Commities for financial support (Contract No. ST 2J-0090-1-F).

Registry No. 1, 119326-02-2; **2**, 119326-03-3; **3**(CF_3SO_3), 119326-05-5; **4**(BF_4), 119326-07-7; **5**(CF_3SO_3), 119326-09-9; **6**(BF_4)$_2$, 119326-11-3; **6**(BF_4)$_2$·((CH_3)$_2$CO)$_4$, 119326-12-4; **7**, 119297-92-6; **8**, 119297-93-7; PhC≡CPh, 501-65-5.

Supplementary Material Available: Tables of bond lengths, bond angles, atomic coordinates, and thermal parameters for **6** (18 pages); a listing of observed and calculated structure factors for **6** (28 pages). Ordering information is given in any current masthead page.

σ,π Complexes of Benzene[1]

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Summary: A series of electron-rich polymetallic complexes of benzene, namely, $C_6H_{6-n}Fp_n$ and (η^6-$C_6H_{6-n}Fp_n$)Cr(CO)$_3$ (Fp = (η^5-C_5H_5)Fe(CO)$_2$ and n = 2 or 3), have been prepared. The X-ray crystal structure of (η^6-1,3,5-$C_6H_3Fp_3$)Cr(CO)$_3$·CH_2Cl_2 confirms that the arene ring is σ-bound to iron and π-bound to chromium.

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] Although most of these ligands contain an aromatic core (e.g. pyrazine, diaminobenzene, dicyanobenzene, diethylnylbenzene, etc.), remarkably few contain direct metal to arene–carbon σ bonds.[3] I now wish to report the synthesis of a number of such polymetallic complexes.

During the course of our studies, we have found that for many organometallic fragments such as (η^5-C_5H_5)Fe(CO)$_2$, Fp, direct metathesis reactions, i.e. eq 1 and 2, fail to

$$2\mathrm{NaFp} + 1{,}4\text{-}\mathrm{C_6H_4Br_2} \xrightarrow[-78\ ^\circ\mathrm{C}]{\mathrm{THF}} 1{,}4\text{-}\mathrm{C_6H_4Fp_2} + 2\mathrm{NaBr} \quad (1)$$

$$2\mathrm{FpI} + 1{,}4\text{-}\mathrm{C_6H_4Li_2} \xrightarrow[-78\ ^\circ\mathrm{C}]{\mathrm{Et_2O}} 1{,}4\text{-}\mathrm{C_6H_4Fp_2} + 2\mathrm{NaI} \quad (2)$$

produce the desired phenylene-bridged complexes in synthetically useful yields. Fortunately, they are readily preparable via acyl intermediates, i.e. eq 3 and 4. Thus,

$$2\mathrm{NaFp} + 1{,}4\text{-}\mathrm{C_6H_4(COCl)_2} \xrightarrow[-78\ ^\circ\mathrm{C}]{\mathrm{THF}} 1{,}4\text{-}\mathrm{C_6H_4(COFp)_2} + 2\mathrm{NaCl} \quad (3)$$

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

addition of terephthaloyl chloride (1.10 g, 5.50 mmol) to a solution of NaFp (11.30 mmol)[4] in THF (60 mL) at −78 °C produces a tan precipitate. This solid may be collected by filtration in air, washed with Et_2O (50 mL) and H_2O (100 mL), and dried in vacuo to give 1,4-C_6H_4(COFp)$_2$ (**1a**)[5] in 94% yield. Gentle reflux of a suspension of this diacyl complex (0.51 mmol) in Bu_2O (60 mL) for 5.5 h, removal of solvent in vacuo, and recrystallization of the resultant product from CH_2Cl_2/hexanes results in the isolation of the desired complex 1,4-$C_6H_4Fp_2$ (**2a**)[6] in 68% yield. The related complexes 1,3-$C_6H_4Fp_2$ (**2b**) and 1,3,5-$C_6H_3Fp_3$ (**2c**) may be prepared in a similar fashion from 1,3-C_6H_4(COCl)$_2$ and 1,3,5-C_6H_3(COCl)$_3$, respectively.[7] These new phenylene-bridged complexes are tan crystalline solids exhibiting remarkable thermal and air stability. Their spectroscopic characteristics[6,7] are analogous to those reported for related iron aryls[8] and indicate that they retain the substitution geometry of the parent aroyl chlorides.

Although these phenylene complexes are very sterically crowded, they retain the ability of free arenes to form π complexes with Cr(CO)$_3$,[9] i.e. eq 5. Thus, when a sus-

$$\mathrm{C_6H_4Fp_2} + \text{excess } \mathrm{Cr(CO)_6} \xrightarrow[\Delta]{\mathrm{Bu_2O}} (\eta^6\text{-}\mathrm{C_6H_4Fp_2})\mathrm{Cr(CO)_3} + \mathrm{CO}\uparrow \quad (5)$$

pension of 1,4-C_6H_4(COFp)$_2$ (0.50 g, 1.02 mol)[10] is refluxed with excess Cr(CO)$_6$ (1.00 g, 4.54 mmol) in Bu_2O (50 mL) for 14 h, a yellow microcrystalline precipitate forms upon cooling to room temperature. This may be fractionally recrystallized from CH_2Cl_2/hexanes to give the new po-

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(1) (a) Organometallic Complexes with Electronic Bridges. 1. (b) Hunter, A. D. Presented in part at the Third Chemical Congress of North America, Toronto, Canada, June 1988; paper 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*, 98. (l) Takahashi, S.; Murata, 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) (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.; Ioganson, A. A. *Dokl. Akad. Nauk SSSR* **1967**, *175*, 358 (English translation p 627). (c) Cohen, S. C. *J. Chem. Soc., Dalton Trans.* **1973**, 553. (d) Bruce, M. I. *J. Organomet. Chem.* **1970**, *21*, 415.

(4) King, R. B. *Organometallic Syntheses*; Academic Press: New York, 1965; Vol. 1, p 151.

(5) **1a**: IR (CH_2Cl_2) ν_{CO} 2030 (m), 1962 (m), 1606 (w, br) cm^{-1}; fast atom bombardment mass spectrum, m/z 487 (P^+ + H). Anal. Calcd for $C_{22}H_{14}O_6Fe_2$: C, 54.37; H, 2.90; O, 19.75. Found: C, 54.51; H, 2.79; O, 20.03.

(6) **2a**: IR (CH_2Cl_2) ν_{CO} 2014 (s), 1959 (s) cm^{-1}; high-resolution mass spectrum, m/z calcd 429.9591, found 429.9603; ^{1}H NMR ((CD_3)$_2$SO) δ 6.95 (s, 4 H, C_6H_4), 5.07 (s, 5 H, C_5H_5) ppm. Anal. Calcd for $C_{20}H_{14}O_4Fe_2$: C, 55.86; H, 3.28. Found: C, 56.30; H, 3.58.

(7) Yields: **1b**, 88%; **1c**, 80%; **2b**, 51%; **2c**, 30%; **3b**, 35%; **3c**, 15%. Analytical and Spectroscopic data for these products are presented in the supplementary material.

(8) See, for example: (a) Butler, I. R.; Lindsell, W. E.; Thomas, M. J. K. *J. Organomet. Chem.* **1984**, *262*, 59. (b) Butler, I. R.; Lindsell, W. E.; Preston, P. N. *J. Chem. Res., Miniprint* **1981**, 2573. (c) Gansow, O. A.; Schexnayder, D. A.; Kimura, B. Y. *J. Am. Chem Soc.* **1972**, *94*, 3406. (d) Stewart, R. P.; Treichel, P. M. *J. Am. Chem. Soc.* **1970**, *92*, 2710. (e) Nesmeyanov, A. N.; Leshcheva, I. F.; Polovyanyuk, I. V.; Ustynyuk, Y. A.; Makarova, L. G. *J. Organomet. Chem.* **1972**, *37*, 159. (f) Nesmeyanov, A. N.; Makarova, L. G.; Polovyanyuk, I. V. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1972**, 609 (English translation p 567). (g) Denisovich, L. I.; Polovyanyuk, I. F.; Lokshin, B. V.; Gubin, S. P. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1971**, 1964 (English translation p 1851). (h) Bolton, E. S.; Knox, G. R.; Robertson, C. G. *J. Chem. Soc., Chem. Commun.* **1969**, 664. (i) Nesmeyanov, A. N.; Chapovskii, Yu. A.; Denisovich, L. I.; Lokshin, B. V.; Polovyanyuk, I. V. *Dokl. Akad. Nauk SSSR* **1967**, *174*, 1342 (English translation p 576). (j) King, R. B.; Bisnette, M. B. *J. Organomet. Chem.* **1964**, *2*, 15.

(9) A wide variety of (arene)Cr(CO)$_3$ compounds have been prepared and characterized, see for example: (a) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987. (b) Sneedon, R. P. A. *Organochromium Compounds*; Academic Press: New York, 1975.

(10) These Cr(CO)$_3$ adducts are best prepared from the phenylene complexes (i.e. 1,4-$C_6H_4Fp_2$) generated in situ from the acyl intermediates (i.e. 1,4-C_6H_4(COFp)$_2$).

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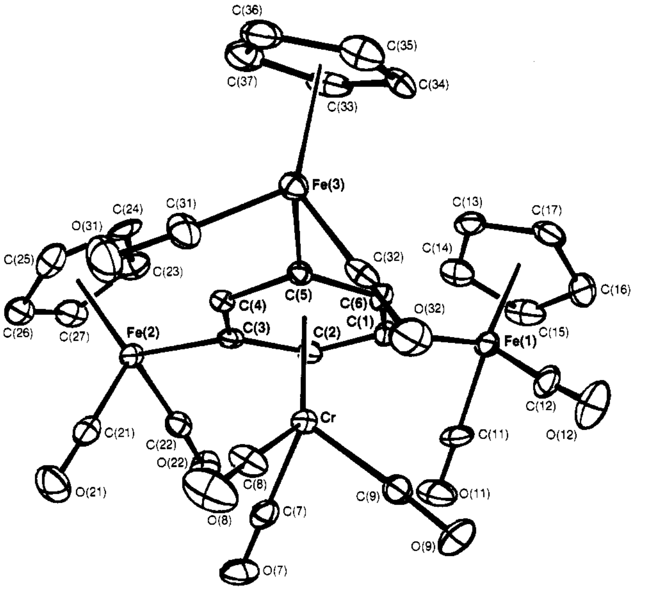

Figure 1. ORTEP plot of the molecular structure of **3c** (η^6-1,3,5-$C_6H_3Fp_3$)$Cr(CO)_3 \cdot CH_2Cl_2$. Selected bond lengths (Å) and angles (deg): Fe(1)–C(1) = 1.993 (8), Fe(2)–C(3) = 2.033 (8), Fe(3)–C(5) = 2.005 (8), Cr–C(1) = 2.282 (8), Cr–C(2) = 2.252 (8), Cr–C(3) = 2.261 (8), Cr–C(4) = 2.237 (8), Cr–C(5) = 2.300 (8), Cr–C(6) = 2.227 (8), Fe–C(carbonyl) = 1.71–1.77 (1.74 av), C–O(Fe) = 1.14–1.17 (1.16 av), Cr–C (carbonyl) = 1.81–1.82 (1.81 av), C–O(Cr) = 1.15–1.18 (1.17 av), C(1)–C(2) = 1.42 (1), C(1)–C(6) = 1.40 (1), C(2)–C(3) = 1.42 (1), C(3)–C(4) = 1.40 (1), C(4)–C(5) = 1.44 (1), C(5)–C(6) = 1.41 (1), Fe–C(C_5H_5) = 2.10 (av), C–C-(C_5H_5) = 1.39 (av), Fe–C–O = 177.1 (av), Cr–C–O = 178.1 (av), C–Fe–C(carbonyl) = 92.8–94.5 (93.4 av), C–Cr–C(carbonyl) = 84.4–89.5 (87.2 av). Hydrogen atoms and the CH_2Cl_2 of solvation are omitted for clarity.

lymetallic product (η^6-1,4-$C_6H_4Fp_2$)$Cr(CO)_3$ (**3a**)[11] in 45% yield. The related complexes, (η^6-1,3-$C_6H_4Fp_2$)$Cr(CO)_3$ (**3b**) and (η^6-1,3,5-$C_6H_3Fp_3$)$Cr(CO)_3$ (**3c**) are prepared similarly.[7] These yellow heterometallic complexes are more air sensitive but less thermally sensitive than their phenylene precursors. Their spectroscopic features[7,11] confirm the proposed σ,π structures[12] as does a single-crystal X-ray analysis of **3c** (vide infra). Thus, in these yellow crystalline complexes[7,10] the benzene ring is σ-bound to iron and π-bound to chromium.[12] Of particular interest are their IR spectra[6,7,11] which unambiguously indicate substantial transfer of electron density from the iron-containing fragment to $Cr(CO)_3$ upon complexation (e.g. for **2a** ν_{CO} (CH_2Cl_2) 2014, 1959 cm^{-1} and for **3a** ν_{CO} (CH_2Cl_2) 2030, 1981, 1937, 1853 cm^{-1}).[13,15] Indeed, the chromium carbonyl bands of **3c** (ν_{CO} ($Cr(CO)_3$ (CH_2Cl_2) 1921, 1838 cm^{-1})[7] are among the lowest reported[16] and suggest that the Fp group is as strong a net electron donor to the arene ring as is NMe_2.[17]

The structure of these complexes has been confirmed by the single-crystal X-ray crystallographic analysis of a representative example, **3c** (Figure 1).[18,19] Thus the Fp group is σ-bound to the benzene ring while the $Cr(CO)_3$ fragment is attached in an η^6-π fashion. The (η^5-C_5H_5)-$Fe(CO)_2$ and $Cr(CO)_3$ fragments are normal,[9,12a,16] their most notable feature being the metal carbonyl linkages which are considerably shorter for iron (1.74 Å) than for chromium (1.81 Å). The extreme steric crowding expected is, in fact, observed and appears to control the molecular geometry. Thus, all three (η^5-C_5H_5) rings are oriented away from the $Cr(CO)_3$ fragment and the chromium carbonyls are nested between each pair of iron carbonyls to create a "molecular gear". The arene bridge shows no significant bond length alternation, but it is distorted from planarity to give a crown-like geometry. Thus, the arene carbons bonded to iron exhibit somewhat longer Cr–arene bonds than do those bound to H (2.28 (av) vs 2.24 (av) Å, respectively), and the iron atoms are displaced by ≈0.3 Å (with respect to the arene plane) away from the $Cr(CO)_3$ group. It seems likely that these distortions are due to the steric crowding on the $Cr(CO)_3$ face of the molecule. The most chemically interesting feature of the structure is the orientation of the "pseudo mirror plane" which bisects the Fp fragment and is perpendicular to the arene ring. The electronic effect of this orientation is that the best π-donor orbital on the iron fragment is in the arene plane, and therefore only weak dπ–pπ back-bonding to the arene π^* orbitals is expected.[20] This expectation is confirmed by the observed Fe–aryl bond lengths (1.993 (8), 2.033 (8), and 2.005 (8) Å) which are in the range typically reported[21] for other Fe–C(sp^2) single bonds (1.98–2.00 Å). This suggests that the substantial Fe to Cr electron transfer observed in these heterometallic complexes has a significant inductive component, although a direct Fe to Cr interaction, even over ~4 Å, cannot be entirely ruled out.[22] Studies are currently in progress to elucidate the extent and nature of the Fe–Fe and Fe–Cr electronic linkages in these and related complexes and the factors that control these interactions.

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(11) These $Cr(CO)_3$ adducts generally crystallize from CH_2Cl_2 as solvates ($^1/_4$ CH_2Cl_2 for **3a** and 1 CH_2Cl_2 for **3c**). **3a**: IR (CH_2Cl_2) ν_{CO} 2030 (s), 1981 (s), 1937 (s), 1853 (s, br) cm^{-1}; high-resolution mass spectrum, m/z calcd 565.8845 (for $C_{23}H_{14}O_7CrFe_2$), found 565.8841; ^1H NMR (CD_2Cl_2) δ 5.32 (CH_2Cl_2), 5.22 (s, 4 H, C_6H_4), 4.95 (s, 5 H, C_5H_5) ppm. Anal. Calcd for $C_{23.25}H_{14.5}O_7Cl_{0.5}CrFe_2$: C, 47.55; H, 2.49. Found: C, 47.62; H, 2.53.

(12) A few complexes of the type (η^6-aryl-Fp)$Cr(CO_3)$ have been reported, see: (a) Heppert, J. A.; Morgenstern, M. A.; Scherubel, D. M.; Takusagawa, F.; Shaker, M. R. *Organometallics* **1988**, *7*, 1715. (b) Kolobova, N. E.; Goncharenko, L. V. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1979**, 900 (English translation p 843). (c) Nesmeyanov, A. N.; Polovyanyuk, I. V.; Makarova, L. G. *Dokl. Akad. Nauk. SSSR* **1976**, *230*, 1351 (English translation p 650).

(13) Analysis of the relative intensity and position of the carbonyl bands as a function of increasing numbers of Fp substituents around the ring unambiguously indicates[1b,12a,14] that those bands above 1970 cm^{-1} are due to the Fp and those below 1970 cm^{-1} are due to the $Cr(CO)_3$ fragments.

(14) Hunter, A. D.; Wichrowska, N. M., unpublished observation.

(15) Compare with (η^6-C_6H_6)$Cr(CO)_3$ (ν_{CO} (CH_2Cl_2) 1973, 1893 cm^{-1}) and (η^6-C_6H_5Fp)$Cr(CO)_3$ (ν_{CO} (CH_2Cl_2) 2030, 1980, 1951, 1869 cm^{-1}).[14]

(16) The only comparable values are those reported for (η^6-C_6H_3-$(NR_2)_3$)$Cr(CO)_3$ complexes. See: Schöllkopf, K.; Stezowski, J. J.; Effenberger, F. *Organometallics* **1985**, *4*, 922.

(17) For a discussion of substituent effects in (arene)$Cr(CO)_3$ chemistry see: (a) Bitterwolf, T. E. *Polyhedron* **1988**, *7*, 407. (b) Solladié-Cavallo, A. *Polyhedron* **1985**, *4*, 901. (c) van Meurs, F.; Baas, J. M. A.; van Bekkum, H. *J. Organomet. Chem.* **1977**, *129*, 347. (d) van Meurs, F.; Baas, J. M. A.; van Bekkum, H. *J. Organomet. Chem.* **1976**, *113*, 353. (e) Neuse, E. W. *J. Organomet. Chem.* **1975**, *99*, 287.

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

(19) Thermal ellipsoids enclose 20% probabilities.

(20) (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) Crocco, G. L.; Gladysz, J. A. *J. Am. Chem. Soc.* **1988**, *110*, 6110. (d) Albright, T. A.; Hofmann, P.; Hoffmann, R. *J. Am. Chem. Soc.* **1977**, *99*, 7546 and references cited therein.

(21) O'Connor, E. J.; Helquist, P. *J. Am. Chem. Soc.* **1982**, *104*, 1869.

(22) Analogous long-range interactions have been previously invoked to rationalize the stabilization of Ar_2CH^+ and $ArCH_2^+$ carbocations upon $Cr(CO)_3$ complexation, see: (a) Top, S.; Jaouen, G.; Sayer, B. G.; McGlinchey, M. J. *J. Am. Chem. Soc.* **1983**, *105*, 6426. (b) Top, S.; Jaouen, G. *J. Organomet. Chem.* **1980**, *197*, 199. (c) Seyferth, D.; Merola, J. S.; Eschback, C. S. *J. Am. Chem. Soc.* **1978**, *100*, 4124. (d) Ceccon, A.; Grobbo, A.; Venzo, A. *J. Organomet. Chem.* **1978**, *162*, 311.

Acknowledgment. The author is grateful to the Natural Sciences and Engineering Research Council of Canada and the University of Alberta for support of this work. I also thank Professor M. Cowie of this department for the use of his diffractometer and for helpful discussions on the X-ray crystallographic analysis.

Supplementary Material Available: Analytical and spectroscopic data for **1b**, **1c**, **2b**, **2c**, **3b**, and **3c** and tables of crystal data and details of intensity collection, positional parameters, anisotropic thermal parameters, least-squares planes, and bond lengths and angles (17 pages); a listing of observed and calculated structure factor amplitudes (12 pages). Ordering information is given on any current masthead page.

Flash Photolysis Studies of Lewis Base Addition to $CpFe(CO)(\eta^3\text{-}CH_2C_6H_5)$

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Summary: Flash photolysis studies on $CpFe(CO)_2(\eta^1\text{-}CH_2C_6H_5)$ in hexane confirm formation of $CpFe(CO)(\eta^3\text{-}CH_2C_6H_5)$ following flash photolysis. Decay proceeds with a rate of 151 (10) M^{-1} s^{-1} for added CO and of 1.34 (5) $\times$ 10^3 M^{-1} s^{-1} for added PPh_3.

The $CpM(CO)_x(\eta^1\text{-}CH_2C_6H_5)$ (M = Fe, x = 2; M = Mo or W, x = 3) system has provoked interest because loss of carbon monoxide leads to the corresponding η^3-benzyl complex[1] in analogy to the $CpM(CO)_x(\eta^1\text{-}C_3H_5)$ allyl system.[2] Recent work has concentrated on the iron derivative which, unlike the corresponding molybdenum and tungsten derivatives,[1] does not have a stable η^3-benzyl intermediate. Wrighton and co-workers[3] have examined the low-temperature infrared spectroscopy of $CpFe(CO)(\eta^3\text{-}CH_2C_6H_5)$ which was prepared photochemically from $CpFe(CO)_2(\eta^1\text{-}CH_2C_6H_5)$. Brookhart and co-workers[4] have reported some preliminary measurements on the nano- and microsecond flash photolysis of $CpFe(CO)(\eta^1\text{-}CH_2C_6H_5)$ and examined the kinetics of trapping of the η^3-benzyl intermediate by phosphines at low temperature. We wish to report a kinetic study of the room-temperature reaction of $CpFe(CO)(\eta^3\text{-}CH_2C_6H_5)$ with carbon monoxide or PPh_3 which clarifies the role of the η^3-intermediate.

Flash photolysis[5] of $CpFe(CO)_2(\eta^1\text{-}CH_2C_6H_5)$ in hexane at 22 °C under 1 atm of carbon monoxide produces a transient which decays exponentially back to the original base line in approximately 3 s (Figure 1). The transient is completely formed by the end of the lamp pulse. The transient absorption spectrum, obtained by measuring absorbance changes as a function of wavelength, shows the previously recorded value of 460 nm ± 5 nm as λ_{max}.[3] Solutions under CO are nearly photochromic, but continued flashing produces a new transient which decays much more rapidly. This is attributed to formation of the exo form of $(\eta^4\text{-}C_5H_5CH_2C_6H_5)Fe(CO)_3$ which was observed as a minor product following low-temperature continuous photolysis of $CpFe(CO)_2(\eta^1\text{-}CH_2C_6H_5)$ under a CO atmosphere.[3] Similar experiments with excess PPh_3 under a nitrogen atmosphere produce an exponential decay to a new base line of increased absorbance. Solutions containing PPh_3 change from yellow to orange following a single flash. An intense band appearing at 1917 cm^{-1} (hexane) indicates formation of $CpFe(CO)(PPh_3)(\eta^1\text{-}CH_2C_6H_5)$.[4,6]

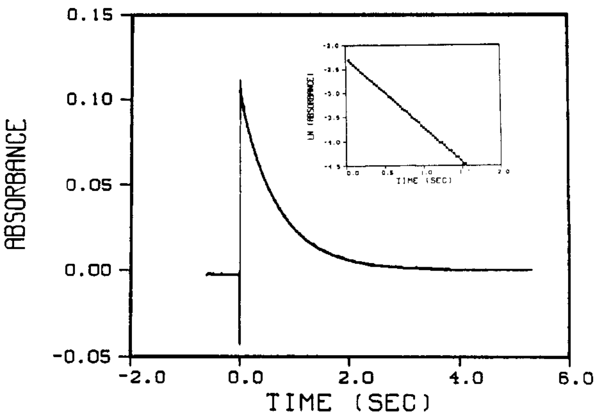


Figure 1. Change in absorbance vs time at 460 nm on flash photolysis of a CO saturated hexane solution of $CpFe(CO)_2(\eta^1\text{-}CH_2C_6H_5)$. The line through the decay curve represents the nonlinear first-order least-squares fit of the data for the disappearance of the transient. Insert: linear least-squares first-order fit of the data to 3.1 half-lives; R = −0.9998.

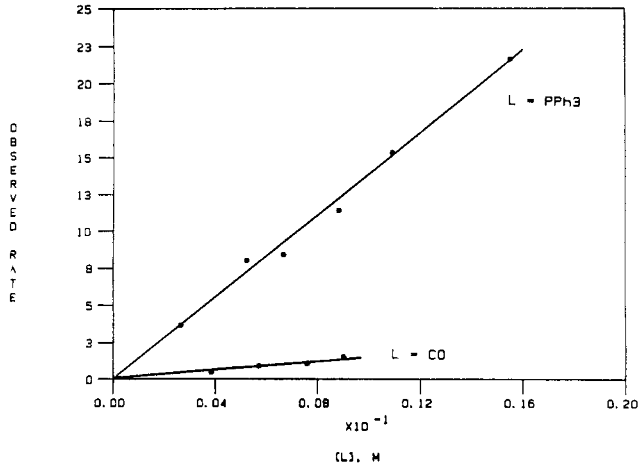
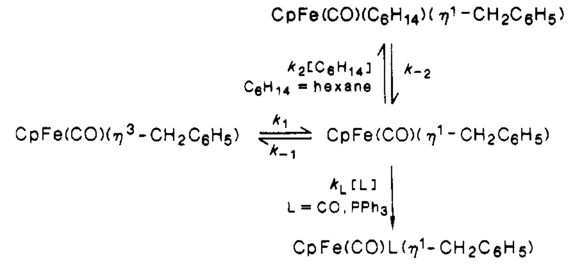


Figure 2. Plot showing the linear dependence of the observed rate constant against PPh_3 concentration (top line) and CO concentration (bottom line) for disappearance of the transient following flash photolysis of $CpFe(CO)_2(\eta^1\text{-}CH_2C_6H_5)$.

Scheme I



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[1] Selected examples include: (a) King, R. B.; Fronzaglia, A. *J. Am. Chem. Soc.* **1966**, *88*, 709. (b) Cotton, F. A.; La Prade, M. D. *J. Am. Chem. Soc.* **1968**, *90*, 5418. (c) Cotton, F. A.; Marks, T. J. *J. Am. Chem. Soc.* **1969**, *91*, 1339.

[2] (a) Green, M. L. H.; Nagy, P. L. I. *J. Chem. Soc.* **1963**, *189*. (b) Dub, M. *Organometallic Compounds*, 2nd ed.; Springer-Verlag: Berlin, 1966; Vol. 1. (c) Gibson, D. H.; Hsu, W. L.; Lin, D. S. *J. Organomet. Chem.* **1979**, *172*, C7.

[3] Blaha, J. P.; Wrighton, M. S. *J. Am. Chem. Soc.* **1985**, *107*, 2694.

[4] (a) Brookhart, M.; Buck, R. C. *J. Am. Chem. Soc.* **1989**, *111*, 559. (b) Brookhart, M.; Buck, R. C.; Danielson, E. *J. Am. Chem. Soc.* **1989**, *111*, 567.

[5] See: Herrick, R. S.; Peters, C. H.; Duff, R. R. *Inorg. Chem.* **1988**, *27*, 2214 for a description of the flash photolysis setup.

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