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Reaction of *o*-Fluorolithiobenzene with Dicarbonyl(η^5-cyclopentadienyl)iodoiron: Single-Crystal X-ray Structure of $[(\eta^5\text{-}C_5H_5)Fe(CO)(C_6H_4\text{-}2\text{-}C(O)\text{-}C_6H_4\text{-}2'\text{-}C_6H_4\text{-}2''\text{-}F)]\text{-}\eta^6\text{-}Cr(CO)_3$, a Metalated Benzophenone

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The reaction of 3 molar equiv of *o*-fluorolithiobenzene with dicarbonyl(η^5-cyclopentadienyl)iodoiron results in an intramolecular cyclization to give the metallacyclic product $[(\eta^5\text{-}C_5H_5)Fe(CO)(C_6H_4\text{-}2\text{-}C(O)\text{-}C_6H_4\text{-}2'\text{-}C_6H_4\text{-}2''\text{-}F)]$. Characterization was made by derivatization with tris(acetonitrile)tricarbonylchromium to give $[(\eta^5\text{-}C_5H_5)Fe(CO)(C_6H_4\text{-}2\text{-}C(O)\text{-}C_6H_4\text{-}2'\text{-}C_6H_4\text{-}2''\text{-}F)]\text{-}\eta^6\text{-}Cr(CO)_3$ (**3a**). Compound **3a** crystallizes in the monoclinic space group $P2_1/c$ with lattice parameters a = 7.1633 (18) Å, b = 13.669 (6) Å, c = 24.116 (3) Å, β = 95.763 (3)°, V = 2349.33 (12) Å^3, ρ(calc) = 1.584 g cm^{-3}, and Z = 4. Least-squares refinement gave a final R_F value of 0.065 for 1864 ($I > 2.5\sigma(I)$) of 3071 unique reflections (R_w = 0.036, GOF = 2.08).

Introduction

The metathesis of coordinated metal halides with group I metal alkyls and aryls is of fundamental importance in synthetic organometallic chemistry. One such well-documented reaction is that of dicarbonyl(η^5-cyclopentadienyl)iron halides (FpX) with lithium alkyls and aryls (eq 1).

$$(\eta^5\text{-}C_5H_5)Fe(CO)_2X + LiR \rightarrow \underset{\mathbf{1}}{(\eta^5\text{-}C_5H_5)Fe(CO)_2R} + LiX \quad (1)$$

R = 2-C_6H_4X etc.; X = F, Cl, Br, I, H, CH_2Ph, Me

We had previously been interested in the synthesis of derivatives of **1** in which the R group was a 2-halogenophenyl ring,[1,2] since such compounds could be possible precursors to iron–benzyne complexes.[3] The organolithium compounds used in such cases are the particularly reactive 2-LiC_6H_4X (X = halogen) compounds, which undergo lithium halide extrusion to form benzyne at low temperature.[4] During the course of the synthesis of $(\eta^5\text{-}C_5H_5)Fe(CO)_2(2\text{-}FC_6H_4)$ we observed a small quantity of an unidentified byproduct possessing unusual spectroscopic properties. This paper outlines our attempts to characterize this compound.

Experimental Section

All solvents were dried with use of conventional procedures and were freshly distilled under nitrogen. Standard Schlenk glassware was used throughout. Neutral alumina (Brockman grade I) and *n*-butyllithium in hexane were obtained from the Aldrich Chemical Co. Hexacarbonylchromium was obtained from the Strem Chemical Co. Dicarbonyl(η^5-cyclopentadienyl)iodoiron was prepared by using the literature method.[5] ^{1}H NMR spectra were recorded with use of Bruker WH-400, Varian XL-300, and Bruker WP-80 instruments. All spectra reported were recorded in chloroform-*d*, unless mentioned otherwise (bt = broad triplet, at = asymmetric triplet). Mass spectra were recorded on Kratos MS-50 or VG Analytical 7070E instruments and are reported in the format *m*/*e* (relative intensity) for the most prominent peaks.

Preparation of 2. A solution of *o*-fluorolithiobenzene was prepared from *o*-bromofluorobenzene (5.85 g, 30 mmol) and *n*-butyllithium (18.75 mL of a 1.6 M solution) in diethyl ether (100 mL) at −70 °C as previously described.[1] After the mixture was stirred for 30 min, dicarbonyl(η^5-cyclopentadienyl)iodoiron[5] (3.04 g, 10 mmol) was added. The solution was stirred at −70 °C for 30 min before being warmed slowly over a period of 8 h to room temperature. The solvent was removed to leave a black oil, which was dissolved in the minimum quantity of diethyl ether. The filtered solution was applied directly to a neutral alumina chromatographic column. The green/brown product band was collected (eluted with diethyl ether/hexane, 80/20) and the solvent removed under vacuum to give a black oil (3.3 g, 78%). The compound is pure by ^{1}H NMR spectroscopy but may be crystallized in diminished yield by dissolving in a small quantity of diethyl ether, diluting with hexane, and cooling the mixture to −20 °C for 2–3 days. The product **2** is obtained as black nodules. ^{1}H NMR (δ): 4.41 (s, 5); 6.92 (bt, 1); 7.00–7.20 (m's, 4); 7.28 (m, 1); 7.39 (t, 1); 7.43 (d, 2); 7.54 (at, 1); 7.61 (bd, 1); 7.95 (bd, 1). ^{13}C NMR (δ): 82.01 (Cp); 115.37; 115.58; 121.33; 123.35; 124.01; 127.23; 128.44; 129.32; 129.39; 129.52; 120.31; 131.50; 131.68; 132.07; 133.48; 143.12; 146.81; 216.62. ^{19}F NMR (δ): −36.51 (septet, relative to TFA). Anal. Calcd for $C_{25}H_{17}FFeO_2$: C, 70.77; H, 4.14. Found: C, 71.19; H, 4.16. Mass spectrum (accurate masses): 425.063 (1.76);

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424.056 (8.84, $M^{\bullet+}$); 396.062 (100.00); 395.055 (57.42); 394.063 (6.26); 378.053 (13.78); 340.127 (18.87); 303 (10.62); 302.111 (16.39); 301.033 (39.85).

The reaction described above was repeated on the same scale with *o*-bromofluorobenzene being replaced by *o*-bromochlorobenzene; however, only small amounts of a yellow/brown compound with a molecular ion at *m/e* 440/442 ($C_{25}H_{17}ClFeO_2$) could be isolated under reaction conditions (except for a lower initial reaction temperature, −90 °C) and workup conditions identical with those used above.

Preparation of 3a and 3b. A sample of $(CH_3CN)_3Cr(CO)_3$ (2.0 g, 7.7 mmol) prepared by the literature procedure[6] was dissolved in THF, and **2** (1.0 g, 2.4 mmol) was added. The solution was stirred overnight. The solvent was removed, and a TLC examination (50/50, hexane/ether) showed some **2** and three new compounds with lower R_f values in comparison to that of **2**. Column chromatography, as reported above, was used to separate the products. The two isomeric products **3a** (34%) and **3b** (19%) were isolated and crystallized. A third isomeric product, **3c**, was collected, but there was insufficient material for crystallization. Unreacted **2** (31%) was also recovered.

3a (deep violet): ^1H NMR (δ) 4.19 (s, 5), 5.12 (t, 1), 5.62 (t, 1), 5.72 (d, 1), 6.04 (d, 1), 7.11 (t, 1), 7.50–7.60 (2 m, 2), 7.46 (td, 1), 7.35–7.41 (2 m, 2), 7.22–7.30 (2 m, 2); mass spectrum *m/e* 532 ($M^{\bullet+}$ − CO, 1.45), 519 (9.24), 518 (23.09), 476 (2.51), 448 (10.95), 396 (4.60), 357 (10.18), 356 (24.78), 328 (10.20), 308 (5.42), 276 21.24), 257 (13.19), 243 (14.64), 242 (11.19), 241 (32.27), 239 (20.09), 208 (10.66), 199 (23.57), 186 (48.39), 121 (100.00). Anal. Calcd for $C_{28}H_{17}CrFFeO_5$: C, 60.03; H, 3.06. Found: C, 59.52; H, 3.32.

3b (black-green): ^1H NMR (δ) 4.47 (s, 5), 4.88 (td, 1), 5.64 (td, 1), 5.66 (dd, 1), 5.86 (dd, 1), 7.02–7.57 (m, 8); mass spectrum *m/e* 532 (M − CO, 0.5), 519 (10.3), 510 (23.3), 501 (1.6), 500 (2.5), 499 (2.1), 498 (4.7), 481 (2.3), 480 (5.3), 473 (2.0), 449 (2.8), 448 (7.2), 446 (16.6), 428 (1.4), 426 (17), 424 (1.3), 422 (1.2), 396 (3.1), 328 (14.6), 315 (6.1), 274 (9.2), 276 (39.5), 275 (13.3), 215 (12.7), 201 (10.1), 200 (10.9), 199 (49.7), 186 (42.6), 121 (78.7), 105 (42.3), 64 (11.7), 61 (18.2), 56 (46.4), 52 (33.1), 51 (14.5), 49 (28.3), 39 (14.1), 28 (100). Anal. Calcd for $C_{28}H_{17}CrFFeO_5$: C, 60.03; H, 3.06. Found: C, 59.62; H, 2.65.

3c (brown/black): mass spectrum *m/e* 532 ($M^{\bullet+}$ − CO, trace product).

Crystallographic Analysis of 3a. The first violet/black needles of compound **3a** studied by X-ray diffraction appeared to be orthorhombic, but the intensities displayed systematic absences that could not be explained by any orthorhombic space group. However, they could be explained by twinning of a monoclinic lattice. Careful morphological examination of the terminations of the crystals under the microscope showed that most crystals had faces consistent with orthorhombic symmetry, but others indicated lower symmetry. A crystal of the latter type with dimensions 0.08 × 0.10 × 0.22 mm was selected and studied by X-ray diffraction of Mo Kα radiation on a Nonius CAD-4 diffractometer controlled by the NRCCAD system of programs.[7] The crystal was monoclinic with space group $P2_1/c$ and cell dimensions a = 7.1633 (18) Å, b = 13.669 (6) Å, c = 24.116 (3) Å, β = 95.763 (3)°. These cell dimensions were obtained from 48 reflections with 2θ angles in the range 30.00–40.00°, and the wavelength 0.709 30 Å was used. Assuming four molecules per cell, the calculated density was 1.584 g cm^{-3}, while the linear absorption coefficient μ was 1.11 mm^{-1}. Intensity data were measured for 5561 Bragg reflections by the $\theta/2\theta$ scan method up to 45.0° Bragg angle. Data reduction produced 3071 unique reflections, of which 1864 had $I_{net} > 2.5\sigma(I_{net})$ and were considered to be observed. In view of the low absorption coefficient, no correction was made for absorption. Structure solution by direct methods followed by least-squares refinement and one difference Fourier map showed the 36 non-hydrogen atoms. Hydrogen atom positions were then calculated and not refined. All other atoms were refined anisotropically together with the scale and an extinction parameter. The last least-squares cycle was calculated with 53 atoms, 326 parameters, and 1864 out of 3071 reflections. Weights based on counting statistics only were used. The residuals on significant reflections were R_F = 0.065, R_w = 0.036, and GOF = 2.08, while they were R_F = 0.116 and R_w = 0.038 for all reflections, where $R_F = \sum|(F_o - F_c)|/\sum(F_o)$, $R_w = [\sum(w(F_o - F_c)^2)/\sum(wF_o^2)]^{1/2}$, and GOF = $[\sum(w(F_o - F_c)^2/((\text{no. of reflections}) - (\text{no. of parameters}))]^{1/2}$.

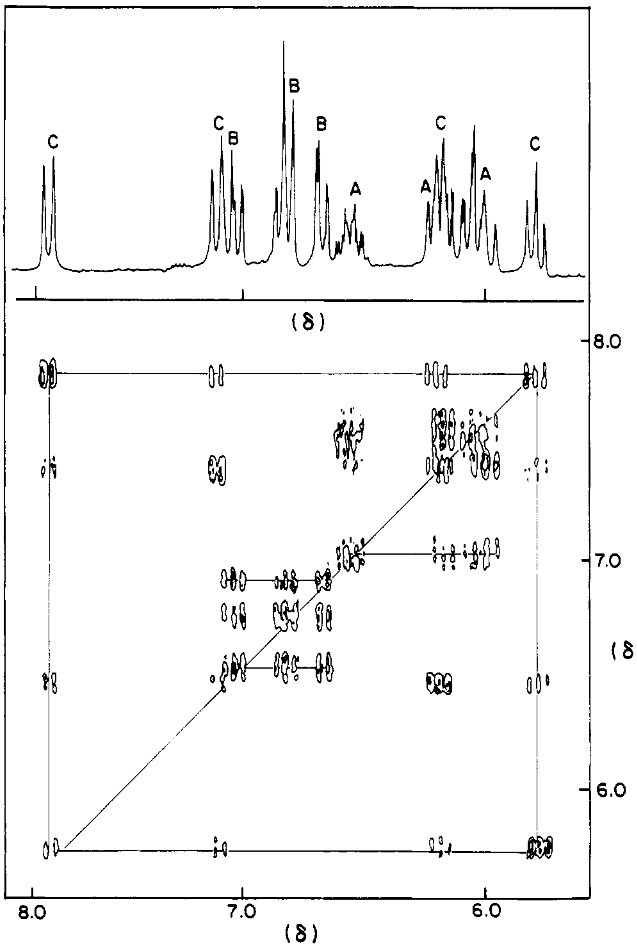

Figure 1. COSY ^1H NMR spectrum of **2** (aromatic region). A, B, and C identify individual aromatic rings referred to in the text.

The maximum Δ/σ ratio was 0.026. In the last D-map, the deepest hole was −0.660 e Å^{-3} and the highest peak 0.480 e Å^{-3}, indicating the absence of solvent molecules, in agreement with the elemental analysis.

Results and Discussion

The stoichiometric reaction of $2\text{-}FC_6H_4Li$, prepared in situ from *o*-bromofluorobenzene and *n*-butyllithium, with FpI at −70 °C gives, as expected, $2\text{-}FC_6H_4Fp^1$ in addition to biphenyls and Fp_2. When the ratio of $2\text{-}FC_6H_4Li$ was increased, we observed the formation of a black byproduct. Maximum yields (~75%) of this compound are obtained when the ratio of the lithio compound to iron is increased to ~3.2:1. The compound was isolated with use of column chromatography on a neutral alumina support under nitrogen and on crystallization gave black nodules. The compound could be formulated as $C_{25}H_{17}FFeO_2$ by elemental analysis. One terminal CO (1940 cm^{-1}, chloroform) was observed by infrared spectroscopy, and three overlapping 1,2-disubstituted phenyl groups, one of which was fluorine-substituted, and one cyclopentadienyl ring were found by ^1H NMR spectroscopy. The 2-D COSY ^1H NMR spectrum of **2** is shown in Figure 1. In the spectrum the three individual phenyl rings A, B, and C are readily

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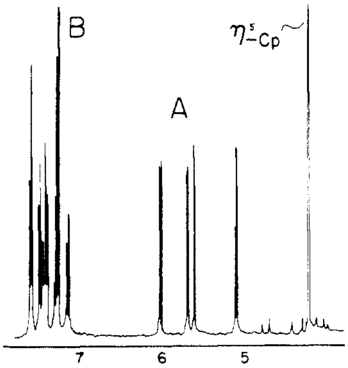


Figure 2. ^{1}H NMR spectrum of **3a**, indicating the effect of the coordination of η^6-Cr(CO)$_3$ on the aromatic protons.

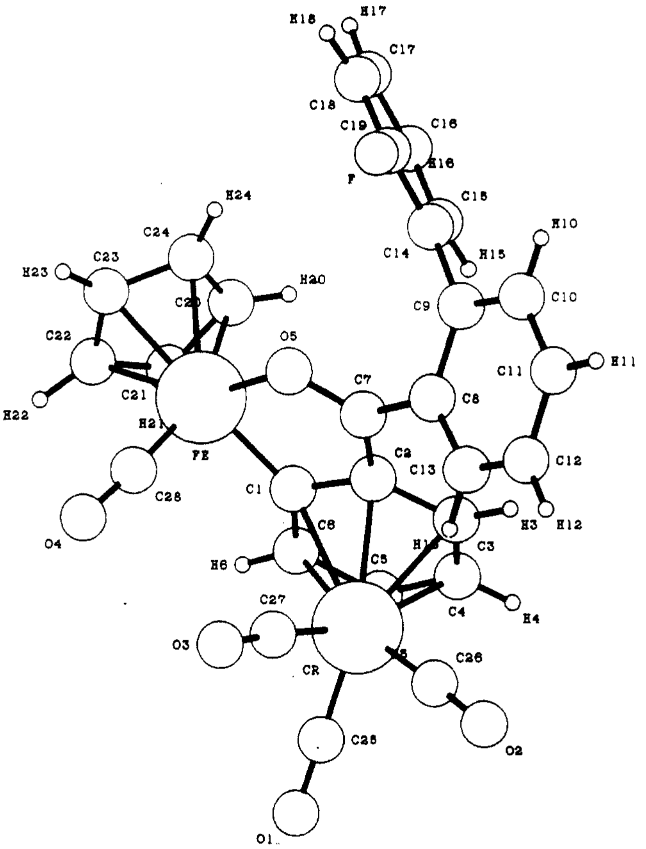
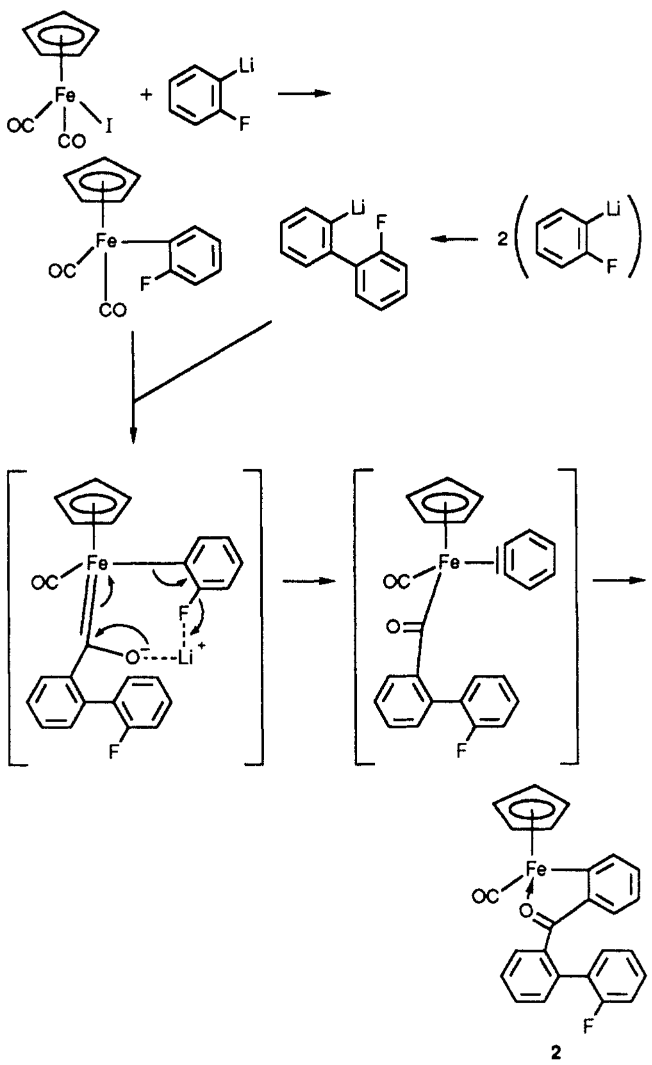
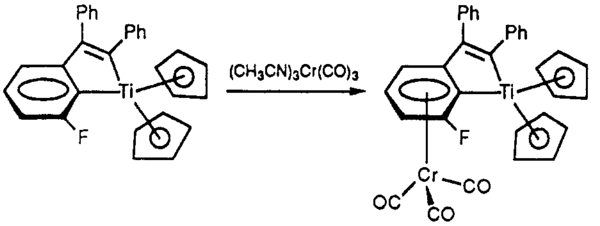


Figure 3. PLUTO drawing of **3a**.

discerned. Ring A exhibits the widest chemical shift range, indicating dipolar substitution, and ring C exhibits additional ^{19}F couplings. The compound is moderately soluble in hexane and is soluble in diethyl ether and more polar organic solvents. Attempts at crystallization of this compound from a large number of different solvent mixtures were unsuccessful in obtaining a crystalline material suitable for X-ray diffraction. It was decided to derivatize the compound in an attempt to obtain a crystalline material. Initial attempts at derivatization by ligand substitution were unsuccessful.[10] Previously we had experienced similar problems of identification of a related titanium metallacycle containing aryl groups. In that case we were able to obtain a full characterization by a derivatization of the compound with tris(acetonitrile)tricarbonylchromium to give a crystalline product (eq 2).[11]

Scheme I





(2)

This technique is, of course, used routinely in the activation of organic aryl derivatives.[12] This method has the advantage of being nondestructive to the original molecule. In addition, coordination of the aryl ring has the effect of simplifying the NMR analysis in the aromatic region of the spectrum since the normal upfield shift of the ring η^6-bound to chromium is observed. This effect, in the present case, is demonstrated in Figure 2, in which the original compound **2** is derivatized with tris(aceto-

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[10] Attempts at derivatizing the product with various ligands were unsuccessful. In the case of reaction with triphenylphosphine, however, we did observe a product that was formulated as an adduct by mass spectroscopy; however, we were unable to completely characterize this product. Recent work suggests that the less bulky phosphine displaces the acyl oxygen.

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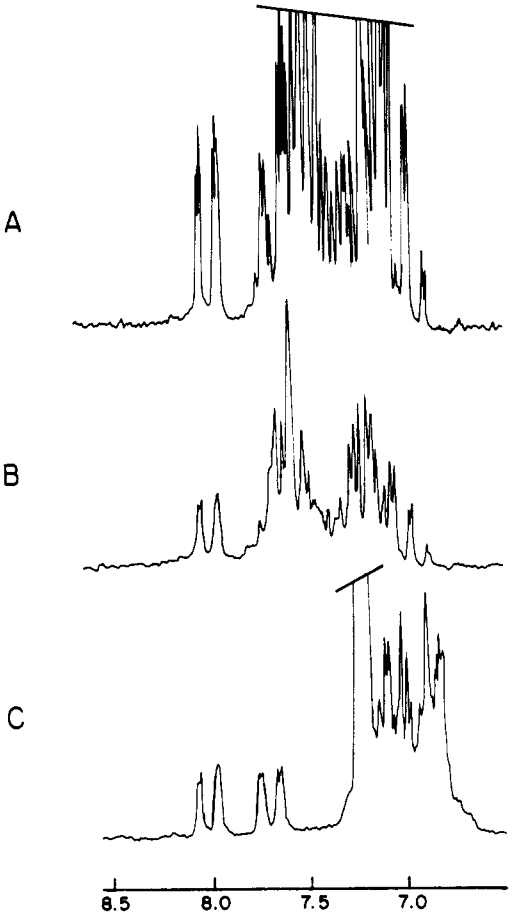
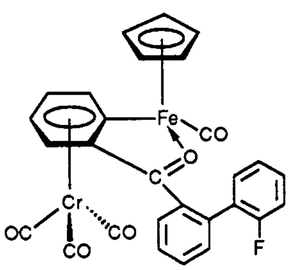


Figure 4. ^{1}H NMR spectra of 2 in (A) chloroform-*d*, (B) dichloromethane-d_2, and (C) acetone-d_6.

nitrile)tricarbonylchromium. On reaction of the unknown compound with the latter reagent a mixture is obtained, including three new complexes, with one predominating and one present in trace quantities. The two major products were isolated following separation by column chromatography. Crystallization from dichloromethane/hexane by slow diffusion gave crystals of the major product present, **3a**, suitable for X-ray analysis.



3a

Table I. Atomic Parameters x, y, z, and B_{iso}[a]

	x	y	z	B_{iso}, Å^2
Fe	0.87338 (22)	0.96575 (11)	0.10076 (5)	4.12 (8)
Cr	1.05271 (24)	0.86716 (12)	0.25551 (6)	4.19 (10)
F	1.1942 (10)	0.6747 (5)	−0.04226 (23)	7.5 (4)
O(1)	1.0936 (12)	0.9907 (6)	0.3566 (3)	7.9 (5)
O(2)	1.3465 (12)	0.7453 (6)	0.3155 (3)	7.6 (5)
O(3)	1.3619 (11)	0.9899 (7)	0.2203 (3)	8.7 (6)
O(4)	1.1657 (12)	1.1047 (6)	0.1331 (3)	7.6 (6)
O(5)	1.0348 (8)	0.8524 (4)	0.08844 (21)	4.0 (3)
C(1)	0.8733 (14)	0.9014 (8)	0.1725 (4)	4.3 (6)
C(2)	0.9501 (13)	0.8088 (8)	0.1744 (4)	3.6 (5)
C(3)	0.9253 (15)	0.7389 (7)	0.2156 (4)	5.2 (6)
C(4)	0.8183 (16)	0.7656 (9)	0.2582 (4)	5.2 (7)
C(5)	0.7502 (16)	0.8577 (10)	0.2608 (4)	5.8 (7)
C(6)	0.7723 (15)	0.9272 (7)	0.2185 (4)	5.5 (6)
C(7)	1.0533 (14)	0.7890 (7)	0.1260 (4)	3.8 (6)
C(8)	1.1754 (14)	0.7021 (7)	0.1190 (4)	3.4 (5)
C(9)	1.1430 (13)	0.6438 (7)	0.0702 (4)	3.3 (5)
C(10)	1.2714 (15)	0.5676 (8)	0.0654 (4)	4.3 (6)
C(11)	1.4077 (15)	0.5484 (7)	0.1062 (5)	5.1 (6)
C(12)	1.4391 (17)	0.6046 (9)	0.1537 (4)	6.0 (7)
C(13)	1.3161 (17)	0.6794 (8)	0.1587 (4)	5.3 (6)
C(14)	0.9891 (15)	0.6606 (6)	0.0272 (4)	3.4 (5)
C(15)	0.8033 (17)	0.6642 (7)	0.0393 (4)	4.9 (6)
C(16)	0.6599 (16)	0.6820 (7)	−0.0013 (5)	5.6 (7)
C(17)	0.6913 (20)	0.6964 (8)	−0.0570 (5)	5.6 (7)
C(18)	0.8765 (19)	0.6941 (8)	−0.0695 (4)	4.8 (7)
C(19)	1.0107 (17)	0.6761 (7)	−0.0283 (5)	4.5 (6)
C(20)	0.6038 (18)	0.9242 (10)	0.0673 (6)	6.8 (8)
C(21)	0.5990 (19)	1.0109 (13)	0.0973 (4)	6.9 (8)
C(22)	0.6970 (19)	1.0799 (8)	0.0731 (5)	6.2 (7)
C(23)	0.7696 (13)	1.0366 (11)	0.0270 (4)	4.9 (7)
C(24)	0.7124 (19)	0.9420 (9)	0.0248 (4)	5.7 (7)
C(25)	1.0735 (16)	0.9411 (8)	0.3170 (4)	5.6 (6)
C(26)	1.2274 (16)	0.7921 (8)	0.2905 (4)	5.1 (6)
C(27)	1.2375 (14)	0.9414 (9)	0.2322 (4)	4.9 (7)
C(28)	1.0492 (17)	1.0455 (8)	0.1210 (4)	5.0 (6)
H(3)	0.978	0.676	0.214	5.5
H(4)	0.791	0.720	0.286	5.9
H(5)	0.691	0.877	0.292	5.9
H(6)	0.726	0.991	0.221	5.5
H(10)	1.259	0.528	0.034	5.3
H(11)	1.487	0.494	0.102	5.7
H(12)	1.541	0.592	0.180	6.4
H(13)	1.325	0.716	0.192	5.8
H(15)	0.778	0.653	0.075	5.5
H(16)	0.537	0.684	0.009	6.4
H(17)	0.595	0.706	−0.084	6.4
H(18)	0.907	0.707	−0.106	5.6
H(20)	0.550	0.866	0.076	6.9
H(21)	0.533	1.023	0.127	7.4
H(22)	0.725	1.146	0.085	6.5
H(23)	0.846	1.069	0.002	5.6
H(24)	0.745	0.898	−0.003	6.4

[a] Esd's refer to the last significant digit. B_{iso} is the mean of the principal axes of the thermal ellipsoid.

The refined atomic positions are given in Table I and selected distances and angles in Table II. The anisotropic thermal parameters are in Table III, and the measured and calculated structure factors are in Table IV (supplementary material). The compound **3a** was thus identified, and a PLUTO plot is shown in Figure 3. Of interest is the orientation of the CO originally present as a terminal iron carbonyl group, which is found in the product as part of a complex metallated diaryl ketone. A possible mechanism for the formation of **2** is shown in Scheme I. The proposed mechanistic pathway goes through a carbenoid anionic acyl intermediate followed by an intramolecular rearrangement step. The formation of *o*-halogenobiphenyls by coupling of *o*-halogenolithiobenzene was found during earyl studies;[4,13] thus, the lithiobiphenyl will be generated in high concentration under the experimentally used reaction conditions (i.e. on warming >−70 °C). In previous studies on the synthesis of aryltitanium complexes from *o*-halogenolithiobenzenes we had observed the formation of significant amounts of σ-bound halogenobiphenyls,[2] again substantiating this argument. A nucleophilic substitution on a coordinated carbonyl ligand is well established in the synthesis of Fischer type carbenes.[14] A novel step in this proposed reaction mechanism is the intramolecular displacement of fluoride ion, as LiF, from the coordinated 2-FC_6H_4 group and the migration of the acyl ligand. In effect, a benzyne unit has been inserted into the Fe–acyl

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Table II. Selected Bond Lengths (Å) and Angles (deg) for 3a

Fe–O(5)	1.974 (6)	Cr–C(6)	2.268 (11)	C(2)–C(3)	1.404 (14)	C(12)–C(13)	1.363 (17)
Fe–C(1)	1.941 (9)	Cr–C(25)	1.788 (11)	C(2)–C(7)	1.467 (13)	C(14)–C(15)	1.392 (16)
Fe–C(20)	2.095 (12)	Cr–C(26)	1.766 (11)	C(3)–C(4)	1.391 (16)	C(14)–C(19)	1.379 (15)
Fe–C(21)	2.054 (12)	Cr–C(27)	1.802 (11)	C(4)–C(5)	1.354 (18)	C(15)–C(16)	1.367 (17)
Fe–C(22)	2.075 (11)	F–C(19)	1.389 (14)	C(5)–C(6)	1.414 (16)	C(16)–C(17)	1.400 (17)
Fe–C(23)	2.094 (9)	O(1)–C(25)	1.168 (13)	C(7)–C(8)	1.495 (14)	C(17)–C(18)	1.389 (20)
Fe–C(24)	2.090 (11)	O(2)–C(26)	1.182 (13)	C(8)–C(9)	1.420 (14)	C(18)–C(19)	1.334 (17)
Fe–C(28)	1.700 (12)	O(3)–C(27)	1.170 (14)	C(8)–C(13)	1.355 (15)	C(20)–C(21)	1.391 (23)
Cr–C(1)	2.316 (9)	O(4)–C(28)	1.177 (14)	C(9)–C(10)	1.402 (15)	C(20)–C(24)	1.369 (20)
Cr–C(2)	2.172 (9)	O(5)–C(7)	1.251 (11)	C(9)–C(14)	1.453 (13)	C(21)–C(22)	1.343 (22)
Cr–C(3)	2.158 (10)	C(1)–C(2)	1.379 (14)	C(10)–C(11)	1.339 (16)	C(22)–C(23)	1.404 (18)
Cr–C(4)	2.185 (11)	C(1)–C(6)	1.429 (14)	C(11)–C(12)	1.381 (16)	C(23)–C(24)	1.356 (20)
Cr–C(5)	2.187 (12)						

O(5)–Fe–C(1)	80.3 (3)	C(1)–Cr–C(27)	88.7 (4)	Fe–C(1)–C(6)	128.7 (7)	F–C(14)–C(9)	92.2 (7)
O(5)–Fe–C(20)	105.1 (5)	C(2)–Cr–C(3)	37.8 (4)	Cr–C(1)–C(2)	66.5 (5)	F–C(14)–C(15)	145.9 (7)
O(5)–Fe–C(21)	143.4 (5)	C(2)–Cr–C(4)	66.6 (4)	Cr–C(1)–C(6)	70.0 (5)	F–C(14)–C(19)	32.3 (6)
O(5)–Fe–C(22)	152.8 (4)	C(2)–Cr–C(5)	77.5 (4)	C(2)–C(1)–C(6)	115.6 (8)	C(9)–C(14)–C(15)	122.0 (9)
O(5)–Fe–C(23)	113.5 (4)	C(2)–Cr–C(6)	64.7 (4)	Cr–C(2)–C(1)	77.9 (6)	C(9)–C(14)–C(19)	124.4 (10)
O(5)–Fe–C(24)	91.5 (3)	C(2)–Cr–C(25)	161.3 (5)	Cr–C(2)–C(3)	70.5 (6)	C(15)–C(14)–C(19)	113.6 (9)
O(5)–Fe–C(28)	96.8 (4)	C(2)–Cr–C(26)	112.2 (4)	Cr–C(2)–C(7)	129.2 (7)	C(14)–C(15)–C(16)	121.5 (10)
C(1)–Fe–C(20)	97.9 (5)	C(2)–Cr–C(27)	96.8 (4)	C(1)–C(2)–C(3)	124.8 (9)	C(15)–C(16)–C(17)	122.1 (11)
C(1)–Fe–C(21)	95.0 (5)	C(3)–Cr–C(4)	37.4 (4)	C(1)–C(2)–C(7)	112.0 (8)	C(16)–C(17)–C(18)	116.9 (10)
C(1)–Fe–C(22)	124.9 (5)	C(3)–Cr–C(5)	66.5 (4)	C(3)–C(2)–C(7)	123.2 (9)	F–C(18)–C(17)	150.8 (8)
C(1)–Fe–C(23)	159.1 (4)	C(3)–Cr–C(6)	78.5 (4)	Cr–C(3)–C(2)	71.6 (6)	F–C(18)–C(19)	32.3 (6)
C(1)–Fe–C(24)	131.4 (5)	C(3)–Cr–C(25)	145.6 (4)	Cr–C(3)–C(4)	72.4 (6)	C(17)–C(18)–C(19)	118.4 (10)
C(1)–Fe–C(28)	95.8 (5)	C(3)–Cr–C(26)	89.4 (4)	C(2)–C(3)–C(4)	117.6 (9)	F–C(19)–C(14)	115.7 (10)
C(20)–Fe–C(21)	39.2 (6)	C(3)–Cr–C(27)	127.6 (5)	Cr–C(4)–C(3)	70.3 (6)	F–C(19)–C(18)	116.8 (10)
C(20)–Fe–C(22)	64.7 (5)	C(4)–Cr–C(5)	36.1 (5)	Cr–C(4)–C(5)	72.1 (7)	C(14)–C(19)–C(1)	127.5 (11)
C(20)–Fe–C(23)	64.1 (4)	C(4)–Cr–C(6)	65.7 (4)	C(3)–C(4)–C(5)	120.4 (9)	Fe–C(20)–C(21)	68.8 (7)
C(20)–Fe–C(24)	38.2 (6)	C(4)–Cr–C(25)	109.5 (4)	Cr–C(5)–C(4)	71.9 (7)	Fe–C(20)–C(24)	70.7 (7)
C(20)–Fe–C(28)	155.8 (5)	C(4)–Cr–C(26)	97.3 (5)	Cr–C(5)–C(6)	74.6 (6)	C(21)–C(20)–C(24)	106.5 (11)
C(21)–Fe–C(22)	38.0 (6)	C(4)–Cr–C(27)	163.4 (4)	C(4)e–C(5)–C(6)	121.7 (9)	Fe–C(21)–C(20)	72.0 (7)
C(21)–Fe–C(23)	64.5 (4)	C(5)–Cr–C(6)	37.0 (4)	Cr–C(6)–C(1)	73.6 (6)	Fe–C(21)–C(22)	71.9 (7)
C(21)–Fe–C(24)	64.5 (5)	C(5)–Cr–C(25)	89.2 (4)	Cr–C(6)–C(5)	68.4 (6)	C(20)–C(21)–C(22)	109.3 (10)
C(21)–Fe–C(28)	119.8 (6)	C(5)–Cr–C(26)	126.6 (5)	C(1)–C(6)–C(5)	119.7 (9)	Fe–C(22)–C(21)	70.2 (7)
C(22)–Fe–C(23)	39.4 (5)	C(5)–Cr–C(27)	144.5 (5)	O(5)–C(7)–C(2)	115.0 (9)	Fe–C(22)–C(23)	71.1 (6)
C(22)–Fe–C(24)	64.6 (4)	C(6)–Cr–C(25)	96.8 (5)	O(5)–C(7)–C(8)	119.2 (8)	C(21)–C(22)–C(23)	107.4 (11)
C(22)–Fe–C(28)	91.1 (5)	C(6)–Cr–C(26)	162.8 (5)	C(2)–C(7)–C(8)	125.8 (8)	Fe–C(23)–C(22)	69.6 (6)
C(23)–Fe–C(24)	37.8 (5)	C(6)–Cr–C(27)	108.8 (4)	C(7)–C(8)–C(9)	119.4 (8)	Fe–C(23)–C(24)	70.9 (6)
C(23)–Fe–C(28)	97.9 (5)	C(25)–Cr–C(26)	86.3 (5)	C(7)–C(8)–C(13)	120.2 (9)	C(22)–C(23)–C(24)	107.4 (10)
C(24)–Fe–C(28)	132.8 (6)	C(25)–Cr–C(27)	86.4 (5)	C(9)–C(8)–C(13)	120.4 (9)	Fe–C(24)–C(20)	71.1 (7)
C(1)–Cr–C(2)	35.6 (4)	C(26)–Cr–C(27)	88.2 (5)	C(8)–C(9)–C(10)	115.5 (8)	Fe–C(24)–C(23)	71.3 (6)
C(1)–Cr–C(3)	66.8 (4)	C(14)–F–C(18)	62.9 (4)	C(8)–C(9)–C(14)	123.4 (9)	C(20)–C(24)–C(23)	109.4 (10)
C(1)–Cr–C(4)	78.1 (4)	C(14)–F–C(19)	32.0 (6)	C(10)–C(9)–C(14)	121.1 (9)	Cr–C(25)–O(1)	177.4 (9)
C(1)–Cr–C(5)	66.1 (4)	C(18)–F–C(19)	30.9 (6)	C(9)–C(10)–C(11)	121.5 (9)	Cr–C(26)–O(2)	177.1 (9)
C(1)–Cr–C(6)	36.3 (3)	Fe–O(5)–C(7)	117.1 (6)	C(10)–C(11)–C(12)	123.1 (10)	Cr–C(27)–O(3)	176.1 (8)
C(1)–Cr–C(25)	126.5 (5)	Fe–C(1)–Cr	144.4 (5)	C(11)–C(12)–C(13)	115.9 (10)	Fe–C(28)–O(4)	176.2 (9)
C(1)–Cr–C(26)	146.7 (4)	Fe–C(1)–C(2)	114.2 (7)	C(8)–C(13)–C(12)	123.5 (10)		

bond, although this may not be a discrete intermediate. This leaves a coordinatively unsaturated iron center to which the ketonic oxygen coordinates. During the course of the synthesis it was observed that the color change from yellow to black (due to the formation of the final product, **2**) in the reaction solution only occurred at relatively high temperature (between −10 °C and room temperature). Such a change may indicate that the final reaction step is relatively slow in comparison to the nucleophilic attack on the carbonyl carbon. Attempts to carry out the same chemistry with use of the *o*-chloro analogue led to only very low product yields. This is readily accounted for since the stability of *o*-chlorolithiobenzene is well-known to be significantly less than that of its fluoro counterpart, leading to salt extrusion with the formation of benzyne intermediates and biphenyls. In acetone-d_6 (Figure 4) a significant chemical shift of the aromatic ring protons is observed in comparison to a similar spectrum in chloroform-*d*: it is possible that this may be due to competitive coordination to the iron by the carbonyl oxygen of the acetone for the oxygen coordination site in **2**. The ^{19}F NMR spectrum of **2** indicates a septet at approximately δ −36.5, which is shifted upfield from the similar ^{19}F resonance of 1 (δ 5.5). This shift is in line with similar chemical shifts in fluoroaromatics, for example, pentafluorobromobenzene (δ 0.02, −6.02, −56.8).

The preferential coordination of the chromium to the metalated ring is an expected, since this ring will have the highest available electron density due to the iron substituent. The predominant isomer **3a** is that which has the least steric interaction with the cyclopentadienyl ring. In the solid state the fluorine-substituted phenyl ring is twisted away from the cyclopentadienyl ring to minimize steric interaction. The dihedral angle between the two rings of the biphenyl moiety is 55.73°. The distance from Cr to the plane of the η^6-aromatic ring is 1.718 (5) Å, and that from the iron to the cyclopentadienyl ring is 1.723 (7) Å. These are both normal.[15] The η^6-coordinated aryl ring is slightly distorted into a boat shape with the vertices directed away from the chromium atom. The chromium is significantly removed from the position below the centroid of the aryl ring, presumably due to the proximity to the cyclopentadienyl ring. The angles around iron in the piano-stool arrangement are 80.3, 95.8, and 96.8° corre-

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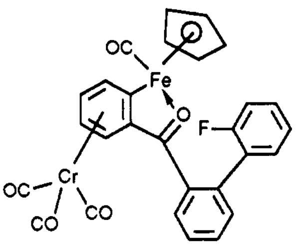
Table III. ***U*(*ij*) Values (×100)**[a]

	U(11)	*U*(22)	*U*(33)	*U*(12)	*U*(13)	*U*(23)
Fe	6.40 (12)	5.85 (11)	3.48 (8)	1.69 (11)	0.80 (8)	0.53 (9)
Cr	6.16 (14)	6.58 (13)	3.25 (10)	−0.07 (11)	0.83 (9)	0.72 (9)
F	10.7 (6)	11.6 (6)	6.6 (4)	−0.4 (5)	2.3 (4)	0.6 (4)
O(1)	12.2 (8)	11.4 (8)	6.9 (5)	−1.0 (6)	2.3 (5)	−2.7 (5)
O(2)	11.1 (8)	9.9 (7)	7.6 (6)	2.2 (6)	0.1 (5)	2.3 (5)
O(3)	6.3 (7)	16.9 (10)	10.2 (6)	−1.6 (6)	2.0 (5)	4.9 (6)
O(4)	12.8 (9)	6.7 (7)	8.8 (6)	−0.5 (6)	−1.9 (6)	0.4 (5)
O(5)	6.3 (5)	6.3 (5)	2.7 (4)	1.1 (4)	1.0 (3)	0.8 (3)
C(1)	6.8 (9)	6.7 (8)	2.9 (6)	2.6 (7)	0.6 (6)	0.3 (6)
C(2)	3.9 (7)	6.1 (8)	3.8 (7)	1.3 (6)	1.7 (5)	0.9 (6)
C(3)	8.8 (10)	5.8 (8)	5.5 (7)	0.5 (7)	1.6 (7)	0.7 (6)
C(4)	7.0 (10)	9.3 (10)	3.7 (7)	−0.8 (8)	0.6 (6)	2.4 (7)
C(5)	8.3 (10)	10.5 (11)	3.5 (7)	1.0 (9)	1.7 (6)	0.3 (8)
C(6)	9.7 (10)	6.9 (9)	4.6 (7)	2.9 (7)	2.8 (7)	0.6 (6)
C(7)	5.8 (8)	5.4 (8)	3.4 (6)	0.3 (7)	0.7 (6)	0.4 (6)
C(8)	4.5 (8)	4.9 (7)	3.6 (6)	0.9 (6)	0.4 (6)	0.7 (6)
C(9)	4.0 (7)	4.8 (7)	3.9 (6)	−0.4 (6)	0.2 (5)	1.4 (6)
C(10)	5.0 (8)	5.6 (8)	5.7 (7)	−0.1 (6)	0.7 (6)	−0.6 (6)
C(11)	6.4 (9)	5.1 (8)	8.0 (9)	2.0 (7)	0.3 (7)	1.7 (7)
C(12)	9.0 (11)	6.9 (10)	6.7 (8)	1.8 (8)	−0.3 (7)	0.2 (7)
C(13)	8.3 (10)	6.4 (9)	5.0 (7)	2.2 (7)	−0.6 (7)	0.5 (6)
C(14)	5.6 (9)	3.6 (7)	3.6 (6)	−0.6 (6)	0.0 (6)	−0.2 (5)
C(15)	4.5 (8)	6.7 (9)	7.3 (8)	0.4 (7)	0.1 (7)	1.0 (6)
C(16)	6.3 (9)	5.3 (8)	9.8 (10)	−0.4 (7)	0.9 (8)	−0.1 (8)
C(17)	10.2 (12)	4.8 (8)	5.9 (8)	0.2 (8)	−1.1 (8)	0.1 (6)
C(19)	8.5 (10)	6.5 (8)	3.2 (7)	−0.6 (8)	−0.4 (7)	0.3 (6)
C(19)	6.3 (10)	5.6 (8)	5.2 (8)	−0.7 (7)	1.8 (7)	−1.1 (6)
C(20)	7.8 (11)	9.3 (12)	8.6 (11)	−2.0 (9)	1.3 (8)	3.7 (9)
C(21)	8.6 (12)	12.9 (14)	5.0 (8)	3.9 (10)	2.4 (7)	1.6 (9)
C(22)	11.3 (13)	7.1 (9)	4.9 (8)	3.5 (9)	0.7 (7)	−0.3 (7)
C(23)	4.3 (8)	9.9 (11)	4.3 (7)	0.7 (8)	1.0 (6)	3.0 (8)
C(24)	10.0 (12)	6.5 (10)	5.3 (8)	2.0 (8)	0.9 (7)	−0.4 (7)
C(25)	7.5 (9)	9.0 (10)	4.8 (7)	−3.3 (7)	1.3 (7)	0.7 (7)
C(26)	7.9 (10)	5.6 (9)	5.4 (8)	0.2 (7)	−1.1 (7)	1.0 (6)
C(27)	2.2 (7)	12.3 (12)	4.3 (7)	1.3 (7)	0.3 (6)	1.2 (7)
C(28)	8.1 (10)	4.6 (8)	5.6 (7)	2.2 (7)	−2.1 (7)	0.3 (7)

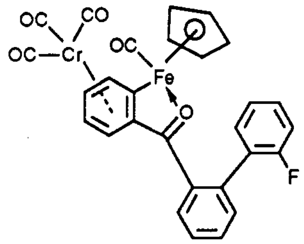
[a] Esd's refer to the last significant digit.

sponding to C(1)–Fe–O(5), C(1)–Fe–C(28), and C(28)–Fe–O(5), respectively. The fused aromatic ring and the metallacycle are distorted slightly from planarity by an angle of 12.23°. The bond distance of the coordinated oxygen to iron is 1.974 Å, which is slightly shorter than those (1.98, 1.99 Å) reported in the cases of related allylacyl complexes.[16]

The structure of the isomeric product **3b** was assigned on the basis of its ^{1}H NMR spectrum, which indicates the same phenyl ring is coordinated to chromium as in **3a**.



3a

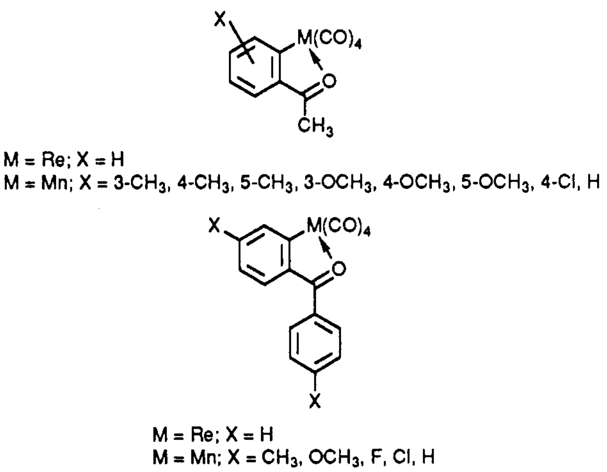


3b

The lower yield is explained by the fact that a greater degree of steric interaction between tricarbonylchromium and the cyclopentadienyl ring would be expected. The exact identity of the third isomer **3c** was not pursued, although clearly it is a compound with the tricarbonylchromium functionality bound to a different aromatic ring.

There exist several related complexes of alkyl and aryl ketones.[17,18] For example Kaesz and co-workers[17] have reported a series of related manganese and rhenium metal carbonyl complexes of acetophenone, benzophenone, and their substituted derivatives, prepared by the direct reaction of the aromatic ketones with σ-bonded methylmetal carbonyls at elevated temperatures (Chart I).

Chart I



We are currently investigating the reaction chemistry of **2** and **3** and the direct synthesis of related complexes by the reaction of activated benzophenones with FpX compounds.

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Note Added in Proof. At the suggestion of a reviewer the generality of the reaction was tested by carrying out the reaction of *o*-FFp with phenyllithium. The dark brown/black product obtained was characterized by mass spectroscopy and ^{1}H NMR as an analogue of **2** with the phenyl group replacing the *o*-fluorobiphenyl moiety. The yield was >90%.

Supplementary Material Available: A table of observed and calculated structure factors (15 pages). Ordering information is given on any current masthead page.

Notes

Mixed Rhenium and Chromium Carbonyl Complexes of Aroylcyclopentadienyl Ligands

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Summary: A series of (aroylcyclopentadienyl)rhenium tricarbonyls ((η^5-$RC_6H_4COC_5H_4$)$Re(CO)_3$, R = H, *o*-CH_3, *p*-CH_3, *p*-OCH_3, *o*-F, *p*-Cl) and their $Cr(CO)_3$ ((η^6-arene)$Cr(CO)_3$) complexes have been prepared and characterized and studied by IR and ^{1}H NMR spectroscopy. The carbonyl stretching frequencies of the $Re(CO)_3$ group and the cyclopentadienyl proton resonances indicate π-electron withdrawal through the ligand system by the $Cr(CO)_3$ group.

Complexes with two or more π-donor sites have been of interest in our laboratory for a number of years. A major reason for studying such complexes has been to determine the extent of electron delocalization through an extended π-system and particularly to study the effect of metal complexation on electron delocalization. All of the complexes reported so far by us have involved only first-row transition metals.

There are many examples in the literature of organometallic complexes with two metal atoms, at least one of which is a second- or third-row element. Almost all of these have the two metal atoms directly bonded, such as $Cp_2Re(H)Mn(CO)_4$,[1] or joined by simple bridging groups such as hydrido and alkenyl.[2] Pyrazine had also been used as a bridging ligand.[3] Another interesting example of a bridging ligand is in $CpCoC_8H_8Mo(CO)_3$, which has two forms, one of which has the metals joined by the cyclooctatetraene ring without a metal–metal bond.[4] None of these compounds have extended bridging ligands, particularly extended π-systems, and hence do not lend themselves to the study of through-ligand metal–metal interaction.

Table I. Elemental Analyses, Melting Points, and Percent Yields of $RC_6H_4COC_5H_4Re(CO)_3$

			C		H	
R	yield, %	mp, °C	found	calcd	found	calcd
H	23.0	97–98	41.16	40.93	2.24	2.06
o-CH_3	37.1	114–115	42.23	42.31	2.47	2.44
p-CH_3	52.7	89–90	42.77	42.31	2.57	2.44
p-OCH_3	23.2	134–135	40.99	40.87	2.52	2.36
o-F	40.0	100–101	39.27	39.32	1.90	1.76
p-Cl	34.0	107–108	39.24	37.96	2.31	1.70

Fulvalene lends itself to the formation of dimetalla complexes, most of which have the metals directly bonded. There are some examples without metal–metal bonding, and some of these involve heavier metals.[5]

Recently Helvenston and Lynch[6] reported three triindenyl complexes in which two or three $Re(CO)_3$ groups are η^5-bonded to the five-membered rings. These molecules do lend themselves to the study of through-ligand metal–metal interaction (or intramolecular metal–metal cooperativity). The report, however, was of only one ligand and involved only one metal, so no comparisons were possible across a series of ligands or between metals.

The most extensive series of complexes with two or more π-donor sites reported so far have been (η^5-aroylcyclopentadienyl)manganese tricarbonyls[7] and their $Cr(CO)_3$ complexes.[8] In this paper the preparation and IR and ^{1}H NMR spectra of similar $Re(CO)_3$ complexes are reported and discussed and the results are compared with those of the corresponding manganese complexes.

Results and Discussion

(Aroylcyclopentadienyl)rhenium tricarbonyls are white crystalline materials with melting points in the range of 97–135 °C (Table I). The C and H analyses are in good

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