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Open Fp Chemistry: Synthesis, Structure, and Chemistry of (2,4-Dimethylpentadienyl)iron Dicarbonyl Iodide

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The syntheses and properties of 2,4-dimethylpentadienyl (2,4-C_7H_{11}) analogues of $(C_5H_5)Fe(CO)_2X$ (Fp) complexes have been investigated. Thus, reaction of $(2,4\text{-}C_7H_{11})Fe(CO)_3^+$ with KI in acetone leads to $Fe(2,4\text{-}C_7H_{11})(CO)_2I$, for which NMR spectroscopy indicates an unsymmetric structure ($\Delta G^\ddagger = 11.45$ kcal/mol). Reduction with sodium amalgam leads to the dimer $[(2,4\text{-}C_7H_{11})Fe(CO)_2]_2$, for which an ESR signal can be observed in solution. An unsymmetric dimer, $[(C_5H_5)Fe(CO)_2][(2,4\text{-}C_7H_{11})Fe(CO)_2]$, can be prepared from the iodide on reaction with $(C_5H_5)Fe(CO)_2^-$. Treatment of the iodide complex with an excess of sodium amalgam leads to the apparent formation of $(2,4\text{-}C_7H_{11})Fe(CO)_2^-$, which can be converted to the thermally unstable liquid $(2,4\text{-}C_7H_{11})Fe(CO)_2(CH_3)$ with CH_3I. Like the analogous iodide complex, this species also exists in an unsymmetric configuration, as indicated by NMR spectroscopy ($\Delta G^\ddagger = 12.75$ kcal/mol). The methyl compound reacts with $P(CH_3)_2(C_6H_5)$ to yield a solid η^1-acyl complex, which is itself thermally converted to at least two other products, which appear to involve acyl–pentadienyl coupling. A single-crystal X-ray diffraction study on $(2,4\text{-}C_7H_{11})Fe(CO)_2I$ has confirmed the unsymmetric coordination environment, in which the iodide and one carbonyl ligand reside under the C(2) and C(4) positions, with the second carbonyl under the open edge of the pentadienyl ligand. The average Fe–CO and Fe–I bond distances are 1.780 (5) and 2.645 (1) Å, while the Fe–C(pentadienyl) bond distances range from 2.100 (6) to 2.158 (8) Å, averaging 2.133 Å. The space group is C_{2h}^5—$P2_1/n$ (No. 14), with $a = 8.034$ (2) Å, $b = 16.589$ (4) Å, $c = 8.485$ (2) Å, $\beta = 91.24$ (2)°, and $V = 1130.7$ (4) Å^3, for $Z = 4$ and $D_{calcd} = 1.96$ g/cm^3. The final agreement indices are $R = 0.037$ and $R_w = 0.031$ for the 1595 independent observed reflections.

A large body of chemistry has been developed for species of the general formula $[(C_5H_5)Fe(CO)_2X]^{n+}$ ($n = 0, 1$), often referred to as Fp (fip) complexes.[3] We have demonstrated that a wide variety of metal-pentadienyl complexes may be synthesized, many of which are quite analogous to known cyclopentadienyl compounds.[4] Often, the chemical reactivity differs markedly from the cyclopentadienyl analogs, however, particularly towards coupling reactions with unsaturated molecules. Thus, attempts to prepare $(2,4\text{-}C_7H_{11})Mo(CO)_3(CH_3)$ (C_7H_{11} = dimethylpentadienyl) led instead to a novel dimeric complex in which the pentadienyl ligand had undergone a coupling reaction of both of its ends to an acyl group.[5] Likewise, the reaction of the "half-open titanocene" complex, $Ti(C_5H_5)(2,4\text{-}C_7H_{11})(PEt_3)$ with acetonitrile also leads to a dimeric complex, in which one end of the pentadienyl ligand has coupled to the quaternary carbon atom of the acetonitrile fragment.[6] It was therefore of interest to explore the syntheses, structures, and reactions of $[(2,4\text{-}C_7H_{11})Fe(CO)_2X]^{n+}$ complexes, which are described herein. Williams and coworkers have recently reported some related compounds involving cyclic dienyl ligands.[7]

Experimental Section

All operations involving organometallics were carried out under a nitrogen atmosphere in prepurified Schlenk apparatus or in a glovebox. Nonaqueous solvents were thoroughly dried and deoxygenated in a manner appropriate to each and were distilled immediately before use. Elemental analyses were performed by Micanal Laboratories. Melting points are uncorrected.

Spectroscopic Studies. Infrared spectra were recorded with a Perkin-Elmer 298 spectrophotometer. Mulls were prepared with dry Nujol in a glovebox. ^1H, ^{13}C, and ^{31}P nuclear magnetic resonance spectra were recorded on Varian EM-360, EM-300, and SC-300 spectrometers. ^{31}P NMR spectra are referenced relative to external H_3PO_4. Mass spectra were performed on a Varian MAT 112 spectrometer at 17 or 70 eV. Except for the parent fragment, peaks are only quoted if their relative intensities are at least 10% of the intensity of the strongest peak.

(2,4-Dimethylpentadienyl)iron Dicarbonyl Iodide. The product was prepared by a modification of a previous procedure, which had been used for the cyclohexadienyl analogue.[8] (2,4-Dimethylpentadienyl)iron tricarbonyl tetrafluoroborate[9] (1.8 g, 5.6 mmol) and potassium iodide (1.0 g, 6.0 mmol) were dissolved in acetone (100 mL) and stirred for 3 h at room temperature. The solution was then evaporated to dryness in vacuo, and the residue was dissolved in benzene (3 × 20 mL), filtered through Celite, and again evaporated. The product (1.65 g, 88%; mp 87.5–89 °C) crystallized as dark red crystals on cooling from toluene–hexane solutions. The C–O stretching vibrations were observed at 2039 and 1984 cm^{-1}. ^1H NMR ($CDCl_3$): δ 6.5 (s, 1 H), 2.5 (s, 8 H), 0.57 (d, 2 H, $J = 4$ Hz). ^{13}C NMR (C_6D_6): δ 214.3 (CO), 114.8 (s), 95.8 (d, $J = 172$ Hz), 56.9 (t, $J = 167$ Hz), 28.3 (q, $J = 129$ Hz). Mass spectrum: m/e (relative intensity) 39 (24), 41 (43), 43 (28), 53

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(19), 55 (43), 56 (28), 59 (15), 67 (26), 69 (13), 77 (17), 79 (37), 81 (19), 83 (12), 91 (14), 93 (18), 95 (54), 96 (20), 97 (33), 107 (11), 121 (18), 135 (15), 139 (100), 140 (10), 148 (31), 144 (20), 151 (18), 179 (13), 183 (18), 276 (29), 278 (32), 306 (20), 334 (3.1). Anal. Calcd for $C_9H_{11}FeIO_2$: C, 32.37; H, 3.32. Found: C, 32.53; H, 3.31.

(2,4-Dimethylpentadienyl)iron Dicarbonyl Dimer. Sodium amalgam (3.0 g, 1%, 1.3 mmol of Na) and the above product (0.40 g, 1.2 mmol) in 25 mL of THF were stirred for 30 min at room temperature. The solvent was removed under reduced pressure and the residue extracted with toluene (3 × 20 mL). The extracts were then filtered and concentrated after which an equal volume of hexane was added. On cooling to −20°, approximately 0.18 g (72%) of the dimer was obtained as dark red crystals, mp 120–121 °C. The C–O stretching modes were observed (as a Nujol mull) at 1970, 1935, 1795, and 1735 cm^{-1}. ^{1}H NMR (C_6D_6): δ 4.0 (s, 1 H), 2.9 (s, 2 H), 1.63 (s, 6 H), 0.7 (s, 2 H). ^{13}C NMR (CD_2Cl_2): δ 218.2 (CO), 114.8 (s), 94.0 (d, J = 169 Hz), 66.0 (t, J = 158 Hz), 25.5 (q, J = 123 Hz). Mass spectrum: m/e (relative intensity) 40 (28), 41 (81), 43 (24), 44 (67), 51 (12), 53 (36), 54 (12), 55 (53), 56 (100), 57 (13), 65 (32), 66 (24), 67 (76), 69 (15), 71 (21), 77 (34), 79 (64), 81 (67), 82 (12), 83 (11), 91 (42), 93 (47), 94 (11), 95 (36), 96 (73), 105 (34), 101 (31), 108 (11), 110 (11), 119 (29), 121 (21), 124 (11), 133 (18), 134 (24), 135 (14), 147 (11), 148 (84), 149 (22), 152 (34), 162 (55), 163 (11), 164 (18), 242 (43), 244 (13), 246 (66), 247 (13), 274 (21), 302 (38), 303 (11), 386 (15), 414 (2.1). Anal. Calcd for $C_{18}H_{22}Fe_2O_4$: C, 52.21; H, 5.36. Found: C, 52.22; H, 5.38.

(Cyclopentadienyl)(2,4-dimethylpentadienyl)diiron Tetracarbonyl. Sodium amalgam (3.5 g, 1%, 1.5 mmol of Na) and (cyclopentadienyl)iron dicarbonyl dimer (0.11 g, 0.31 mmol) in 20 mL of THF were stirred overnight at room temperature. After removal of the excess of the amalgam, 0.20 g (0.60 mmol) of (2,4-dimethylpentadienyl)iron dicarbonyl iodide in 5 mL of THF was added dropwise at −78 °C, then warmed to room temperature, and stirred another hour. The solvent was removed under reduced pressure and the residue extracted with toluene (3 × 15 mL). The extract was then concentrated and an equal volume of hexane added. Upon cooling to −20 °C, 0.20 g (87%) of the product was obtained as dark red crystals, mp 134–135 °C. The CO stretching modes were observed (Nujol mull) at 1965, 1930, and 1748 cm^{-1}. ^{1}H NMR (C_6D_6): δ 4.22 (s, 5 H), 3.78 (s, 1 H), 3.14 (s, 2 H), 1.73 (s, 6 H), 0.86 (s, 2 H). ^{13}C NMR (C_6D_6): δ 217.2 (CO), 211.0 (CO), 114.1 (s), 97.4 (d, J = 157 Hz), 85.8 (d, Cp, J = 176 Hz), 64.7 (t, J = 158 Hz), 24.6 (q, J = 128 Hz). Mass spectrum: m/e (relative intensity) 55 (17), 66 (25), 67 (30), 79 (13), 95 (42), 96 (11), 121 (39), 149 (28), 151 (37), 177 (15), 179 (35), 186 (100), 187 (13), 384 (1.8). Anal. Calcd for $C_{16}H_{16}Fe_2O_4$: C, 50.05; H, 4.20; O, 16.67. Found: C, 49.95; H, 4.14; O, 17.03.

(2,4-Dimethylpentadienyl)methyliron Dicarbonyl. To 17 g of sodium amalgam (1%, 7.4 mmol of Na) in 20 mL of THF was added 0.70 g of (2,4-dimethylpentadienyl)iron dicarbonyl iodide (2.1 mmol) in 5 mL of THF at 0 °C. The mixture was stirred overnight at room temperature. After the excess of the amalgam was removed, 0.4 g of methyl iodide (2.8 mmol) was added at −78 °C. The mixture was stirred and warmed slowly to room temperature, after which the solvent was removed in vacuo, and the residue was extracted with hexane (3 × 15 mL). The extracts were then concentrated and cooled to −78 °C, after which 0.15 g (32%) of the crystalline product was obtained, which melted to a yellow oil by room temperature. The CO stretching modes were observed (neat) at 1999 and 1940 cm^{-1}. ^{1}H NMR (C_6D_6): δ 4.92 (s, 1 H), 2.17 (s, br, 2 H), 1.47 (s, 6 H), 0.28 (s, br, 2 H), −0.29 (s, 3 H). ^{13}C NMR (toluene-d_8, −20 °C): δ 221.7 (CO), 212.3 (CO), 116.8 (s), 109.8 (s), 92.8 (d, J = 162 Hz), 63.5 (t, J = 159 Hz), 59.3 (t, J = 159 Hz), 28.0 (q, J = 127 Hz), 23.9 (q, J = 128 Hz), −4.3 (q, J = 134 Hz). Mass spectrum: m/e (relative intensity) 41 (45), 43 (27), 53 (15), 55 (90), 56 (54), 57 (100), 67 (19), 69 (41), 70 (14), 71 (56), 77 (14), 79 (25), 81 (38), 82 (13), 83 (49), 84 (11), 85 (18), 91 (17), 93 (25), 95 (52), 96 (30), 97 (30), 105 (24), 107 (31), 109 (19), 111 (18), 120 (11), 121 (14), 122 (12), 123 (13), 125 (11), 133 (12), 134 (11), 135 (14), 137 (14), 148 (46), 149 (19), 152 (12), 162 (29), 222.1 (0.9). Anal. Calcd for $C_{10}H_{14}FeO_2$: C, 54.09; H, 6.35. Found: C, 55.53; H, 6.31.

Reaction of $(2,4\text{-}C_7H_{11})Fe(CO)_2(CH_3)$ with $P(CH_3)_2(C_6H_5)$. To 0.20 g (0.90 mmol) of $(2,4\text{-}C_7H_{11})Fe(CO)_2CH_3$ in 20 mL of THF was added 0.12 g (0.87 mmol) of $P(CH_3)_2(C_6H_5)$ by syringe at −78 °C. The reaction solution was warmed to room temperature and continuously stirred for 2 h. After removal of the THF in vacuo, the residue was extracted with hexane (3 × 10 mL). The extracts were concentrated and cooled to −20 °C, and 0.10 g of yellow-brown crystals was isolated (31%). The C–O stretching modes were observed (as a Nujol mull) at 1962, 1912, and 1585 cm^{-1}. ^{1}H NMR (C_6D_6): δ 7–7.5 (m, 5 H), 4.87 (s, 1 H), 2.57 (s, 3 H), 2.49 (s, 1 H), 1.95 (s, 3 H), 1.80 (s, 1 H), 1.71 (d, 3 H, J(P–H) = 9 Hz), 1.63 (s, 3 H), 1.56 (d, 3 H, J(P–H) = 9 Hz), 0.48 (s, 1 H), 0.15 (s, 1 H). Several smaller couplings (≤ ca. 5 Hz) might be present, but they could not be completely resolved. ^{13}C NMR (toluene-d_8, −20 °C): δ 272.9 (d, acyl, J(CP) = 21 Hz), 213.5 (d, CO, J(CP) = 19 Hz), 144.1 (d, aromatic, J(CP) = 41 Hz), 116.4 (s), 111.0 (s), 87.8 (d, J = 162 Hz), 65.9 (t, J = 159 Hz), 61.2 (t, J = 157 Hz), 49.5 (q, J = 128 Hz), 28.6 (q, J = 124 Hz), 25.4 (q, J = 124 Hz), 18.9 (q of d, J = ca. 130 Hz, J(CP) = 31 Hz), 17.5 (q of d, J = ca. 128 Hz, J(CP) = 28 Hz). The three aromatic CH resonances are obscured by the solvent. ^{31}P NMR (toluene-d_8): δ 41.6. Mass spectrum: m/e (relative intensity): 41 (35), 43 (92), 51 (25), 53 (16), 55 (25), 56 (15), 65 (12), 67 (24), 77 (39), 79 (18), 83 (12), 91 (50), 93 (12), 95 (28), 96 (14), 105 (17), 123 (25), 139 (100), 148 (18), 154 (55), 246 (10). No parent fragment was observed. Anal. Calcd for $C_{18}H_{25}FeO_2P$: C, 60.02; H, 7.00; O, 8.88. Found: C, 60.52; H, 7.15; O, 8.94.

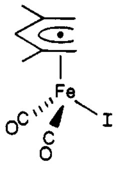
X-ray Diffraction Study of $(2,4\text{-}C_7H_{11})Fe(CO)_2I$. Well-formed single crystals of this compound could be isolated by slowly cooling concentrated solutions in toluene–hexane. Unit cell data were determined from a combination of oscillation photographs and standard Nicolet software programs. Accurate cell constants and their standard deviations were derived from a least-squares refinement of 25 centered reflections using the Mo K$\bar{\alpha}$ peak at 0.71069 Å. The unit cell parameters are a = 8.034 (2) Å, b = 16.589 (4) Å, c = 8.485 (2) Å, β = 91.24 (2)°, and V = 1130.7 (4) Å^3 for Z = 4. Systematic absences uniquely determined the space group as C_{2h}^5—$P2_1/n$ (No. 14).

For data collection, a crystal of approximate dimensions 0.25 × 0.3 × 0.3 mm was selected. Data were collected by using θ–2θ scans in the range 3° ≤ 2θ ≤ 60°, leading to 1818 reflections, of which 1595 unique ones were judged to be observed ($I \geq 2.5\sigma(I)$). All data were processed by using the SHELXTL version 4.1 programs. An empirical absorption correction was applied from psi scan data, leading to a range in relative transmission factors of 0.671–1.000. The calculated linear absorption coefficient is 40.04 cm^{-1}. The function minimized in least-squares refinements was $\sum w(|F_o| - |F_c|)^2$, with $w = 1/\sigma^2(F)$.

The position of the iodine atom was determined from a Patterson map, after which the remaining non-hydrogen atoms were readily located from Fourier maps. After subsequent refinement, the hydrogen atoms were located and subjected to isotropic refinement. Final refinement led to agreement indices of R = 0.037 and R_w = 0.031. A final difference Fourier map revealed no peaks greater than 0.72 e/Å^3, and no unusual intermolecular contacts were observed. In addition to the tables presented herein, tables of thermal parameters, hydrogen atom parameters, and structure amplitudes may be obtained (see supplementary material).

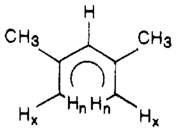
Synthetic and Spectroscopic Results

The reaction of $(2,4\text{-}C_7H_{11})Fe(CO)_3^+$ with KI in acetone leads to a high yield of $(2,4\text{-}C_7H_{11})Fe(CO)_2I$, analogous to the previously reported cyclohexadienyl and cycloheptatrienyl analogues.[8] The deep reddish purple complex can be sublimed in vacuo just above room temperature and can be handled in air for at least brief periods. Spectroscopic characterization proved straightforward and appeared initially consistent with the expected structure I,

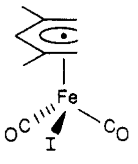


I

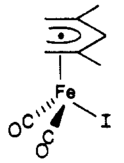
having the large iodine atom located by the open edge of the pentadienyl ligand, so that pseudooctahedral coordination is provided by the three formally changed pentadienyl positions (1, 3, and 5) and the three additional ligands. Thus, four resonances were observed in the ^1H NMR spectrum, but surprisingly they all were noticeably broad, except for that of the hydrogen atom attached to the central carbon atom. This behavior was reminiscent of that of the bis(2,4-dimethylpentadienyl) compounds of titanium, iron, ruthenium, and osmium, all of which possess unsymmetric ground-state conformations, characterized by seven-line ^1H NMR patterns at lower temperatures, yet display symmetric (four-line) ^1H NMR patterns at higher temperatures due to rapid ligand oscillation on the NMR time scale.[10] Indeed, for $(2,4\text{-}C_7H_{11})Fe(CO)_2I$ at low temperatures, further broadening of the H(endo), H(exo), and CH_3 resonances (as in II) was observed, leading to a seven-line pattern by −60 °C (300 MHz). This indicated that the ground-state conformation was unsymmetric, as in III, with the iodine atom actually eclipsing one of the methyl groups. This was subsequently confirmed by X-ray diffraction (vide infra). From the observed coalescence temperatures, a value for $\Delta G^{\ddagger}$ of 11.45 ± 0.1 kcal/mol was determined for the ligand oscillation process,[11] although it could not be ascertained whether the oscillation process involves I or IV as the symmetric intermediate.



II



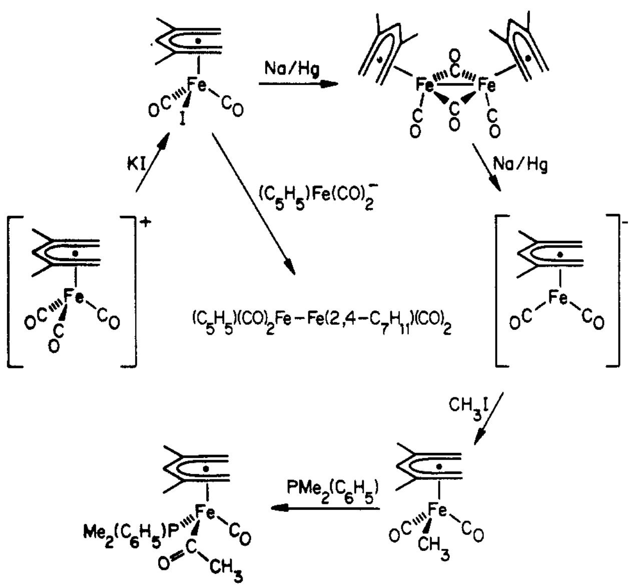
III

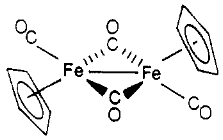


IV

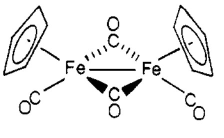
The iodide complex has proven to be very useful as a starting point for further chemistry (Scheme I). Reduction with a slight excess of sodium amalgam led to the formation of the metal–metal bonded dimer $[Fe(2,4\text{-}C_7H_{11})(CO)_2]_2$ in good yield. A Nujol mull infrared spectrum indicated the presence of both terminal (1970 and 1935 cm^{-1}) and bridging (1795 and 1735 cm^{-1}) carbonyl ligands, although the terminal modes seemed more dominant in solution spectra. At least in the solid state, then, the complex probably exists in a form similar to that of $[Fe(C_5H_5)(CO)_2]_2$,[12] e.g., V. Related cyclic η^5-dienyl dimers have also been reported.[13]

Scheme I





Va



Vb

In addition, it was found possible to prepare the unsymmetric dimetallic compound $[Fe(C_5H_5)(CO)_2][Fe(2,4\text{-}C_7H_{11})(CO)_2]$ in good yield from the reaction of the iodide compound 1 with the $Fe(C_5H_5)(CO)_2$ anion. Spectroscopic features for this metal–metal bonded species were similar to those for the symmetric $[Fe(2,4\text{-}C_7H_{11})(CO)_2]_2$ compound, suggesting a related dimeric structure with both bridging and terminal carbonyl ligands, at least in the solid state. Naturally it would be of interest to compare the related metal–metal bond strengths in these complexes with $[Fe(C_5H_5)(CO)_2]_2$, especially given the fact that a much longer bond is found in the open allyl compound $[(C_3H_5)Fe(CO)_3]_2$[14] relative to $[(C_5H_5)Fe(CO)_2]_2$[12] (3.138 (3) vs. ca. 2.51 Å, respectively). While structural data are not yet in hand, there are several indications that the metal–metal bonding in the pentadienyl species is also weaker than that in $[(C_5H_5)Fe(CO)_2]_2$. For example, while no ESR signal is readily detected for a solution of $[(C_5H_5)Fe(CO)_2]_2$ in toluene at room temperature, a strong signal is readily observable for $[(2,4\text{-}C_7H_{11})Fe(CO)_2]_2$, with g = 2.044. Similarly, the metal–metal bond in the unsymmetric complex also appears weak—isolation of the

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[11] (a) $\Delta G^{\ddagger}$ (J/mol) = $19.14(T_c)(9.97 + \log (T_c/\delta\nu))$.[11b] (b) Günther, H. *NMR Spectroscopy*; Wiley: New York, 1980; p 243. (c) The coalescence temperature for the methyl groups is −27 °C for $\Delta\nu$ = 138.5 Hz. For the endo protons, T_c = −18 °C and $\Delta\nu$ = ca. 372 Hz (partly obscured by Me_4Si), while for the exo protons, T_c = −25 °C (very roughly due to CH_3 proximity) and $\Delta\nu$ = 224.4 Hz. For the methyl complex, the barrier could best be determined from the endo protons (T_c = −5 °C and $\Delta\nu$ = 103 Hz) due to the proximity of the exo protons (T_c = 8 °C and $\Delta\nu$ = 256 Hz) to the methyl proton resonances.

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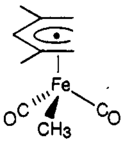
[14] (a) It should be noted that this compound possesses only terminal carbonyl ligands.[14b] (b) Putnik, C. F.; Welter, J. J.; Stucky, G. D.; D'Aniello, M. J., Jr.; Sosinsky, B. A.; Kirner, J. F.; Muetterties, E. L. *J. Am. Chem. Soc.* **1978**, *100*, 4107.

mixed complex from solutions which have been left standing a while leads to contamination by some $[(C_5H_5)Fe(CO)_2]_2$. These solutions also display the same ESR signal as observed for $[(2,4\text{-}C_7H_{11})Fe(CO)_2]_2$. It is quite possible that the presence of open pentadienyl (or allyl) ligands will generally have a weakening effect on metal–metal bonds relative to the cyclopentadienyl ligand. Further structural and theoretical studies should help clarify these observations.

Various organic moieties may also be incorporated into the iron coordination sphere. Treatment of the iodide complex with an excess of sodium amalgam leads to the apparent formation of the $(2,4\text{-}C_7H_{11})Fe(CO)_2$ anion, which is converted to $(2,4\text{-}C_7H_{11})Fe(CO)_2CH_3$ on reaction with CH_3I. The compound could be isolated by low temperature crystallization but melts to an oil below room temperature. The complex is thermally unstable, decomposing on standing at room temperature.[15] In contrast to some other (pentadienyl)metal carbonyl complexes,[16] the C–O stretching vibrations (1940 and 1999 cm^{-1}) were observed at lower frequencies than those for the cyclopentadienyl analogue (1955 and 2010 cm^{-1}).[17] This is, however, more in accord with the observed electron affinities and ionization potentials of the C_5H_5 and C_5H_7 groups.[18] ^1H and ^{13}C NMR spectra provide support for the above formulation, with the metal-bound methyl resonances occurring at −0.29 and −4.3 ppm, respectively (cf. 0.15 and −23.5 ppm for $(C_5H_5)Fe(CO)_2CH_3$[17]). However, while four pentadienyl resonances were observed in the ^1H NMR spectrum at room temperature, all appeared somewhat broad with the exception of the central proton resonance, reminiscent of the behavior of the related iodide compound and again suggesting the presence of an unsymmetric ground state, VI. Indeed, at lower temperatures, the ^1H NMR spectrum exhibited seven resonances for the pentadienyl ligand, indicative of VI, and a value for $\Delta G^{\ddagger}$ of 12.75 ± 0.2 kcal/mol was found for the ligand oscillation process. Also consistent with structure VI was the observation of two carbonyl resonances (221.7 and 212.3 ppm) in the ^{13}C NMR spectrum. That a higher barrier would be observed for the more covalent methyl compound is not surprising, in that a ligand for which the bonding is more polar (i.e., partially ionic) should naturally exhibit less of a directional preference, which could allow for more facile rearrangement of the other ligands.



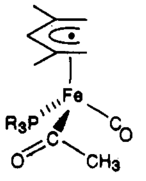
VI

Table I. Comparison of ^{13}C NMR Spectral Data for the Pentadienyl Fragments in VI, the Phosphine Adduct, and X[a]

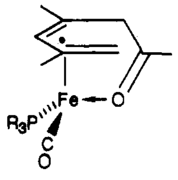
	VI	adduct	X
δ(CO)	212, 222	214	213
δ(C)	110, 117	111, 117	72, 103
δ(CH)	93	88	92
δ(CH_2)	59, 64	61, 66	37, 44
δ(CH_3)	24, 28	26, 29	24, 31
J(CH_2)	159, 159	157, 159	130, 159

[a] Chemical shifts are given in ppm, while coupling constants are in Hz.

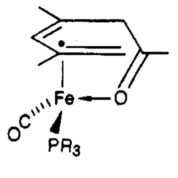
While $(2,4\text{-}C_7H_{11})Fe(CO)_2CH_3$ is somewhat difficult to fully characterize due to its liquid nature and thermal sensitivity, it does react cleanly with $PMe_2(C_6H_5)$ to yield a solid, analytically pure complex of stoichiometry $(2,4\text{-}C_7H_{11})Fe(CO)_2[PMe_2(C_6H_5)]CH_3$ which possesses substantially higher thermal stability than the starting compound, although it too "decomposes" (vide infra) on standing at room temperature. Conceivably, a number of different possible formulations can be considered for the product. Perhaps the simplest possibility would involve accommodating the incorporation of the phosphine ligand by a conversion of the η^5-pentadienyl ligand to an η^3 form. Spectroscopic data clearly excludes this possibility; most notably, while five methyl resonances were observed in both the ^1H and ^{13}C NMR spectra, none were located anywhere near the expected position for a metal-bound methyl group (cf. $(2,4\text{-}C_7H_{11})Fe(CO)_2CH_3$). A variation of this formulation could involve η^3-pentadienyl coordination but conversion of the methyl group and one carbonyl ligand to an η^2-acyl bonding mode. Spectroscopic data, particularly the absence of a C=C stretching mode in the infrared spectrum, also exclude this possibility. At the other extreme, one could envision a three-step coupling reaction taking place, similar to that observed on the attempted preparation of $(2,4\text{-}C_7H_{11})Mo(CO)_3CH_3$.[5] However, the infrared spectrum of the product contained a band at 1585 cm^{-1}, indicative of a C=O linkage, whereas a three-step coupling process would lead to the formation of an alkoxide ligand. Two other possibilities exist, both of which are consistent with the above data. In structure VII, the conversion of the methyl group and a carbonyl ligand to an η^1-acyl ligand allows for the incorporation of the phosphine ligand,[19] while in the VIIIa and VIIIb diastereomers (each present as an enantiomeric pair), coupling has occurred between the acyl group and one end of the pentadienyl ligand, necessitating coordination by the ketonic oxygen atom. Given that a multistep coupling reaction took place spontaneously in $(2,4\text{-}C_7H_{11})Mo(CO)_3C$-



VII



VIIIa



VIIIb

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(15) (a) The related (cycloheptadienyl)$Fe(CO)_2(CH_3)$ has been reported[7b] and is also thermally unstable. An analogue in which a modified alkyl ligand is attached to a cycloheptadienyl ligand has been reported and possesses higher thermal stability,[15b] as does the crystallographically characterized (cycloheptadienyl)$Fe(CO)(P(OC_6H_5)_3)(CH_3)$.[7b] (b) Davis, R. E.; Dodds, T. A.; Hseu, T.-H.; Wagnon, J. C.; Devon, T.; Tancrede, J.; McKennis, J. S.; Pettit, R. *J. Am. Chem. Soc.* **1974**, *96*, 7562.

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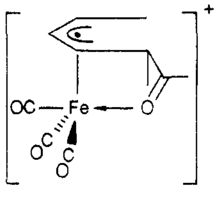
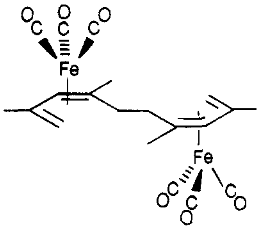
(19) It must be noted that the actual ground state of the acyl complex could involve an alternative conformation. By analogy to the reported structure of (cycloheptadienyl)$Fe(CO)(P(OC_6H_5)_3)(CH_3)$,[7b] it might be expected that the ligand residing under the open pentadienyl edge is actually the unchanged carbonyl ligand. In fact, the ^1H NMR resonances for the methyl compound at low temperature (δ 4.9, 2.6, 1.8, 1.6 (3 H), 1.4 (3 H), 0.5, 0.1, −0.3) are nearly identical with those of the acyl complex, except for (at least) one of the methyl resonances.

H_3, at first glance it appeared most likely that addition of the phosphine ligand to VI would bring about a coupling reaction involving one end of the pentadienyl ligand. However, the C–O stretching frequency of 1585 cm^{-1} is reasonably close to that of 1601 cm^{-1} observed in $(C_5H_5)Fe(CO)(P(C_6H_5)_3)(\eta^1\text{-}COCH_3)$,[20] although not necessarily too much unlike that of 1637 cm^{-1} in IX,[21] which



IX

might be a reasonable model for VIII. However, more revealing is the comparison of the ^{13}C NMR resonances of the phosphine adduct with those in VI and X,[9] the latter



X

one probably providing a reasonable model for the η^4-pentadiene portion in VIII. As can be seen in Table I, the resonances of the adduct differ greatly from those of X but are actually very similar to those in VI. Even more telling are the relative values of the ^{13}C–H coupling constants for the CH_2 groups. For typical pentadienyl complexes such as VI, the value is ca. 159 Hz, whereas for IX, two values are observed, 130 and 159 Hz. A value of ca. 130 Hz is quite normal for a quaternized carbon center, such as that formed by a coupling reaction involving one end of a pentadienyl ligand.[9] The analogous coupling constants observed for the phosphine adduct are 157 and 159 Hz, thereby unambiguously defining its general structure as VII. The presence of a ^{13}C resonance at 272.9 ppm, assigned to metal–acyl carbon atom, provides further support for this formulation (cf. $Fe(C_5H_5)(CO)_2(COCH_3)$, 254.4 ppm[17b,22]). Notably, spectroscopic evidence has been presented for the existence of a related cycloheptadienyl analogue, but the complex was not isolated.[7b]

Interestingly, solutions of the acyl complex at room temperature gradually turn from a bright yellow to a brownish color on standing for a day or so. This same color change takes place for the solid compound, but no change in composition takes place even after standing for an extra day or two.[23] During the solution-phase conversion, the ^{31}P NMR resonance for the acyl complex (41.6 ppm) becomes weaker, while one major (29.6 ppm, 85%) and one minor (28.0 ppm, 15%) resonance grow in. All resonances are in the range expected for coordinated phosphine, and not even traces of free phosphine were observed. The product is more difficult to isolate than the acyl complex,

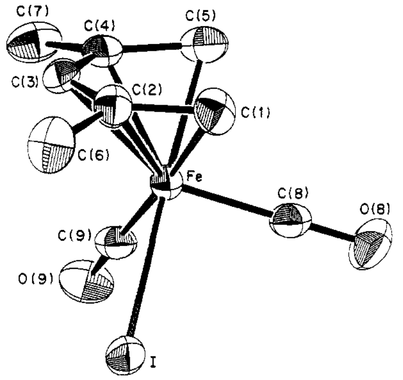


Figure 1. Perspective view and numbering scheme for $(2,4\text{-}C_7H_{11})Fe(CO)_2I$.

Table II. Positional Parameters for the Non-Hydrogen Atoms of $(2,4\text{-}C_7H_{11})Fe(CO)_2I$

atom	x	y	z
Fe	-0.01502 (10)	0.16419 (5)	-0.20522 (9)
I	0.06265 (6)	0.17319 (3)	0.09881 (5)
C(1)	0.2370 (10)	0.1516 (5)	-0.2847 (11)
C(2)	0.1789 (8)	0.0768 (4)	-0.2402 (7)
C(3)	0.0239 (8)	0.0453 (3)	-0.2886 (7)
C(4)	-0.1003 (8)	0.0850 (4)	-0.3825 (7)
C(5)	-0.0740 (9)	0.1597 (4)	-0.4515 (7)
C(6)	0.2753 (9)	0.0292 (4)	-0.1194 (9)
C(7)	-0.2726 (10)	0.0490 (5)	-0.3916 (9)
C(8)	0.5091 (9)	0.2300 (4)	0.2754 (7)
C(9)	-0.2215 (8)	0.1657 (4)	-0.1313 (6)
O(8)	0.5246 (7)	0.1622 (3)	0.2634 (6)
O(9)	-0.3530 (6)	0.1692 (3)	-0.0843 (5)

and the ^1H and ^{13}C NMR spectra are also more complex, in part due to the presence of the minor product. Nevertheless, in the ^{13}C NMR spectrum of this mixture, one can clearly recognize that at least one coupled product is present. Thus, a major new CH_2 resonance at 46.4 ppm has grown in, for which $J(^{13}C\text{–}H) = 126$ Hz, and a minor new CH_2 resonance at 49.0 ppm is characterized by the $J(^{13}C\text{–}H)$ value of 128 Hz. One could speculate that these two resonances might be associated with the two new ^{31}P NMR resonances and that these might be due to species VIIIa and VIIIb. However, the actual formulations of the complexes remain to be established, and further studies employing other phosphine ligands will probably be required.[24]

Crystallographic Results

To confirm the expected unsymmetric structural formulation of $Fe(2,4\text{-}C_7H_{11})(CO)_2I$, a single-crystal X-ray study was undertaken. A perspective drawing and numbering scheme for the structure may been seen in Figure 1, and the atomic positional and thermal parameters are presented in Tables II–IV. Pertinent bond distances and angles and least-squares plane information may be found in Tables V and VI, respectively. It can be seen from Figure 1 that the complex does indeed exist in the expected unsymmetric configuration, with η^5 coordination by the 2,4-dimethylpentadienyl ligand. As indicated in Table VI,

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[20] Forschner, T. C.; Cutler, A. R. *Organometallics* **1985**, *4*, 1247.

[21] (a) Greaves, E. O.; Knox, G. R.; Pauson, P. L. *J. Chem. Soc., Chem. Commun.* **1969**, 1124. (b) Greaves, E. O.; Knox, G. R.; Pauson, P. L.; Toma, S.; Sim, G. A.; Woodhouse, D. I. *Ibid.* **1974**, 257.

[22] Todd, L. J.; Wilkinson, J. R.; Hickey, J. P.; Beach, D. L.; Barnett, K. W. *J. Organomet. Chem.* **1978**, *154*, 151.

[23] Anal. Calcd for $C_{18}H_{25}FeO_2P$: C, 60.02; H, 7.00; O, 8.88. Found: C, 59.63; H, 7.02; O, 9.00.

[24] Should the complex involve coupling at only one end of the pentadienyl ligand, as in VIII, there should remain CH_2 resonances in the ^{13}C NMR spectrum for which larger $J(^{13}C\text{–}H)$ values should be observed. While at least one such resonance was present, it could not be completely established that this did not derive from the starting acyl complex. Thus, at the present time the possibility of coupling of both ends of the pentadienyl ligands cannot be ignored. To resolve this problem, a more rigid phosphine or phosphite will probably need to be employed, so that the various species may be separated from one another. Note that Williams et al. have observed acyl coupling to cycloheptadienyl ligands.[7b]

Table V. Pertinent Bond Distances (Å) and Angles (deg) for $(2,4\text{-}C_7H_{11})Fe(CO)_2I$

Bond Distances

Fe–C(1)	2.158 (8)	Fe–C(5)	2.134 (6)	C(8)–O(8)	1.136 (8)	C(1)–C(2)	1.382 (10)
Fe–C(2)	2.153 (6)	Fe–C(8)	1.774 (7)	C(9)–O(9)	1.139 (7)	C(2)–C(3)	1.403 (9)
Fe–C(3)	2.121 (6)	Fe–C(9)	1.786 (6)	C(2)–C(6)	1.497 (9)	C(3)–C(4)	1.425 (9)
Fe–C(4)	2.100 (6)	Fe–I	2.645 (1)	C(4)–C(7)	1.508 (11)	C(4)–C(5)	1.389 (9)

Bond Angles

I–Fe–C(1)	96.1 (2)	C(8)–Fe–C(5)	88.0 (3)	Fe–C(9)–O(9)	177.9 (9)
I–Fe–C(3)	110.1 (2)	C(9)–Fe–C(1)	174.7 (3)	C(1)–C(2)–C(3)	123.9 (6)
I–Fe–C(5)	178.5 (2)	C(9)–Fe–C(3)	105.9 (3)	C(1)–C(2)–C(6)	119.2 (6)
I–Fe–C(8)	90.6 (2)	C(9)–Fe–C(5)	99.0 (3)	C(3)–C(2)–C(6)	116.6 (6)
I–Fe–C(9)	81.8 (2)	C(1)–Fe–C(3)	70.1 (3)	C(2)–C(3)–C(4)	126.7 (5)
C(8)–Fe–C(9)	97.1 (3)	C(1)–Fe–C(5)	83.1 (3)	C(3)–C(4)–C(5)	122.5 (6)
C(8)–Fe–C(1)	87.8 (3)	C(3)–Fe–C(5)	70.9 (3)	C(3)–C(4)–C(7)	118.4 (6)
C(8)–Fe–C(3)	150.7 (3)	Fe–C(8)–O(8)	179.8 (8)	C(5)–C(4)–C(7)	118.7 (6)

the five backbone carbon atoms for this ligand are planar to within 0.03 Å. The methyl group carbon atoms (C(6) and C(7)), however, are located 0.173 and 0.310 Å out of the ligand plane in a direction toward the iron atom, corresponding to bends of 6.6 and 11.9°, respectively. This is typical of other metal–pentadienyl complexes and appears due to an attempt by the large ligand to improve overlap with the metal orbitals.[25,26] The metal–carbon bond distances for the pentadienyl ligand vary somewhat, being 2.158 (8), 2.153 (6), 2.121 (6), 2.100 (6), and 2.134 (6) Å, respectively, for C(1)–C(5). The clear preference for bonding to the C(4)–C(5) end of the ligand can be attributed to the fact that the C(5) atom is situated opposite to the iodine atom, while C(1) is opposite to a carbonyl ligand, which exerts a much stronger trans weakening influence. The internal carbon–carbon bond distances (C(2)–C(3) and C(3)–C(4)) average 1.414 (6) Å, which appears longer than the average value for the external bonds (C(1)–C(2) and C(4)–C(5)), 1.386 (7) Å. Such differences are normal[25a] and can be correlated with resonance hybrid XI for the pentadienyl anion. Also normal are the relative values of the pentadienyl C–C–C bond angles. As is generally observed, the presence of an attached methyl group brings about a contraction in such an angle.[25] In this case, the C(2)–C(3)–C(4) bond angle is 126.7 (5)°, compared to an average value of 123.2 (4)° for the C(1)–C(2)–C(3) and C(3)–C(4)–C(5) bond angles. Even in the presence of an iodine atom, the hydrogen atom positions could still be refined, leading to C–H bond distances ranging from 0.829 (74) to 1.092 (61) Å, averaging 0.96 (2) Å.

XI

The remaining three ligands are essentially situated in such a way that they complete an approximate octahedron with the formally charged C(1), C(3), and C(5) carbon atoms around the iron atom. In fact, the C(1)–Fe–C(9) and C(5)–Fe–I bond angles are nearly linear (174.7 (3)° and 178.5 (2)°, respectively), but the C(3)–Fe–C(8) bond angle differs noticeably at 150.7 (3)°. This formal distortion from approximate octahedral symmetry should significantly alter the electronic environment of the site under the open pentadienyl edge relative to the sites under C(2) and C(4), and most likely this leads to the preference for the I or CH_3 groups to occupy one of the latter sites.[27] The distortion corresponds to an approximate tilt of the Fe–C(8) bond by 28° toward the pentadienyl ligand, as the Fe–C(8), Fe–C(9), and Fe–I vectors make angles of 133.3, 106.7, and 135.9° with the pentadienyl ligand plane perpendicular. Despite the nonequivalency of the carbonyl ligands, their respective Fe–C and C–O bond distances are essentially identical, averaging 1.780 (5) and 1.138 (5) Å. The Fe–C–O bond angles are nearly linear, averaging 178.8 (5)°.

Discussion

It has proven possible to prepare a variety of Fp analogues, $(2,4\text{-}C_7H_{11})Fe(CO)_2X$, in which the 2,4-dimethylpentadienyl ligand has replaced the cyclopentadienyl ligand. Included in this group are the iodide complex, metal–metal bonded species, and methyl and acyl complexes. A key to the isolation of such complexes seems to be the utilization of the 2,4-dimethylpentadienyl ligand, which, even as an anion, tends to adopt the "U" conformation.[4b,28] In fact, the use of 1,5-disubstituted pentadienyl ligands in similar reactions has been reported to lead to much different products.[7c]

Variable-temperature NMR studies on $(2,4\text{-}C_7H_{11})Fe(CO)_2X$ ($X = I, CH_3$) have demonstrated that both complexes exist in unsymmetric structures, with $\Delta G^\ddagger$ for ligand oscillation equal to 11.45 and 12.75 kcal/mol, respectively. These barriers are in the range observed for various other metal–pentadienyl complexes, e.g., M(pentadienyl)$_2$ (Fe, ca. 8.4–9.15 kcal/mol;[29] Ru, ca. 9.7–10.2 kcal/mol;[30] Os, ca. 13.35 kcal/mol;[31] Ti, ca. 15.3 kcal/mol[32]), and a variety of mono(pentadienyl)metal complexes (9.5–13.4 kcal/mol[33]).[34]

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(25) (a) Ernst, R. D. *Struct. Bonding (Berlin)* **1984,** *57,* 1. (b) Haaland, A. *Acc. Chem. Res.* **1979,** *12,* 415.

(26) H(1A), H(3), and H(5A) are also bent out of the pentadienyl ligand plane toward the iron atom by 0.339, 0.071, and 0.386 Å or 22.6, 4.5, and 20.7°, respectively. The endo hydrogen atoms H(1B) and H(5B) are bent out of the ligand plane away from the iron atom by 0.579 and 0.400 Å or 37.9 and 24.5°, respectively.

(27) (a) The observed geometry may be rationalized as follows. The pentadienyl ligand occupies essentially five positions of a hexagon. The three alternating (charged positions) form the strongest metal–carbon bonds,[27b,c] and hence the other three ligands could be expected to be opposite to them, leading to the octahedral description. However, the other two carbon atoms will also engage in some bonding to the metal, but this will not occur in the unoccupied sixth position, where unused metal orbital density remains. Hence, the ligand opposite the central carbon atom of the pentadienyl ligand could be expected to move somewhat toward the empty sixth position, as is indeed observed. (b) Böhm, M. C.; Eckert-Maksic, M.; Ernst, R. D.; Wilson, D. R.; Gleiter, R. *J. Am. Chem. Soc.* **1982,** *104,* 2699. (c) Böhm, M. C.; Ernst, R. D.; Gleiter, R.; Wilson, D. R. *Inorg. Chem.* **1983,** *22,* 3815.

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(31) Stahl, L.; Ernst, R. D., unpublished results.

(32) Stahl, L.; Wilson, D. R.; Ernst, R. D., unpublished results.

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An X-ray diffraction study has confirmed the unsymmetric nature of the iodide complex.

The thermally unstable complex $Fe(2,4\text{-}C_7H_{11})(CO)_2CH_3$ was found to react readily with dimethylphenylphosphine, leading to an acyl complex. While $(C_5H_5)Fe(CO)_2CH_3$ will also incorporate additional ligands, leading to an acyl, the process requires much more forcing conditions.[3] At first glance it would appear that the greater facility for bringing about η^5–η^3 transformations in pentadienyl complexes has aided the acyl formation by allowing initial phosphine coordination, and a similar conclusion has been reached by Williams et al.[7b] However, the fact that a spontaneous acyl formation and coupling reaction took place on the attempted preparation of $(2,4\text{-}C_7H_{11})Mo(CO)_3CH_3$ indicates that the situation may actually be more complex. It should be noted that in the case of the molybdenum complex, the spontaneous coupling reaction actually led to trialkylation of a carbonyl ligand, thereby converting it to a bridging alkoxide ligand in a dimeric complex.[5] The reason for the much greater facility for coupling in the molybdenum complex is not clear yet but may involve the larger size of the molybdenum atom. A related, but thermally more stable, acyl complex has been reported previously in which the acyl carbon atom is connected to the 2-position of a cyclohexadienyl ligand by a *cis*-C_2H_2 bridge.[35]

As noted above, even the introduction of a dimethylphenylphosphine ligand into the $(2,4\text{-}C_7H_{11})Fe(CO)_2CH_3$ complex did not lead spontaneously to a coupling reaction, but instead to an isolable acyl. However, after 1–2 days of standing, this acyl itself is converted to at least two products, which appear to involve some sort of coupling to the pentadienyl ligand. Unfortunately, the products could not be readily isolated, and their superimposed spectra were too complex to be fully interpreted. Thus, further studies with alternate phosphine ligands will need to be carried out. However, it is apparent that the nonaromatic pentadienyl ligands display a high degree of allyl-like reactivity (such as coupling and naked-metal reactions[4–6a]), even while often behaving structurally very much like the cyclopentadienyl ligand.[25a] It is clear that metal–pentadienyl complexes will prove quite useful in a variety of applications,[36] and our studies in this area are continuing.

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Registry No. $[(2,4\text{-}C_7H_{11})Fe(CO)_3]BF_4$, 103533-90-0; $(2,4\text{-}C_7H_{11})Fe(CO)_2I$, 106251-34-7; $[(2,4\text{-}C_7H_{11})Fe(CO)_2]_2$, 106266-48-2; $[(C_5H_5)Fe(CO)_2]_2$, 12154-95-9; $(2,4\text{-}C_7H_{11})(C_5H_5)Fe_2(CO)_4$, 106251-35-8; $(2,4\text{-}C_7H_{11})Fe(CO)_2Me$, 106251-36-9; $P(CH_3)_2(C_6H_5)$, 672-66-2.

Supplementary Material Available: Listings of the hydrogen atom parameters (Table III), non-hydrogen atom anisotropic thermal parameters (Table IV), and least-squares plane data (Table VI) (3 pages); and the structure amplitude table (10 pages). Ordering information is given on any current masthead page.

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(34) (a) An alternative process, involving initial conversion of the η-pentadienyl ligand to an η^3-bonding mode, seems unlikely, in that the expected trans effect of a methyl ligand should promote such a conversion relative to an iodide ligand. To be consistent with the observed values, such a rotation process for a hypothetical $(\eta^3\text{-}2,4\text{-}C_7H_{11})Fe(CO)_2CH_3$ intermediate would therefore have to have an even greater barrier (relative to the iodide analogue) than just the net 1.3 kcal/mol difference observed. However, such a process has been suggested for some (pentadienyl)manganese phosphine complexes.[33d] (b) Related to the possibility of an η^5–η^3 pentadienyl ligand conversion is the fact that reaction of the iodide complex with NaC_5H_5 leads to a product whose IR and (unsymmetric) ^1H NMR spectra are consistent with the formulation $Fe(C_5H_5)(\eta^1\text{-}2,4\text{-}C_7H_{11})(CO)_2$. The compound is thermally unstable, although other related species have been reported (with similar spectral characteristics).[34c] (c) Lush, S.-F.; Liu, R.-S. *Organometallics* **1986**, *5*, 1908.

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