8)Cr(CO)_3$, ν_{CO} (CH_2Cl_2) is 1972 and 1896 cm^{-1} and $\delta(^{13}CO)$ ($CDCl_3$) is 231.6 ppm.[12d]

(25) It has previously been reported that $(\eta^6\text{-}C_6H_5Ph)Cr(CO)_3$ is irreversibly oxidized at 25 °C in $CH_2Cl_2/[n\text{-}Bu_4N]PF_6$/Pt electrode at 0.1 V s^{-1}. See: Van Order, N.; Geiger, W. E.; Bitterwolf, T. E.; Rheingold, A. L. *J. Am. Chem. Soc.* **1987**, *109*, 5680–5690. Under our experimental conditions, particularly with the addition of the ICN Biomedical activated alumina, this becomes a chemically reversible process (i.e., ΔE = 81 mV, $i_{p,c}/i_{p,a}$ = 0.97 V) at 0.1 V s^{-1}. Indeed, in every case we found that the use of this superactivated alumina resulted in increased chemical reversibilities for our $(\eta^6\text{-arene})Cr(CO)_3$ complexes.

(26) For comparison purposes, the NMR spectra of these compounds were recorded in the same solvent as was used for the analogous Fp derivatives (i.e., $(CD_3)_2SO$) and these data have been deposited as supplementary material. The ^{13}C NMR spectra of some of these compounds have been reported previously in other solvents.[12d]

(27) The Fp group has characteristic influence[28] on the ^{13}C NMR chemical shifts of benzene derivatives of Δ_{ipso} = +17.0 ppm, Δ_{ortho} = +17.0 ppm, Δ_{meta} = −1.0 ppm, and Δ_{para} = −6.0 ppm in $(CD_3)_2SO$, and for $(\eta^6\text{-benzene})Cr(CO)_3$ derivatives its characteristic effects are Δ_{ipso} = +30.0 ppm, Δ_{ortho} = +16.0 ppm, Δ_{meta} = +2.0 ppm, and Δ_{para} = −3.0 ppm in $(CD_3)_2SO$.[4b,c] The addition of a $Cr(CO)_3$ to a benzene ligand shields its aromatic carbon atoms by 33.4 ppm (i.e., Δ = −33.4 ppm) in $(CD_3)_2SO$.[4b,c]

(28) For a detailed discussion of ^{13}C NMR substituent effects[29] in these complexes see refs 4*b*,*c*,*e* and work cited therein.

(29) For main-group substituents, the characteristic effects substituents have on the ^{13}C NMR chemical shifts are the same magnitude, to a first approximation, for benzene, biphenyl, and naphthalene derivatives. See, for example: (a) Levy, G. C.; Lichter, R. L.; Nelson, G. L. *Carbon-13 Nuclear Magnetic Resonance Spectroscopy*; Wiley: New York, 1980. (b) Stothers, J. B. *Carbon-13 NMR Spectroscopy*; Academic: New York, 1972. (c) Memory, J. D.; Wilson, N. K. *NMR of Aromatic Compounds*; Wiley: New York, 1982. (d) Ewing, D. F. *Org. Magn. Reson.* **1979**, *12*, 499–524.

(30) Similar long-range substituent effects on the chemical shifts of biphenyl and naphthalene derivatives have been described previously.[29] For these species, they probably arise from π-donor interactions between the 17-electron transition-metal fragments and their aryl ligands.[2,4,17]

(31) Even though the aryl rings in the biphenyl complexes would be expected to be twisted by ≈20–25° with respect to one another, the cosine term governing the degree of conjugation between these rings allows them to retain ≈90% of the maximum amount of conjugation that they would experience if fully coplanar.

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and are much lower than those of the related (η^6-arene)Cr(CO)$_3$ complexes without Fp substituents such as (η^6-C$_{12}$H$_{10}$)Cr(CO)$_3$.[24,25] Indeed, the substitution of the first Fp group onto the "complexed" ring of (η^6-C$_{12}$H$_{10}$)Cr(CO)$_3$ causes its formal oxidation potential to decrease by 330 mV while the substitution of a second Fp group on the other rings causes $E^{\circ\prime}$ to decrease by a further 60 mV even over a distance of eight bonds ($\approx$9 Å).[35] These values are consistent with the IR and ^{13}C NMR data (Tables I and II) and unambiguously confirm our earlier suggestion that the Fp substituents in these complexes transfer substantial electron density to the chromium centers, making them very electron rich. Finally, it is interesting to note that the chemical reversibilities of these oxidations and those of other (η^6-arene)Cr(CO)$_3$ complexes[9d,e,25,34] are substantially increased by the addition of activated alumina to the cyclic voltammetry cell, presumably due to the in situ removal of traces of water or other electroactive impurities.

Conclusions

During this study, we have successfully extended the synthetic methodology that we developed earlier for benzene-bridged complexes of (η^5-C$_5$H$_5$)Fe(CO)$_2$ to the preparation of a series of polymetallic complexes of biphenyl, terphenyl, naphthalene, and anthracene. Thus, homometallic complexes having two direct Fe–C σ bonds to the aryl and acyl bridging groups in these bimetallic complexes were prepared. Three representative heterometallic complexes of iron and chromium having biphenyl and naphthyl bridging groups were also prepared, and it was established that the iron centers in these heterobimetallic complexes transfer substantial electron density to the π-bonded chromium centers. Unfortunately, because the simple arene- and acyl-bridged complexes were not observed to be oxidized reversibly under the conditions employed, we were not able to ascertain if the addition of increased conjugation to the aromatic bridging groups in these complexes resulted in increased iron–iron electronic interactions in the homometallic complexes.

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Supplementary Material Available: NMR data for (η^6-C$_{12}$H$_{10}$)(Cr(CO)$_3$)$_n$ (where n = 1 and 2), C$_{12}$H$_{10}$, C$_{18}$H$_{14}$, C$_{10}$H$_8$, and C$_{14}$H$_{10}$ recorded in (CD$_3$)$_2$SO (2 pages). Ordering information is given on any current masthead page.

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(35) By way of comparison, the addition of a methyl substituent to (η^6-arene)Cr(CO)$_3$ complexes causes $E^{\circ\prime}$ to decrease by approximately 30 mV.[33g,o,p,34]

Multiple η^2-Arene Coordination. Structure and Isomerism of Naphthalene Complexes of [(C$_5$Me$_5$)Rh(PMe$_3$)]

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The fragment [(C$_5$Me$_5$)Rh(PMe$_3$)] reacts with naphthalene to give both C–H bond activation and η^2-naphthalene complexes. Continued thermal reaction eventually leads to the production of the unusual binuclear species [(C$_5$Me$_5$)Rh(PMe$_3$)]$_2$(1,2-η^2-3,4-η^2-C$_{10}$H$_8$), which can be isolated in pure form. The complex crystallizes in monoclinic space group $P2_1/a$ with a = 16.717 (8) Å, b = 16.153 (4) Å, c = 27.721 (8) Å, β = 106.75 (3)°, V = 7167.6 (6.8) Å^3, and Z = 8. The isomerization of the labeled molecule (C$_5$Me$_5$)Rh(PMe$_3$)(2-naphthyl)D has been examined and found to proceed intramolecularly within the same ring.

Introduction

Over the past few years, a variety of new π-arene complexes have been discovered in which the metal interacts with a single double bond of the aromatic ligand.[1-4] These complexes have been found to be important precursors in C–H bond oxidative addition reactions.[5,6] Coordination of the metal to the arene alters its reactivity and has found applications in the selective hydrogenation of benzene to cyclohexene.[7] In the present study, a variety of binding modes for naphthalene have been examined, one of which involves the coordination of two metals to the same aromatic ring.

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