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Phenylene-Bridged Organometallic Complexes of Iron and Manganese[1]

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The synthesis of the complexes 1,3-$C_6H_4(ML_n)_2$, 1,4-$C_6H_4(ML_n)_2$, and 1,3,5-$C_6H_3(ML_n)_3$ (where ML_n = (η^5-C_5H_5)$Fe(CO)_2$, (η^5-C_5H_4Me)$Fe(CO)_2$, or $Mn(CO)_5$) is described. These species are best prepared in two steps by metathesis of the organometallic anion, $NaML_n$, with the appropriate aroyl chloride to give acyl intermediates. These complexes were isolated and then thermally decarbonylated (in refluxing butyl ether and THF for the Fe and Mn complexes, respectively) to give the desired products in 40–90% overall yield. Their perfluoro analogues, 1,4-$C_6F_4Fp^*_2$ (where Fp^* = (η^5-C_5H_5)$Fe(CO)_2$ or (η^5-C_5H_4Me)$Fe(CO)_2$), are prepared in 30–60% yield by the metathesis of 1,4-$C_6F_4Li_2$ with Fp^*I. These new materials have been fully characterized by conventional spectroscopic techniques and are shown to contain metal–arene σ bonds. Evidence is provided for partial dimetalloquinone character in the bonding of the para-substituted species. The reactions of the title compounds with phosphines (to give carbonyl substitution products) and with halogens (to give metal–aryl bond cleavage) are also reported.

Introduction

Over the last several years there has been growing interest in the synthesis of polymetallic complexes whose metal centers are joined by polyfunctional organic ligands having delocalized π systems.[2] Such electronically bridged species are of interest both because of the novel interactions observed between the adjacent metal centers and because of their relationship to one-dimensional conductors. The bridging ligands used to date are generally organic molecules having an aromatic core and two Lewis base sites (i.e., pyrazine, diaminobenzene, or dicyanobenzene).[2a–j] However, surprisingly little work has been reported in which the aromatic core of the bridging ligand is directly joined to the metal centers by metal–carbon σ bonds.[3–6] We are interested in such phenylene-bridged complexes because their metal–ligand–metal bonding interactions are models for those of other complexes which have an aromatic core.[2] In addition, they may serve as models for any phenylene-bridged polymers that may be prepared in the future.

The chemistry of monofunctional metal–arene linkages is well developed[3] but that of the related phenylene-bridged species is not.[4–6] Our initial studies in this area have therefore involved the development of the synthetic technology required to produce such bimetallic linkages in a systematic fashion. Such studies were required because simple extensions of the methods used to prepare monometallic complexes often fail to give the related polymetallic species in satisfactory yields. In addition, we have characterized the polymetallic products of these studies and have used the resulting data to establish the characteristic chemical and spectroscopic properties of such phenylene linkages. In this paper, we report the complete results of these studies and discuss the nature of the resulting arene bridges.

Experimental Section

Unless otherwise noted, all reactions and subsequent manipulations were performed by using conventional techniques for the manipulation of air-sensitive compounds.[7] Thus, anaerobic and anhydrous conditions were maintained by using a prepurified argon or dinitrogen atmosphere. The reagents used were purchased from commercial suppliers (Aldrich) or were prepared according to the published procedures. The chemicals used were of reagent grade or comparable purity and where necessary were purified before use (their purity was ascertained by elemental analyses and/or other suitable methods).[7,8] Solvents used were dried and deaerated by standard procedures and stored under N_2 or Ar.[7,8] Thus CH_2Cl_2 and Bu_2O were distilled from P_2O_5 and CaH_2, respectively, and deaerated prior to use while toluene,[9] benzene,[9] THF,[9] Et_2O,[10] and hexanes[10] were distilled from sodium–benzophenone ketal under an inert atmosphere. Unless specified otherwise, the reactions and any subsequent manipulations described below were effected at ambient temperatures.

Infrared spectra were recorded on a Pye Unicam PU9522 infrared spectrophotometer and were calibrated with the 1601 cm^{-1} band of polystyrene. Nuclear magnetic resonance spectra were recorded on Bruker WH-200, 300, and 400 spectrometers with reference to the deuterium signal of the solvent employed. The ^1H and ^{13}C chemical shifts are reported in parts per million downfield from external Me_4Si, the ^{31}P NMR spectra are reported in parts per million downfield from external 85% H_3PO_4, and the ^{19}F NMR spectra are reported in parts per million downfield from

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[1] (a) Organometallic Complexes with Electronic Bridges. 2. For Part 1 see: Hunter, A. D. *Organometallics* **1989**, *8*, 1118. (b) Presented in part at the "Third Chemical Congress of North America", Toronto, Canada, June 1988, INOR 87.

[2] See for example: (a) Maatta, E. A.; Devore, D. D. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 569. (b) Zulu, M. M.; Lees, A. J. *Inorg. Chem.* **1988**, *27*, 1139. (c) Gross, R.; Kaim, W. *J. Organomet. Chem.* **1987**, *333*, 347. (d) Gross, R.; Kaim, W. *Inorg. Chem.* **1987**, *26*, 3596. (e) Metz, J.; Hanack, M. *Chem. Ber.* **1987**, *120*, 1307. (f) Collman, J. P.; McDevitt, J. T.; Leidner, C. R.; Yee, G. T.; Torrance, J. B.; Little, W. A. *J. Am. Chem. Soc.* **1987**, *109*, 4606. (g) Kaim, W.; Kohlmann, S. *Inorg. Chem.* **1986**, *25*, 3442. (h) Kobel, W.; Hanack, M. *Inorg. Chem.* **1986**, *25*, 103. (i) Toscano, P. J.; Marks, T. J. *J. Am. Chem. Soc.* **1986**, *108*, 437. (j) Feinstein-Jaffe, I.; Frolow, F.; Wackerle, L.; Goldman, A.; Efraty, A. *J. Chem. Soc., Dalton Trans.* **1988**, 469. (k) Hanack, M.; Seelig, F. F.; Strähle, J. *Z. Naturforsch., A* **1979**, *34*, 983. (l) Takahashi, S.; Marata, E.; Sonogashira, K.; Hagihara, N. *J. Polym. Sci., Polym. Chem. Ed.* **1980**, *18*, 661. (m) Sonogashira, K.; Ohga, K.; Takahashi, S.; Hagihara, N. *J. Organomet. Chem.* **1980**, *188*, 237.

[3] See for example: 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.

[4] Buchwald, S. L.; Lucas, E. A.; Dewan, J. C. *J. Am. Chem. Soc.* **1987**, *109*, 4396.

[5] (a) Nesmeyanov, A. N.; Anisimov, K. N.; Kolobova, N. E. *Dokl. Akad. Nauk SSSR* **1967**, *175*, 358 (Engl. transl., 627). (b) Nesmeyanov, A. N.; Anisimov, K. N.; Kolobova, N. E. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1963**, 1348 (Engl. transl., 1225).

[6] (a) Cohen, S. C. *J. Chem. Soc., Dalton Trans.* **1973**, 553. (b) Cohen, S. C. *Org. Mass Spectrom.* **1972**, *6*, 1283. (c) Cohen, S. C. *J. Organomet. Chem.* **1971**, *30*, C15. (d) Cohen, S. C. Abstracts, International Conference on Organometallic Chemistry; 1971; 397. (e) Bruce, M. I. *J. Organomet. Chem.* **1970**, *21*, 415 and references cited therein.

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

[8] Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*, 2nd ed.; Pergamon: New York, 1980.

[9] Approximately 20 mL of heavy paraffin oil was added to these still pots to reduce the hazard of the still pot going dry and causing an organic peroxide explosion.[7,8]

[10] Approximately 20 mL of tetraglyme (tetraethyleneglycol dimethyl ether) was added to these still pots to increase the solubility of the sodium benzophenone ketal drying agent and to reduce the danger from organic peroxides.[7,8]

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

complex[a]	analytical data				low-resolutn mass spectral data m/z^b	infrared data ν_{CO} (CH_2Cl_2, cm^{-1})[c]
	C		H			
	calcd	found	calcd	found		
$1,4\text{-}C_6H_4(COFp)_2$[d]	54.37	54.51	2.90	2.79	486[e,f]	2030 (m), 1962 (m), 1606 (w, br)
$1,4\text{-}C_6H_4(COFp')_2$	56.07	56.04	3.92	3.70	514	2019 (s), 1962 (s), 1604 (w, br)
$1,3\text{-}C_6H_4(COFp)_2$	54.37	54.19	2.90	2.97	486[f]	2028 (m), 1960 (m), 1610 (w, br)
$1,3,5\text{-}C_6H_3(COFp)_3$[g]	52.22	52.24	2.63	2.63	690[f]	2028 (s), 1961 (s), 1612 (m, br)
$1,3,5\text{-}C_6H_3(COFp')_3$	54.12	54.12	3.30	3.41	732	2020 (s), 1963 (s), 1609 (w, br)
$1,4\text{-}C_6H_4(COMn(CO)_5)_2$	41.38	41.12	0.76	0.81	522[f]	2118 (s), 2050 (s), 2043 (s), 2034 (s), 2003 (vs, br), 1986 (vs, br), 1587 (s)[h]
$1,3\text{-}C_6H_4(COMn(CO)_5)_2$	41.38	41.16	0.76	0.88		2120 (m), 2056 (m), 2022 (vs, br), 1613 (w, br)
$1,3,5\text{-}C_6H_3(COMn(CO)_5)_3$	38.74	38.77	0.41	0.50	744[f]	2120 (m), 2062 (m), 2030 (sh), 2008 (vs, br), 1975 (s), 1608 (m, br)
$1,4\text{-}C_6H_4Fp_2$	55.86	56.30	3.28	3.58	430[e]	2014 (s), 1959 (s)
$1,4\text{-}C_6H_4Fp'_2\cdot{}^1/_2CH_2Cl_2$	53.99	54.19	3.83	3.94	458	2010 (s), 1953 (s)
$1,3\text{-}C_6H_4Fp_2$	55.86	55.41	3.28	3.30	430[e]	2016 (s), 1958 (s)
$1,3,5\text{-}C_6H_3Fp_3$	53.52	53.75	2.99	3.31	606[e]	2014 (s), 1958 (s)
$1,4\text{-}C_6H_4(Mn(CO)_5)_2$	41.23	40.61	0.86	0.82	466[e]	2111 (m), 2050 (w, sh), 2020 (vs), 1994 (s), 1946 (w, br)
$1,3\text{-}C_6H_4(Mn(CO)_5)_2$	41.23	41.70	0.86	0.95	466[e]	2108 (m), 2050 (vw, sh), 2024 (vs), 1997 (s)
$1,3,5\text{-}C_6H_3(Mn(CO)_5)_3$	38.21	38.16	0.46	0.73	660[e]	2110 (m), 2055 (sh), 2027 (s), 1987 (m, br)
$1,4\text{-}C_6F_4(Fp')_2$	49.85	49.08	2.66	2.53	530[e]	2029 (s), 1978 (s)
$1,4\text{-}C_6F_4(Fp)_2$	47.85	47.10	2.01	2.49	502	2027 (w), 1981 (w)
$1,4\text{-}C_6F_4(Mn(CO)_5)_2$	35.72	34.59			538	2131 (m), 2076 (w, sh), 2042 (vs), 2014 (s)
$1,4\text{-}C_6Cl_4(COFp)H$	40.05	39.73	1.44	1.73	420[f]	2030 (m), 1977 (m), 1616 (w, br)
$1,4\text{-}C_6Cl_4(Mn(CO)_5)H$	32.23	32.24	0.25	0.30	387[e]	2129 (m), 2036 (vs), 2013 (s), 1975 (w, br)
$1,4\text{-}C_6H_4(Mn(CO)_4(PPh_3))_2$	64.25	64.47	3.67	3.89	934[f]	2064 (m), 2020 (w, sh), 1966 (s, br), 1940 (br, sh)
$1,3\text{-}C_6H_4(Mn(CO)_4(PPh_3))_2$	64.25	59.41	3.67	3.76	934[f]	2058 (m), 2016 (w, sh), 1976 (s, br), 1942 (br, sh)
$1,3\text{-}C_6H_4(Mn(CO)_5)(Mn(CO)_3(dppe))$	59.37	59.33	3.50	3.67	808[f]	2112 (w), 2064 (m), 2018 (vs), 1997 (vs), 1970 (s, br), 1944 (s, br), 1918 (s, br)
$1,3\text{-}C_6H_4(Mn(CO)_4)_2(\mu\text{-dppen})$	59.57	59.73	3.25	3.75	806[f]	2066 (m), 2058 (m), 1982 (s, vbr), 1950 (m, br)

[a] Where Fp = (η^5-C_5H_5)Fe$(CO)_2$, Fp′ = (η^5-C_5H_4Me)Fe$(CO)_2$, dppe = $Ph_2PCH_2CH_2PPh_2$, dppen = *trans*-$Ph_2PCH{=}CHPPh_2$. [b] Probe temperature 100–280 °C. Assignments involve the most abundant naturally occurring isotopes of each species (i.e. ^{55}Mn, ^{56}Fe, ^{35}Cl). All ions displayed peak patterns attributable to the expected isotopomers. [c] Abbreviations: w (weak), m (medium), s (strong), sh (shoulder), v (very), br (broad). [d] Oxygen analysis. Calcd: 19.75. Found: 20.03. [e] Peak assignments confirmed by high-resolution mass spectra. [f] No parent ion observed in low-resolution mass spectrum. Parent ion observed in positive ion, Xe atom, fast atom bombardment mass spectrum (usually as P^+ + H). [g] Oxygen analysis. Calcd: 20.87. Found: 20.70. [h] IR spectrum taken as a Nujol mull.

external $CFCl_3$. G. H. M. Aarts, L. C. Kong, G. Bigam, T. Brisbane, and Dr. T. T. Nakashima assisted in obtaining the NMR data. Low-resolution mass spectra were recorded at 16 or 70 eV on an AEI MS50 spectrometer. High-resolution mass spectra were recorded at 70 eV on an AEI MS12 spectrometer. Positive ion fast atom bombardment mass spectra (FAB-MS) were recorded by using Xe fast atoms on a customized[11] AEI MS9 spectrometer. J. Olekszyk, A. Jodham, D. Morgan, L. Harrower, and/or Dr. A. M. Hogg recorded the MS data. Elemental analyses were performed by D. Mahlow, A. Dunn, and R. N. Swindlehurst of this department.

Caution: Mercury is a volatile substance having well-established human toxicity. Its reactions should therefore be carried out while taking appropriate precautions.[8]

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 reported below.

Preparation of $C_6H_{6-n}(COFp)_n$ (Fp = (η^5-C_5H_5)Fe$(CO)_2$; n = 2, 3). All these reactions were performed in a similar manner. The procedure for $1,3,5\text{-}C_6H_3(COFp)_3$ is described in detail as a representative example.

An excess of solid sodium amalgam[12] (20.0 g, 20.0 mmol of Na) was liquified by the addition of mercury (≈3 mL); then THF (60 mL) and Fp_2[13] (2.00 g, 5.65 mmol) were added. The resultant dark red solution was stirred vigorously for 1 h to produce a solution containing NaFp.[14] Excess amalgam was drained from the reaction through a side arm on the reaction flask.[15] The solution was then filtered through Celite (2 × 3 cm) supported on a medium porosity frit to remove any finely divided amalgam (2 × 10 mL of THF wash). The resulting orange-red solution was cooled to −78 °C (dry ice/acetone), and then $1,3,5\text{-}C_6H_3(COCl)_3$ (0.95 g, 3.58 mmol) was added. This stirred solution was allowed to slowly warm to room temperature (≈1 h) and then taken to dryness in vacuo. To the resulting red tar was added Et_2O (20 mL) producing, upon stirring, a red solution over a tan solid. This solid was collected by filtration in air, washed with Et_2O[16] (30 mL), distilled H_2O (60 mL), Et_2O[16] (10 mL), and hexanes[16] (10 mL), and dried in vacuo to give the desired product, $1,3,5\text{-}C_6H_3(COFp)_3$, in excellent yield (1.98 g, 2.87 mmol, 80%) as an analytically pure tan solid.

The 1,3- and $1,4\text{-}C_6H_4(COFp)_2$ products were similarly produced in 88 and 94% yields, respectively, from isophthaloyl or terephthaloyl chloride. Attempts to prepare $1,2\text{-}C_6H_4(COFp)_2$ by this route (i.e., 2NaFp + $1,2\text{-}C_6H_4(COCl)_2$) resulted in near quantitative formation of Fp_2.

Preparation of $C_6H_{6-n}(COMn(CO)_5)_n$ (n = 2, 3). These syntheses were carried out in the same manner described for their iron analogues (vide supra) with the exception that the additions of the aroyl chlorides to $NaMn(CO)_5$ were performed at ambient temperatures. The analytically pure pale yellow powders were isolated in good yields: $1,3\text{-}C_6H_4(COMn(CO)_5)_2$, 61%; $1,4\text{-}C_6H_4(COMn(CO)_5)_2$, 93%; $1,3,5\text{-}C_6H_3(COMn(CO)_5)_3$, 40%.

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

A suspension of $1,4\text{-}C_6H_4(COFp)_2$ (0.25 g, 0.51 mmol) in Bu_2O (50 mL) was stirred slowly (to avoid splashing the diacyl on the sides of the flask) and was heated at a *gentle* reflux (note: care

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[11] Hogg, A. M. *Int. J. Mass Spectrom. Ion Phys.* **1983**, *49*, 25.

[12] A solid solution of sodium in mercury can be prepared by the rapid addition (~2 min) of sodium chunks (23.0 g, 1 mol) to rapidly stirred metallic mercury in a 500-mL suction flask (under an N_2 stream). *Note*: this step should be done behind an explosion shield in a well-ventilated fume hood while wearing gloves since a gray vapor probably containing Na and Hg is given off by this very exothermic process. Upon cooling to room temperature the resultant silver puck of solid polycrystalline sodium amalgam (1.00 mmol of Na/g) is removed from the flask with a hammer and ground to small pieces in a large mortar and pestle. This material may be stored for extended periods in air with no noticeable hydrolysis and, in fact, is only slowly hydrolyzed by water.

[13] King, R. B. *Organometallic Syntheses*; Academic Press: New York, 1965; Vol. 1, p 114.

[14] Reference 13, p 151 and work cited therein.

[15] Reference 13, p 149.

[16] Wash solvent grade.

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

	^{1}H NMR^{b}		^{13}C NMR^{b} ($^{1}J_{CH}$, Hz)			
				arene		
complex^{a}	Cp^{*}	C_6H_{6-n}	Cp^{*}	Fe–*C*	H–*C*	M–*CO*
1,4-$C_6H_4Fp_2$	5.07 (s, 10 H)	6.95 (s, 4 H)	86.64 (180.7)	134.63	144.98 (154)	217.47
1,4-$C_6H_4Fp'_2$	4.96 (s, 4 H) 4.83 (s, 4 H) 1.60 (s, 6 H)	6.96 (s, 4 H)	105.5 (*C*Me) 85.55 (*C*H) 84.55 (*C*H) 12.65 (*C*H_3)	138	144.42	217.18
1,3-$C_6H_4Fp_2$	5.07 (s, 10 H)	7.46 (t, 1 H, H_A, J_{AB} = 1.5 Hz) 6.87 (dd, 2 H, H_B, J_{BC} = 7.3 Hz) 6.48 (t, 1 H, H_C)	86.45	143.90	161.46 (*C*2) 127.24 (*C*5) 138.98 (*C*4/*C*6)	217.35
1,3,5-$C_6H_3Fp_3$	5.03 (s, 15 H)	6.92 (s, 3 H)	86.35	142.64	155.48	217.16
1,4-$C_6H_4(Mn(CO)_5)_2$		7.28 (s)^{c}				
1,3-$C_6H_4(Mn(CO)_5)_2$		7.65 (s, 1 H, H_A)^{c} 7.10 (d, 2 H, H_B, J_{BC} = 6 Hz) 6.79 (t, 1 H, H_C)		146.48	161.55 (*C*2) 129.63 (*C*5) 140.75 (*C*4/*C*6)	211.66 209.94
1,3,5-$C_6H_3(Mn(CO)_5)_3$		7.28 (s)^{c}		147.53	157.26	211.78 ≈210
1,4-$C_6F_4(Fp)_2$^{d}	5.22 (s)		85.83	*e*	150.77	215.15
1,4-$C_6F_4(Fp')_2$^{f}	5.13 (s, 4 H) 5.02 (s, 4 H) 1.68 (s, 6 H)		106.44 (*C*Me) 84.65 (*C*H) 84.13 (*C*H) 12.68 (*C*H_3)	113.73	150.63 ($^{1}J_{CF}$ = 220)	215.47

^{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′ complexes. ^{b} ^{1}H NMR were measured at 300.135 MHz and ^{13}C NMR were measured at 75.469 MHz unless otherwise specified. ^{c} Recorded in CD_2Cl_2. ^{d} ^{19}F NMR δ −108.27. ^{e} Not observed. ^{f} ^{19}F NMR δ −109.21.

must be taken to avoid local overheating of the solution). 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 2015 and 1960 cm^{-1} grew in intensity. The reaction was stopped upon the appearance of Fp_2 bands (most noticeably that at 1790 cm^{-1}), or when no further increase in product, IR bands was observed (≈5.5 h). The supernatant solution was then removed by filtration from the brown residue (20 mL of CH_2Cl_2 wash), and the combined filtrates were taken to dryness in vacuo. The resulting solid was recrystallized from a mixture of CH_2Cl_2 (20 mL) and hexanes (30 mL) at −40 °C to give 1,4-$C_6H_4Fp_2$ as analytically pure yellow needles in excellent yield (0.15 g, 68%).

The 1,3-$C_6H_4Fp_2$ was prepared similarly but in lower yield (51%) with FpPh and Fp_2 being identified as byproducts by comparison of their IR and mass spectral data with those of authentic samples. Similarly, 1,3,5-$C_6H_3Fp_3$ was isolated in 30% yield and 1,3-$C_6H_4Fp_2$, FpPh, and Fp_2 were identified as byproducts by comparison with authentic samples.

The synthesis of 1,4-$C_6H_4Fp_2$ from its acyl precursor could also be carried out in 59% yield in refluxing butyronitrile (25 h).

Preparation of $C_6H_{6-n}(Mn(CO)_5)_n$ (n = 2, 3). These reactions were performed in an identical fashion. The procedure for 1,3,5-$C_6H_3(Mn(CO)_5)_3$ is described in detail.

A yellow suspension of 1,3,5-$C_6H_3(COMn(CO)_5)_3$ (0.51 g, 0.69 mmol) in THF (40 mL) was refluxed for 0.5 h until the solid had dissolved to give a very pale yellow solution. This solution was taken to dryness in vacuo and the resulting solid recrystallized from Et_2O to give 1,3,5-$C_6H_3(Mn(CO)_5)_3$ in excellent isolated yield (0.40 g, 88%) as an analytically pure, white crystalline solid.

The bimetallic complexes may be isolated in slightly lower yield (58% for 1,4-$C_6H_4(Mn(CO)_5)_2$ and 61% for 1,3-$C_6H_4(Mn(CO)_5)_2$) by crystallization from hexanes. However, IR and NMR spectroscopic monitoring indicates that all three products are formed quantitatively in these reactions. They are therefore generally produced and used in situ.

Preparation of 1,4-$C_6F_4(Fp')_2$ (Fp′ = (η^5-C_5H_4Me)Fe$(CO)_2$). To a suspension of 1,4-$C_6F_4Br_2$ (2.00 g, 6.50 mmol) in Et_2O (50 mL) at −78 °C was added 2 equiv of n-BuLi (2.5 M solution in hexanes, 4.9 mL, 12.2 mmol). After the solution was stirred for 0.5 h, Fp′I[17] (4.13 g, 13.0 mmol) was added to the resultant suspension. This mixture was kept at −78 °C for 1.5 h and then allowed to warm to room temperature over a period of 1 h producing a red solution over a tan solid. This solid was collected by filtration in air, washed with Et_2O[16] (100 mL), H_2O (50 mL), and Et_2O[16] (10 mL), and dried in vacuo to give 1,4-$C_6F_4(Fp')_2$ (2.20 g, 59%).

Preparation of 1,4-$C_6F_4(Fp)_2$. This reaction proceeds analogously to its methylcyclopentadienyl analogue with the exception that here the product, 1,4-$C_6F_4(Fp)_2$, is crystallized from acetone, in air, in 74% yield.

Reaction of 1,4-$C_6F_4Li_2$ with $Mn(CO)_5Br$. To a suspension of 1,4-$C_6F_4Br_2$ (0.31 g, 1.00 mmol) in Et_2O (50 mL) at −78 °C was added 2 equiv of n-BuLi (0.80 mL, 2.00 mmol). After this had been stirred for 0.5 h, $Mn(CO)_5Br$[18] (0.55 g, 2.00 mmol) was added and the solution was allowed to warm to room temperature. The resultant suspension was stirred for 18 h, taken to dryness in vacuo, and chromatographed on alumina (neutral activity 1, 2 × 6 cm) with benzene as eluent. The first band was shown to contain $Mn_2(CO)_{10}$ by IR spectroscopy and was discarded. The second band contained 1,4-$C_6F_4H(Mn(CO)_5)$ which was identified by its spectroscopic properties (low-resolution mass spectrum, m/z 344; ^{1}H NMR (CD_2Cl_2) 6.88 (m) ppm; ^{19}F NMR (CD_2Cl_2) −140.17 (2 F, m), −105.14 (2 F, m)) but was not isolated in an analytically pure form. The third band was collected and taken to dryness to give 1,4-$C_6F_4(Mn(CO)_5)_2$ as a yellow solid in low yield (0.12 g, 22%).

Reaction of 2NaFp with 1,4-$C_6Cl_4(COCl)_2$. Addition of 1,4-$C_6Cl_4(COCl)_2$ (0.48 g, 1.41 mmol) to a solution of NaFp (2.82 mmol) in THF (60 mL) (vide supra) at −78 °C resulted in the formation of a red-brown solution. After being stirred for 2 h at room temperature, this solution was taken to dryness in vacuo. The resulting red oil was chromatographed on alumina (neutral activity 1, 2 × 8 cm) with benzene as eluent to give 1,4-C_6Cl_4(COFp)H (0.11 g, 19%) as the organometallic component of the second band.

Reaction of 2NaMn$(CO)_2$ with 1,4-$C_6Cl_4(COCl)_2$. Addition of 1,4-$C_6Cl_4(COCl)_2$ (0.43 g, 1.26 mmol) to a solution of NaMn$(CO)_5$ (2.56 mmol) in THF (50 mL) caused the solution to become orange in color. After being stirred for 20 h, the solution was taken to dryness, extracted with Et_2O (4 × 20 mL), and taken to dryness in vacuo. Removal of $Mn_2(CO)_{10}$ by sublimation and recrystallization from Et_2O gave 1,4-$C_6Cl_4(Mn(CO)_5)$H in low yield (0.10 g, 19%) as the only new organometallic product identified.

Reaction of 1,4-$C_6H_4(Mn(CO)_5)_2$ with Excess X_2 (X = Br, I). Addition of excess Br_2 (6 drops) to a solution of 1,4-C_6H_4-

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[17] (a) King, R. B.; Stone, F. G. A. *Inorg. Synth.* **1963**, *7*, 110. (b) Reference 13, p 175.

[18] Quick, M. H.; Angeleci, R. J.; Reimer, K. J.; Shaver, A. *Inorg. Synth.* **1979**, *19*, 160.

$(Mn(CO)_5)_2$ (0.10 g, 0.21 mmol) in THF (20 mL) resulted in the rapid loss (≈5 min) of IR bands due to the starting material and their replacement by those attributable to $Mn(CO)_5Br$. This orange solution was taken to dryness in vacuo, and the resulting yellow powder was shown to contain $Mn(CO)_5Br$ and 1,4-$C_6H_4Br_2$ (identified by comparison with authentic samples).

The analogous reaction with excess I_2 proceeds overnight to give $Mn(CO)_5I$ and 1,4-$C_6H_4I_2$ as the only isolable products.

Reaction of 1,4-$C_6H_4(Mn(CO)_5)_2$ with 1 Equiv of I_2. To a solution of 1,4-$C_6H_4(Mn(CO)_5)_2$ (0.45 g, 0.97 mmol) in THF (50 mL) was added 1 equiv of I_2 (0.25 g, 0.98 mmol). After it had been stirred for 1 h, the resulting orange solution was taken to dryness in vacuo. The resulting red oil was found to contain a mixture of 1,4-$C_6H_4(Mn(CO)_5)_2$, 1,4-$Mn(CO)_5(C_6H_4I)$, $Mn(CO)_5I$, and 1,4-$C_6H_4I_2$ by comparison with authentic samples.

Reaction of $C_6H_4(Mn(CO)_5)_2$ with Phosphines. A suspension of 1,4-$C_6H_4(COMn(CO)_5)_2$ (0.25 g, 0.48 mmol) was refluxed for 0.5 h in THF (40 mL) to effect its decarbonylation (vide supra); then PPh_3 (0.25 g, 0.95 mmol) was added. This solution was stirred for 12 h and then taken to dryness in vacuo. The resulting solid was crystallized from CH_2Cl_2/hexanes to give 1,4-$C_6H_4(Mn(CO)_4(PPh_3))_2$ (0.30 g, 67%) as analytically pure pale yellow crystals.

The analogous reactions of 1,3-$C_6H_4(Mn(CO)_5)_2$ with dppe, dppen, and two equiv of PPh_3 (where dppe = $Ph_2PCH_2CH_2PPh_2$ and dppen = *trans*-$Ph_2PCHCHPPh_2$) proceeded in a similar fashion to give 1,3-$C_6H_4(Mn(CO)_5)(Mn(CO)_3(dppe))$, 1,3-$C_6H_4(Mn(CO)_4)_2(\mu$-dppen), and 1,3-$C_6H_4(Mn(CO)_4(PPh_3))_2$, respectively, as the isolated yellow products.

Results and Discussion

Strategies for the Synthesis of the Polymetallic Complexes. Contrary to naive expectations, the synthesis of phenylene bridges is generally much more difficult than is the synthesis of the related monometallic metal–arene bonds. Three general routes have been widely used to synthesize monometallic transition-metal aryls, i.e. eq 1–4

$$L_nMX + ArM' \rightarrow L_nMAr + M'X \quad (1)$$

$$M'[L_nM] + ArX \rightarrow L_nMAr + M'X \quad (2)$$

$$M'[L_nM] + ArCOCl \rightarrow L_nM(COAr) + M'Cl \quad (3)$$

$$L_nM(COAr) \xrightarrow{\Delta \text{ or } h\nu} L_nMAr + CO \quad (4)$$

(where L_nM is a 17-electron metal fragment; X = F, Cl, Br, I; Ar is an aryl group (i.e., C_6H_5, C_6F_5, C_6H_4Me, etc.), and M′ = Na, Li, MgCl, etc.), and each of these methods has been applied to the synthesis of selected polymetallic complexes.[1a,4–6] However, no systematic studies have been carried out to determine the best synthetic route to such species, and low yields are often observed.

Optimization of reaction conditions is particularly important for the synthesis of complexes in which two or more metal atoms are bonded to the same ligand. Consideration of statistical factors suggests that the yields of products in these reactions will decrease as the number of metal–carbon bonds formed increases, all other factors being equal. Thus, a 50% yield for the synthesis of a monometallic complex would suggest yields of 25 and 12% for the syntheses of the related bi- and trimetallic species, respectively. One must, therefore, optimize reaction conditions and carefully pick the synthetic route if useful yields of polymetallic complexes are to be obtained. In particular, the availability of the requisite organic reagents and the relative redox properties and nucleophilicities of the reactants will generally dominate this choice.

Synthesis of the Phenylene-Bridged Complexes. Given the synthetic utility[3,19] and well-developed chemistry of the Fp fragment (where Fp = $(\eta^5\text{-}C_5H_5)Fe(CO)_2$), we began our work by investigating the synthesis of its phenylene-bridged complexes. Extension of the three methods outlined above to the syntheses of polymetallic species met with varying degrees of success. In particular, the reaction of dilithiobenzene[20] with FpI showed the least promise since the iron-containing dimer, Fp_2, was the major product. No evidence for the formation of $C_6H_4(Fp)_2$ was observed, i.e. eq 5. In a similar fashion, nucleophilic attack

$$C_6H_4Li_2 + 2FpI \xrightarrow[Et_2O]{-78\ °C} Fp_2 + 2LiI \quad (5)$$

by NaFp on aryl halides, e.g. eq 6, gave only low yields of

$$2NaFp + C_6H_4I_2 \rightarrow C_6H_4Fp_2 \text{ (trace)} + Fp_2 + 2NaI \quad (6)$$

the desired bimetallic products. Thus, both of these direct metathesis reactions proceed in even lower yields than statistical considerations would predict (i.e. for monometallic Fp aryls these reactions commonly give isolated yields of 30 to 70%[21]). These unexpectedly low yields appear to be the result of the relative redox properties of the transition-metal and organic reagents. Thus, the bifunctional organics $C_6H_4I_2$ and $C_6H_4Li_2$ are stronger oxidizing and reducing reagents, respectively, than are their monofunctional analogues. Since NaFp is very readily oxidized while FpI is very readily reduced,[22] electron transfer[23] (to form the ubiquitous Fp_2), rather than the desired nucleophilic attack, is the predominant reaction pathway in eq 5 and 6.

Fortunately, we have found that the desired phenylene-bridged complexes are readily prepared via acyl intermediates in a two-step procedure.[1] Thus, reaction of the Fp^- anion with the appropriate aroyl chloride, i.e. eq 7 (where n = 2 or 3), generally results in the formation of

$$n NaFp + C_6H_{6-n}(COCl)_n \xrightarrow[THF]{-78\ °C} C_6H_{6-n}(COFp)_n + n NaCl \quad (7)$$

tan-colored acyl complexes in excellent isolated yields of 80–98%. Performing this reaction at low temperature minimizes the formation of the Fp_2 byproduct. These superior isolated yields (compared to those reported for monometallic Fp(COAr) complexes which generally range from 50 to 80%[21,24]) are probably the result of the low solubility of these high molecular-weight products. The air and water stability of the acyl complexes makes their workup very simple. Indeed, the only limitation that we have found to this procedure is that ortho-substituted

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[19] Davies, S. G. *Organotransition Metal Chemistry: Applications to Organic Synthesis*; Pergamon: New York, 1982.

[20] (a) Evleth, E. M.; Freeman, L. D.; Wagner, R. I. *J. Org. Chem.* **1962**, *27*, 2192. (b) Baldwin, R. A. *J. Org. Chem.* **1967**, *32*, 1572.

[21] (a) King, R. B.; Bisnette, M. B. *J. Organomet. Chem.* **1964**, *2*, 15. (b) Butler, I. R.; Lindsell, W. E.; Thomas, M. J. K. *J. Organomet. Chem.* **1984**, *262*, 59. (c) Gansow, O. A.; Schexnayder, D. A.; Kimura, B. Y. *J. Am. Chem. Soc.* **1972**, *94*, 3406. (d) Stewart, R. P., Jr.; Isbrandt, L. R.; Benedict, J. J.; Palmer, J. G. *J. Am. Chem. Soc.* **1976**, *98*, 3215. (e) Jacobson, S. E.; Wojcicki, A. *J. Am. Chem. Soc.* **1973**, *95*, 6962. (f) Severson, R. G.; Leung, T. W.; Wojcicki, A. *Inorg. Chem.* **1980**, *19*, 915. (g) De Luca, N.; Wojcicki, A. *J. Organomet. Chem.* **1980**, *193*, 359. (h) Dizikes, L. J.; Wojcicki, A. *J. Am. Chem. Soc.* **1977**, *99*, 5295. (i) Butler, I. R.; Lindsell, W. E.; Preston, P. N. *J. Chem. Res. Miniprint* **1981**, 2573. (j) Kuhlmann, E. J.; Alexander, J. J. *J. Organomet. Chem.* **1979**, *174*, 81. (k) Ellis, J. E. *J. Organomet. Chem.* **1976**, *111*, 331. (l) Nesmeyanov, A. N.; Kolobova, N. E.; Goncharenko, L. V.; Anisimov, K. N. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1976**, 153 (Engl. transl., 142).

[22] (a) Legzdins, P.; Wassink, B.; Einstein, F. W. B.; Jones, R. H. *Organometallics* **1988**, *7*, 477. (b) Legzdins, P.; Wassink, B. *Organometallics* **1988**, *7*, 482. (c) Dessy, R. E.; Stary, F. E.; King, R. B.; Waldrop, M. *J. Am. Chem. Soc.* **1966**, *88*, 471. (d) Dessy, R. E.; King, R. B.; Waldrop, M. *J. Am. Chem. Soc.* **1966**, *88*, 5112. (e) Denisovich, L. I.; Ioganson, A. A.; Gubin, S. P.; Kolobova, N. E.; Anisimov, K. N. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1969**, 258 (Engl. transl., 218). (f) Pickett, C. J.; Pletcher, D. *J. Chem. Soc., Dalton Trans.* **1975**, 879.

[23] Kochi, J. K. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1227.

[24] The invariance of the IR band positions is consistent with what has been previously reported for other Fp(COAr) complexes.[21]

products are generally not obtained (giving only the Fp_2 dimer), presumably because of steric crowding in the diacyl product (vide infra). All of these iron acyl complexes are diamagnetic solids having the expected analytical and spectroscopic properties (Table I). In particular, their IR spectra exhibit two terminal carbonyl stretching bands at about 2030 and 1961 cm^{-1} and an acyl stretch at about 1610 cm^{-1}.[1,24]

Acyl complexes are generally decarbonylated either photochemically or thermally.[3] At the start of this study, it appeared that for the Fp complexes the route of choice would be photochemical decarbonylation since monometallic Fp aryls have generally been prepared in moderate to excellent yields in this fashion.[21] Unfortunately, pilot studies indicated that photolysis of the bimetallic acyls resulted in the isolation of only low yields of the desired products, e.g. eq 8. The photolysis of complexes con-

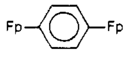
$$1,4\text{-}C_6H_4(COFp)_2 \xrightarrow{h\nu} 1,4\text{-}C_6H_4Fp_2 + C_6H_5Fp + Fp_2 \qquad (8)$$

taining metal–alkyl or metal–aryl bonds often results in the cleavage of the metal–carbon bonds. This is followed by reactions of the free-radical photodegradation products (e.g. dimerization or hydrogen atom abstraction) which produce the observed species.[25] This process causes the low yields of desired products often observed in the photochemical decarbonylations of monometallic Fp acyls (which also produce Fp_2 as the major organometallic byproduct).[21,25] As a result of the low solubilities of their phenyleneacyl precursors (compared with those of monometallic acyls), the relative time that the phenylene products are exposed to the UV light in solution is increased. This exacerbates the photodegradation problem and probably explains the very low yield of the desired product observed in reaction 8.

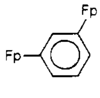
Early studies reported that Fp acyls could not be thermally decarbonylated;[21a] however, we have found[1] that this is not the case and that this reaction can be carried out under sufficiently forcing conditions, i.e. eq 9.[26] This

$$1,4\text{-}C_6H_4(COFp)_2 \xrightarrow[Bu_2O]{\Delta} 1,4\text{-}C_6H_4Fp_2 + 2CO \qquad (9)$$

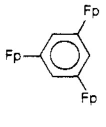
thermal decarbonylation proceeds readily for all the Fp(COAr) complexes that we have tested and is, in fact, the route of choice to phenylene-bridged complexes. The only major experimental difficulty is that the products are somewhat thermally unstable at the elevated temperatures that are required. If overheated, they decompose with the breaking of Fp–aryl bonds and thus give Fp_2 and Fp aryls of lower molecularity (e.g. C_6H_5Fp in eq 9, above). As expected on steric grounds, the 1,3,5 complexes are the most thermally sensitive and the 1,4 complexes are the least. These reactions are best carried out in *gently* refluxing butyl ether (bp 142 °C) and given the desired products in 30–70% isolated yields. The phenylene-bridged products of these reactions, i.e. are pale yellow solids that exhibit remarkable thermal and air stability and may be handled in air, even in solution, for several hours without exhibiting noticeable decomposition. They are quite soluble in most common organic solvents but are only sparingly soluble in nonpolar solvents such as hexanes. Their analytical and mass spectral data (Table I) originally suggested the proposed formulations[1] which were subsequently confirmed by IR and NMR spectroscopy (which will be discussed in detail later). In addition, the X-ray crystal structure of the $Cr(CO)_3$ adduct of the 1,3,5-trisubstituted species (i.e. $(\eta^6\text{-}1,3,5\text{-}C_6H_3Fp_3)Cr(CO)_3$) confirms this geometry.[1a] Of particular utility in determining the molecularity of these species were the mass spectra in which peaks due to the parent ions were observed (unambiguously confirming the bi- or trimetallic nature of these and the other phenylene-bridged complexes described in this paper). The methylcyclopentadienyl complexes $(1,4\text{-}C_6H_4(COFp')_2$ and $1,4\text{-}C_6H_4Fp'_2$ where $Fp' = (\eta^5\text{-}C_5H_4Me)Fe(CO)_2)$ are prepared identically to their cyclopentadienyl analogues and exhibit similar physical properties with the expected small decrease in carbonyl stretching frequencies (Table I) (vide infra).



1,4



1,3



1,3,5

The phenylene-bridged complexes of $Mn(CO)_5$ are prepared by using the same methods used for the iron-containing species. Thus, reaction of a THF solution of the manganese anion with the appropriate aroyl chloride, i.e. eq 10, results in the formation of the manganese acyl

$$n\mathrm{NaMn(CO)_5} + C_6H_{6-n}(COCl)_n \xrightarrow{THF} C_6H_{6-n}(COMn(CO)_5)_n + n\mathrm{NaCl} \qquad (10)$$

species in 40–95% isolated yields. These acyl complexes are pale yellow solids that are air and thermally stable in the solid state. They have the expected physical and spectroscopic properties[5,27] (Table I), and, in particular, they exhibit three or four terminal carbonyl stretches between 2120 and 1975 cm^{-1} and a single acyl band at about 1610 cm^{-1}.[27] Attempts to prepare *o*-phenylene complexes (e.g. $1,2\text{-}C_6H_4(COMn(CO)_5)_2$) again met with failure and gave $Mn_2(CO)_{10}$ as the only organometallic product (vide supra). In contrast to reaction 7, reaction 10 may be performed at ambient temperature with no apparent loss of yield. This is perhaps a reflection of the greater oxidative stability of the manganese anion under these conditions.[22,28]

The manganese acyl complexes are much more readily decarbonylated than are their Fp analogues. Thus, a THF suspension of these manganese acyls may be quantitatively (by IR and NMR spectroscopy) decarbonylated if it is gently refluxed until the solid has completely dissolved (about 15 min), i.e. eq 11. The resulting phenylene-

$$C_6H_{6-n}(COMn(CO)_5)_n \xrightarrow[\Delta]{THF} C_6H_{6-n}(Mn(CO)_5)_n \qquad (11)$$

bridged complexes (the 1,4, 1,3, and 1,3,5 complexes were produced, Table I) are white to pale yellow powders that are considerably more soluble than their acyl precursors but less so than are their iron analogues. They are relatively air-stable in the solid state, and they may be handled, even as solutions, in air for short periods. However, they are much more thermally sensitive than are their iron analogues and decompose on extended heating, even in THF. This explains the thermal decomposition that we have observed when the 1,3 and 1,4 complexes are pre-

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(25) Geoffroy, G. L.; Wrighton, M. S. *Organometallic Photochemistry*; Academic: New York, 1979; Chapter 8.

(26) During our initial studies, Me_3NO was used to promote the decarbonylations (see: Shen, J. K.; Shi, Y. L.; Gao, Y. C.; Shi, Q. Z.; Basolo, F. *J. Am. Chem. Soc.* **1988**, *110*, 2414), but this was latter found to be unnecessary.

(27) (a) Beck, W.; Hieber, W.; Tengler, H. *Chem. Ber.* **1961**, *94*, 862. (b) Hieber, W.; Lindner, E. *Chem. Ber.* **1962**, *95*, 273. (c) Bruce, M. I.; Sharrocks, D. N.; Stone, F. G. A. *J. Chem. Soc. A* **1970**, 680.

(28) Connelly, N. G.; Geiger, W. E. *Adv. Organomet. Chem.* **1984**, *23*, 1 and references cited therein.

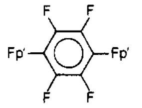
pared by vacuum pyrolysis at elevated temperatures.[5] These syntheses are therefore best performed in refluxing THF. The analytical and spectroscopic properties (Tables I and II) of the phenylene-bridged complexes are in accord with the limited data previously reported for the $C_6H_4(Mn(CO)_5)_2$ complexes[5] and confirm the proposed formulations[27,29] (vide infra).

Synthesis of the Perfluorophenylene-Bridged Complexes. On the basis of substituent electronegativities, one would predict that the dilithium reagent of perfluorobenzene, $C_6F_4Li_2$, would be a weaker reducing agent than is $C_6H_4Li_2$. In accord with this prediction, it has been shown that the reaction between 1,4-$C_6F_4Li_2$ and FpI proceeds not by electron transfer (to give Fp_2 as occurs for 1,4-$C_6H_4Li_2$, vide supra) but rather gives the expected metathesis product,[6a] i.e. eq 12 and 13. The product of

$$1,4\text{-}C_6F_4Br_2 + 2BuLi \xrightarrow[-78\,^{\circ}C]{THF} 1,4\text{-}C_6F_4Li_2 \quad (12)$$

$$1,4\text{-}C_6F_4Li_2 + 2FpI \xrightarrow[-78\,^{\circ}C]{THF} 1,4\text{-}C_6F_4Fp_2 \quad (13)$$

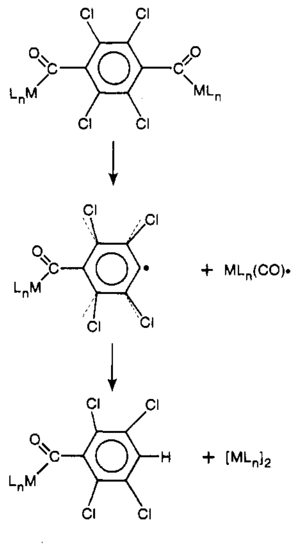
this reaction, 1,4-$C_6F_4Fp_2$,[30] is obtained in 74% yield as a tan powder; however, it is only sparingly soluble in common organic solvents. A more tractable product is its methylcyclopentadienyl analogue, 1,4-$C_6F_4Fp'_2$, which is prepared in an identical fashion by using Fp'I in eq 13. This organge crystalline solid, i.e.



is moderately soluble in most polar organic solvents such as CH_2Cl_2 and is sufficiently air stable to be handled in air, even as a solution, for short periods of time without noticeable decomposition occurring. The physical and spectroscopic properties of these compounds (Tables I and II) are analogous to those of the related monometallic fluoroarene complexes[21,27] and support the bimetallic formulations of these species. These data also indicate that, as expected, these complexes have more electron-poor metal centers than do the analogous phenylene complexes (e.g. the ν_{CO} value for 1,4-$C_6F_4Fp_2$ is 15–20 cm^{-1} higher than it is for 1,4-$C_6H_4Fp_2$).

The reaction of $Mn(CO)_5Br$ with 1,4-$C_6F_4Li_2$ is somewhat more complex than is that of its iron analogue. From it can be isolated a mixture of mono- and bimetallic products, i.e. eq 14. The desired perfluorophenylene-bridged complex was obtained in low yield (22%) as a yellow solid. Its physical properties (Table I) are analogous to those described for its perhydro analogue. Interestingly, the second major product isolated from this reaction mixture was 1,4-$C_6F_4H(Mn(CO)_5)$. This complex was initially identified by its characterstic mass spectrum in which one observes the successive loss of CO from the parent ion at m/z 344. Its structure was confirmed by its ^1H and ^{19}F NMR spectra which exhibit signals attributable to the expected AA'MM'X spin system. Although the exact origin of this product remains unclear, we believe that it was formed by the decomposition of the bimetallic complex and that this was caused by the extreme steric crowding around the $C_6F_4X_2$ center.[31,32]

$$1,4\text{-}C_6F_4Li_2 + 2Mn(CO)_5Br \xrightarrow[-78\,^{\circ}C]{THF} 1,4\text{-}C_6F_4(Mn(CO)_5)_2 + 1,4\text{-}C_6F_4HMn(CO)_5 \quad (14)$$



$ML_n = Mn(CO)_5, (\eta^5\text{-}C_5H_5)Fe(CO)_2$, etc.

Figure 1. Homolytic cleavage of the carbon–carbon bonds of the sterically crowded $C_6Cl_4(ML_n)_2$ complexes would be expected to relieve steric strain and produce the observed products.

Attempts were made to extend the series of $-C_6X_4-$-bridged complexes to their chloro analogues, i.e. eq 15 and 16. Unfortunately, all attempts to synthesize the required bimetallic acyls have met with failure, producing the ubiquitous metal-containing dimers and monometallic aryl complexes instead, i.e. eq 17 and 18. Thus, the iron complex is isolated in its acyl form whereas the manganese derivative is isolated as the aryl (probably reflecting the more facile decarbonylation of the latter[21,27]). These monometallic products were characterized by elemental analysis and by mass and IR spectra (Table I) but were not investigated further. Again, it seems reasonable to assume that the steric requirements of a $C_6X_4(ML_n)_2$ bimetallic complex are greater than can be accommodated around the benzene ring[31,32] (vide supra), and a bond cleavage reaction occurs to relieve the steric strain about the benzene ring (Figure 1).

$$2NaML_n + 1,4\text{-}C_6Cl_4(COCl)_2 \cancel{\xrightarrow[-78\,^{\circ}C]{THF}} 1,4\text{-}C_6Cl_4(COML_n)_2 \quad (15)$$

$$1,4\text{-}C_6Cl_4(COML_n)_2 \xrightarrow{\Delta \text{ or } h\nu} 1,4\text{-}C_6Cl_4(ML_n)_2 \quad (16)$$

$$2NaFp + 1,4\text{-}C_6Cl_4(COCl)_2 \xrightarrow[-78\,^{\circ}C]{THF} 1,4\text{-}C_6Cl_4H(COFp) + Fp_2 \quad (17)$$

$$2NaMn(CO)_5 + 1,4\text{-}C_6Cl_4(COCl)_2 \xrightarrow[-78\,^{\circ}C]{THF} 1,4\text{-}C_6Cl_4H(Mn(CO)_5) + Mn_2(CO)_{10} \quad (18)$$

Spectroscopic Characterization of the Complexes and the Nature of the Phenylene Bridge. The η^1 metal–arene bond in monometallic Fp–aryl complexes has both σ and π components. This interaction is primarily

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[29] The related complex, 1,3,5-$C_6H_3(CORe(CO)_5)_3$, was recently reported, see: Schweiger, M. J.; Nagel, U.; Beck, W. J. *J. Organomet. Chem.* **1988**, *355*, 289.

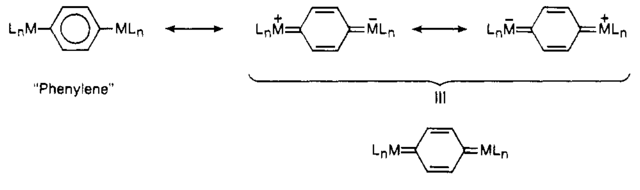
[30] Surprisingly, earlier reports of the preparation of 1,4-$C_6F_4Fp_2$ provided only analytical and mass spectroscopic data for this compound.[6a-d]

[31] For a useful discussion to the structures of perfluorophenyl complexes, see: Jones, P. G. *J. Organomet. Chem.* **1988**, *345*, 405 and references cited therein.

[32] Hexasubstituted arenes are often very sterically crowded which results in distortions of the arene structure, see for example: Ballester, M.; Olivella, S. in *Polychloroaromatic Compounds*; Suschitzky, H., Ed.; Plenum: New York, 1974; p 21 and references cited therein.

σ-bonding in character but contains a significant π component.[21,33] In both of these interactions, the metal containing fragment acts as a donor of electron density toward the arene ring.[33] Thus, the relative electronegativities of these two fragments[33a] result in the σ bond being polarized toward the arene ring to give an electron rich carbon atom that is prone to electrophilic attack.[21e–h] In addition, the highest occupied molecular orbitals, HOMOs, on the metal center are of the correct energy and symmetry to interact with the π*-antibonding orbitals on the arene.[34] Thus, the metal center acts as both a σ and a π donor to the aryl group.[33] This description is confirmed by the various chemical[21] and spectroscopic[21,33] properties of such linkages with the ^{19}F and ^{13}C NMR spectra of such species being particularly informative in this regard[21,33] (vide infra). In addition, X-ray crystallographic characterization of a variety of related compounds containing iron-C(sp^2) linkages has demonstrated the expected shortening of the metal–carbon bond that such a π-donation interaction would produce.[35–38] Indeed, this evidence has been interpreted in terms of partial metal–carbon double-bond character[21,33–38] analogous to that described for organic π-donor and -acceptor substituents. Clearly, the extent of these σ- and π-donor interactions is dependent on both the electronic properties and the relative orientations of the two fragments. Maximum electron transfer is expected, for example, with more electron-releasing substituents on the metal and more electron-withdrawing groups on the arene.[33] The π-back-bonding interaction will be maximized when the metal-centered HOMOs are oriented such that maximum overlap with the arene π* orbitals can occur.[34]

To the best of our knowledge, no molecular orbital calculations have been reported for phenylene-bridged complexes. However, extension of the above arguments to polymetallic complexes should provide a reasonable *qualitative* description of the metal–ligand interactions in such species. In particular, the metal fragments are expected to act as both σ and π donors toward the arene ring and thus it should be particularly electron-rich. As well, π donation from the metals' HOMOs should give the metal–arene bonds in such species partial double-bond character (vide supra) independent of the arene substitution geometry. In the case of the 1,4-phenylene complexes, we would like to suggest that a further synergic bonding interaction may take place. In localized valence bond terms, this interaction could be described as a small contribution from the dimetalloquinone resonance form, i.e.



Any such contribution should be readily apparent due to the expected changes in the metal–arene–metal structure (i.e. metal–carbon and carbon–carbon bond orders) and its spectroscopic properties. Such changes should be most easily observed by comparison of the 1,3- and the 1,4-phenylene complexes since any such simple resonance interaction should be prohibited in the former. The quinoidal character of the 1,4 species should also be enhanced by the factors which produce an increase in dπ–pπ bonding interaction (vide supra). Indeed, evidence for just such a metal–arene–metal synergic interaction is provided by the spectroscopic properties of our Fp complexes (vide infra).

The IR and NMR spectral data for these novel phenylene-bridged complexes are listed in Tables I and II and may be compared with those of their well-characterized monometallic analogues.[21,33] The ^{1}H and ^{13}C NMR signals attributable to the cyclopentadienyl rings of our complexes are observed as singlets in the regions previously reported for those in related monometallic complexes. Similarly, the IR and ^{13}C NMR data for the carbonyl ligands in these complexes are as expected,[21,33] indicating 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 IR and NMR frequencies of the Cp and CO groups are independent of the substitution geometry and the number of Fp groups around the benzene ring. This is not totally surprising given the low sensitivity of these parameters to changes in the Fp substituents.[21,33] However, it is consistent with the suggestion that the arene's ability to accept electron-density in these complexes is not being saturated, even by three strongly electron-donating Fp groups (vide infra).

The ^{1}H 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 using the peak multiplicities, chemical shifts, and homo- and heteronuclear coupling constants of the signals. The ^{13}C assignments were confirmed by consideration of the characteristic substituent effects of the pendant metal fragments (vide infra). The ^{1}H and ^{19}F NMR spectra of the phenylene groups occur in the regions previously reported for their monometallic analogues.[21,27,33] They dis-

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(33) (a) Stewart, R. P.; Treichel, P. M. *J. Am. Chem. Soc.* **1970**, *92*, 2710. (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. (d) Casey, C. P.; Konings, M. S.; Gohdes, M. A.; Meszaros, M. W. *Organometallics* **1988**, *7*, 2103. (e) 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). (f) Batsanov, A. S.; Struchkov, Y. T. *J. Organomet. Chem.* **1984**, *266*, 295. (g) Churchill, M. R.; Wormald, J. *Inorg. Chem.* **1969**, *8*, 1936. (h) Wilford, J. B.; Stone, F. G. A. *Inorg. Chem.* **1965**, *4*, 389. (i) Axe, F. U.; Marynick, D. S. *J. Am. Chem. Soc.* **1988**, *110*, 3728. (j) 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). (k) Denisovich, L. I.; Polovyanyuk, I. V.; Lokshin, B. V.; Gubin, S. P. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1971**, 1964 (Engl. transl., 1851). (l) Nesmeyanov, A. N.; Makarova, L. G.; Polovyanyuk, I. V. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1972**, 607 (Engl. transl., 567).

(34) 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.

(35) The X-ray crystal structures of simple Fp aryls have not been reported;[21b] however, numerous studies of related Fe–C(sp^2) interactions have been completed.[36–39]

(36) For structures of Cp$_3$Fe(CO)(PR$_3$)–aryls see: (a) ref 33e. (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).

(37) For structures of Fp–R (where R is is attached to iron via an sp^2 hybridized carbon atom), see: (a) ref 33d and g. (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.

(38) For structures of FpAr (where the aryl is π bound to a 12-electron metal center), see: (a) ref 1 and 33f. (b) Heppert, J. A.; Morgenstern, M. A.; Scherubel, D. M.; Takusagawa, F.; Shaker, M. R. *Organometallics* **1988**, *7*, 1715. (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.

Table III. ^{13}C Substituent Effects for C_6H_5X[a]

X =	substituent consts[b]					
	Δ_{ipso}	Δ_{ortho}	Δ_{meta}	Δ_{para}	Δ_{π}[b]	ref
NH_2	18.0	−13.3	0.9	−9.8	−10.7	*c*
OMe	31.4	−14.4	1.0	−7.7	−8.7	*c*
F	34.8	−12.9	1.4	−4.5	−5.9	*c*
Me	8.9	0.7	−0.1	−2.9	−2.8	*c*
CN	−15.4	3.6	0.6	3.9	3.3	*c*
CF_3	2.6	−3.3	−0.3	3.2	3.5	*c*
NO_2	20.0	−4.8	0.9	5.8	4.9	*c*
Fp	17.5	17.0	−0.5	−5.2	−5.7	*d*
Fp	16.9	16.5	−1.0	−5.7	−4.7	*e*
Fp	17.0	17.0	−1.0	−6.0	−5.0	*f*
$Mn(CO)_5$	17.5	16.5	0.7	−4.3	−5.0	*f, g*

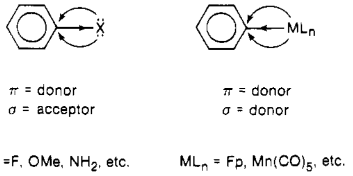
[a] Where the values for the substituent constants, Δ, are quoted in ppm relative to benzene at 128.5 ppm and positive shifts indicate deshielding. [b] The Δ values are the substituent chemical shifts, $\Delta = \delta_{arene\ carbon} - 128.5$ ppm and $\Delta_{\pi} = \Delta_{para} - \Delta_{meta}$. [c] Reference 39a in text (CCl_4). [d] Reference 21b in text, derived from the data for FpPh ($CDCl_3$). [e] Reference 21d in text, derived from the data for FpPh ($CHCl_3$). [f] This work, derived so as to give the most consistent set of values from the data for the phenylene complexes ($(CD_3)_2SO$). [g] For $C_6H_5Re(CO)_5$ the reported data (ref 39i in text, $CDCl_3$) indicate a value of −4.4 ppm for Δ_{π}.

play 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.[21,27,33,39]

Because they are directly related to the arene–carbon electron density and they have been used to elucidate the nature of arene–substituent bonding interactions, the ^{13}C NMR chemical shifts of the arene carbons are particularly useful.[39] They are best understood in terms of the substituent effects of the Fp and $Mn(CO)_5$ 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.[39] They have, therefore, been widely used to assign the ^{13}C NMR spectra of substituted arenes. In Table III are presented some representative values for the substituent constants of a variety of common functional groups in C_6H_5X species (where X = NH_2, OMe, F, Me, CN, CF_3, and NO_2)[39a] along with some values that have been used previously for Fp.[21b,d,39c,f]

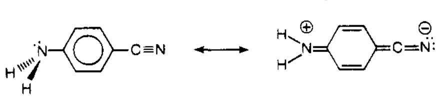
Substituent constants are a measure of the effect that a substituent will have on the chemical shifts of the four types of arene carbon. The interpretation of the ipso and ortho values is, in general, quite complicated while those for the meta position show little systematic variation.[39a,b] The para 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.[39]

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 III) can be obtained that both predicts the observed chemical shifts to within an average error of less than 0.5 ppm (with the exception of the ipso carbon of 1,4-$C_6H_4Fp_2$ (vide infra)) and agrees with the values previously reported for Fp. The fact that our substituent effects are generally linearly additive for these complexes suggests that (as we previously proposed on the basis 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.[39] Inspection of the derived Δ_{π} values for both Fp and $Mn(CO)_5$ indicates that it is −5 ppm for both and thus that they are both 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, F. Because of their electronegativities, non-transition-metal π-donor substituents almost always withdraw electron density inductively from the ring through the aryl–X σ bond. Transition-metal substituents, on the other hand, are less electronegative than is carbon and are therefore σ donors.[33a] Substituents such as Fp and $Mn(CO)_5$ (and probably most other related 17-electron fragments[33a]) are therefore rather unique in being both good σ donors and strong π donors,[39f] i.e.



This explains why the phenylene-bridged complexes have such unusually electron-rich arene rings.[1]

The most unexpected finding of this study was that the observed chemical shift of the ipso carbons of 1,4-$C_6H_4Fp_2$ are shielded by about 5 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 −6 to about −11 ppm (i.e. π donation increases). This is very surprising since when organic π-donor substituents (such as NMe_2 or F) are arranged 1,4, the apparent para-substituent effects decrease due to electronic saturation of the arene's π system.[39–41] Increases are only observed when π donors are arranged opposite to π acceptors. This produces a cross-ring substituent interaction, resulting in a synergic conjugation of the substituents' π systems and thus a quinoidal contribution to the bonding interaction, e.g.



Since our 1,4-phenylene complexes appear to be exhibiting the opposite effect to what would be expected if arene saturation was occurring, it seems probable that a conjugative interaction such as occurs for 1,4-donor–acceptor substituents accounts for the apparent increase in Δ_{π} (vide supra). It therefore seems reasonable to propose that this enhancement is due to a synergic increase in π donation that would be described, in valence bond terms, as an

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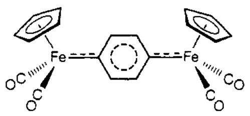
(39) (a) Levy, G. C.; Lichter, R. L.; Nelson, G. L. *Carbon-13 Nuclear Magnetic Resonance Spectroscopy*; John Wiley and Sons: New York, 1980. (b) Stothers, J. B. *Carbon-13 NMR Spectroscopy*; Academic: New York, 1972. (c) Mann, B. E. *Adv. Organomet. Chem.* **1974**, *12*, 135. (d) Ernst, L.; Wray, V.; 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. Engl.* **1970**, *9*, 87. (h) Nelson, G. L.; Williams, E. A. *Prog. Phys. Org. Chem.* **1976**, *12*, 229. (i) Webb, M. J.; Graham, W. A. G. *J. Organomet. Chem.* **1975**, *93*, 119.

(40) A similar saturation effect is observed for 1,4-disubtituted organic π-acid groups such as NO_2 and CN.[41]

(41) (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.

increase in the dimetalloquinone resonance hybrid contribution to the bonding in the phenylene complexes, i.e.



Unfortunately, with the data at hand, 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.[41] Nevertheless, preliminary electrochemical studies of some of these complexes supports our proposal of quinoidal character to the metal-arene-metal interaction in the 1,4 species.[42] In addition, we have recently observed evidence for similar quinoidal interactions in a variety of other 1,4-substituted systems.[42,43] However, confirmation of this must await crystallographic characterization of a number of such complexes, spectroscopic analysis of related species and a detailed molecular orbital analysis of the bonding in these unusual phenylene-bridged complexes.

Reactivity of the Complexes. The complexes synthesized in this study have electron-rich phenylene bridges and would be expected to exhibit chemical reactivity broadly analogous to that displayed by their monometallic analogues.[3,21,27] Thus one would expect to see reactivity of the arene ring, of the metal–arene bonds, and on the metal centers. Our investigations confirm that this is the case.

One of the most characteristic reactions of arenes in organometallic chemistry is their ability to act as π-donor ligands to 12-electron metal containing fragments such as "$Cr(CO)_3$". Thus, the reaction of these compounds with $Cr(CO)_6$ produces the desired σ,π complexes, e.g. eq 19.[1,43a]

$$1,3,5\text{-}C_6H_3Fp_3 + Cr(CO)_6 \xrightarrow{\Delta} (\eta^6\text{-}1,3,5\text{-}C_6H_3Fp_3)Cr(CO)_3 \quad (19)$$

Indeed, the resultant polymetallic complexes are among the most electron-rich (arene)chromium tricarbonyl complexes known[1] (vide supra) and display very interesting derivative chemistry in their own right.[43]

The metal–arene σ bonds in these complexes also exhibit behavior characteristic of their more well-known monometallic analogues. For example, the metal–arene bonds in these species are readily cleaved by a variety of electrophilic reagents such as Br_2 and I_2, e.g. eq 20. In fact,

$$1,4\text{-}C_6H_4(Mn(CO)_5)_2 + \text{excess } Br_2 \rightarrow 2Mn(CO)_5Br + 1,4\text{-}C_6H_4Br_2 \quad (20)$$

if these reactions are carried out stoichiometrically, one obtains a mixture of products and unchanged starting materials, i.e. eq 21, which indicates that the rate of cleavage of the first and second manganese groups from the arene are similar.

$$1,4\text{-}C_6H_4(Mn(CO)_5)_2 + I_2 \rightarrow 1,4\text{-}C_6H_4(Mn(CO)_5)_2 + 1,4\text{-}C_6H_4I(Mn(CO)_5) + 1,4\text{-}C_6H_4I_2 + Mn(CO)_5I \quad (21)$$

The metal centers in these phenylene-bridged complexes also retain much of their characteristic reactivity. For example, they undergo carbonyl substitution reactions under similar conditions to their monometallic analogues.[21,27] Thus, the manganese complexes react readily with mono- and bidentate phosphines to give the expected substitution products, i.e. eq 22. The new products of

$$1,3\text{-}C_6H_4(Mn(CO)_5)_2 + 2PPh_3 \xrightarrow[25\ °C]{12\ h} 1,3\text{-}C_6H_4(Mn(CO)_4(PPh_3))_2 \quad (22)$$

these reactions exhibit the expected analytical and spectroscopic properties (Table I), but their complete characterization has been hampered somewhat by their relatively low solubilities. Interestingly, it appears that the bidentate phosphines may either chelate or bridge the two metal centers depending on the steric requirements of the phosphine to produce both asymmetrically substituted and cyclic products (e.g. $1,3\text{-}C_6H_4(Mn(CO)_5)(Mn(CO)_3(Ph_2PCH_2CH_2PPh_2))$ and $1,3\text{-}C_6H_4(Mn(CO)_4)_2(\mu\text{-}trans\text{-}Ph_2PCHCHPPh_2)$, respectively).

Conclusions

These studies have shown that phenylene-bridged complexes can be synthesized in a systematic fashion if the relative redox properties of the reagents used are taken into consideration. Specifically, the synthesis of complexes with electron-rich phenylene bridges generally requires a two-step synthetic procedure involving the acyl intermediates. We have shown that these can be decarbonylated conveniently in refluxing butyl ether or THF for the Fe and Mn complexes, respectively. Complexes containing more electron-deficient phenylene bridges may be more directly prepared by metathesis. The only general limitation to these reactions that we have found is that sterically crowded phenylene bridges are difficult to prepare, tending to give monometallic products instead. Thus these general synthetic methods should be readily applicable to the synthesis of a wide variety of structurally divergent arene-bridged complexes, and such studies are currently underway.

Our spectroscopic studies of the phenylene-bridged complexes have indicated that the benzene rings in these species are very electron-rich because the metal fragments are both σ and π donors to the arene. In addition, the data suggest the existence of a novel dimetalloquinone contribution to the bonding in the 1,4-phenylene-bridged complexes. Although we acknowledge that this proposal is somewhat speculative, we believe that it merits further study. To this end, we are now in the process of investigating the existence and nature of any such bonding interaction. We are also using cyclic voltammetry to elucidate the electrochemical properties of the phenylene linkages. This will help both to clarify the existence of any such synergic interaction and to elucidate the factors controlling the degree of electronic linkage between adjacent metal centers in all of these phenylene-bridged complexes. It is hoped that the resultant insight will allow the synthesis of organometallic polymers having predictable electronic properties and potential as one-dimensional conductors and semiconductors. We are also exploring the derivative chemistry of these novel electron-rich phenylene linkages and, in particular, their applications to organic synthesis and the synthesis of organometallic liquid crystals.

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

Registry No. dppe, 1663-45-2; dppen, 983-81-3; Fp_2, 38117-54-3; $1,3\text{-}C_6H_4(COFp)_2$, 119923-99-8; $1,3,5\text{-}C_6H_3(COFp)_3$,

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(42) In particular, our preliminary data indicate that the 1,4 complexes exhibit successive, reversible one-electron oxidations (giving rise to the radical cations and the dimetalloquinone dications) in contrast to the related monometallic Fp–arenes which generally exhibit a single irreversible oxidation. Richter-Addo, G. B.; Hunter, A. D., unpublished observations.

(43) (a) Hunter, A. D.; McLernon, J. L. *Organometallics*, following paper in this issue. (b) Richter-Addo, G. B.; Hunter, A. D. *Inorg. Chem.*, submitted for publication. (c) Richter-Addo, G. B.; Hunter, A. D.; Wichrowska, N. *Can. J. Chem.*, submitted for publication.

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-$C_6H_4(Mn(CO)_4)_2(\mu\text{-dppen})$, 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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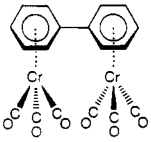
The synthesis of the complexes $(\eta^6\text{-}1,3\text{-}C_6H_4Fp_2)Cr(CO)_3$ (Fp = $(\eta^5\text{-}C_5H_5)Fe(CO)_2$), $(\eta^6\text{-}1,4\text{-}C_6H_4Fp_2)M(CO)_3$ (M = Cr, Mo, or W), $(\eta^6\text{-}1,3,5\text{-}C_6H_3Fp_3)M(CO)_3$ (M = Cr or Mo), $(\eta^6\text{-}1,4\text{-}C_6H_4Fp'_2)Cr(CO)_3$ (Fp′ = $(\eta^5\text{-}C_5H_4Me)Fe(CO)_2$), and $(\eta^6\text{-}1,3,5\text{-}C_6H_3Fp'_3)Cr(CO)_3$ 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 $(\eta^6\text{-}1,4\text{-}C_6H_4Fp_2)Cr(CO)_3$.

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



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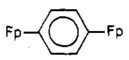
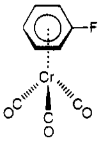


2a



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 $(\eta^6\text{-aryl–}ML_n)M(CO)_3$, 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 $(\eta^5\text{-}C_5H_4(ML_n))M(CO)_3$ 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.

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