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Notes

Mono- and Trinuclear Aroyl Complexes of Iron: Crystal Structure of $Hg[Fe\{C(=O)C_6H_3Me_2\text{-}2,6\}(CO)_3(PPh_3)]_2$

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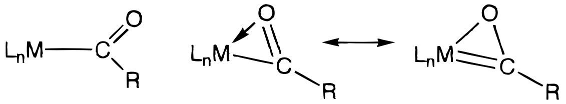
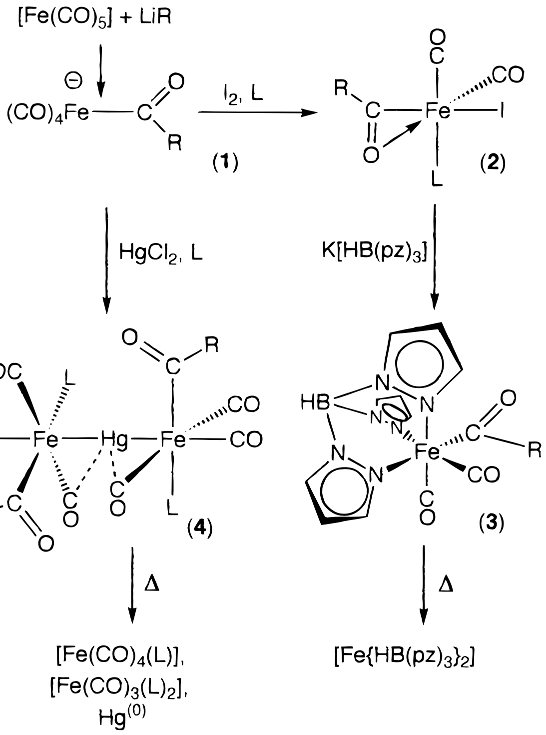
Summary: The reaction of $[Fe(CO)_5]$ *with LiR* ($R = C_6H_3Me_2$-2,6) *provides* $[Fe\{C(OLi)R\}(CO)_4]$*, which reacts with* I_2 *or* $HgCl_2$ *in the presence of* PPh_3 *to provide respectively* $[Fe(\eta^2\text{-}OCR)I(CO)_2(PPh_3)]$ *or* $Hg[Fe\{C(=O)R\}(CO)_3(PPh_3)]_2$*; the latter has been characterized by X-ray diffraction. The reaction of* $[Fe(\eta^2\text{-}OCR)I(CO)_2(PPh_3)]$ *with* $K[HB(pz)_3]$ *(pz = pyrazol-1-yl) leads to* $[Fe\{C(=O)R\}(CO)_2\{HB(pz)_3\}]$ *which is converted thermally to* $[Fe\{HB(pz)_3\}_2]$*.*

The carbamoylferrate complex $[Fe\{C(OLi)N^iPr_2\}(CO)_4]$ reacts with a variety of electrophiles ("E^+") and triphenylphosphine,[2] leading in general to bidentate carbamoyl complexes of the form $[Fe(\eta^2\text{-}OCN^iPr_2)(CO)_2(PPh_3)(E)]$ (E = Br, I, CF_3, $SnPh_3$) or the aminomethylidyne complex $[Fe(\equiv CN^iPr_2)(CO)_3(PPh_3)](O_2CCF_3)$.[3] In general, though not exclusively, electrophilic attack occurs at the iron center rather than the carbamoyl oxygen, although it is the latter site which provides access to alkylidene or alkylidyne ligands.[3] Given the unexpected propensity for bidentate coordination of the carbamoyl ligand to iron(II), we have investigated the suitability of this synthetic methodology for the preparation of aroyl complexes of iron(II), via the reactions of the xyloylferrate $[Fe\{C(OLi)C_6H_3Me_2\text{-}2,6\}(CO)_4]$ (**1**) toward electrophiles. We find that the reactivity of this complex differs substantially from that reported for related acylates derived from the reactions of Collman's reagent $[Fe(CO)_4]Na_2$ and alkyl halides.[4] We describe here (i) the convenient preparation of mononuclear η^2- and η^1-aroyl complexes of iron (Chart 1) and (ii) the preparation and crystallographic characterization of a trimetallic aroyl complex of iron and mercury.

Chart 1. Coordination Modes for Acyl Ligands



Scheme 1[a]



[a] Legend: L = PPh_3; R = $C_6H_3Me_2$-2,6; pz = pyrazol-1-yl.

Iron pentacarbonyl reacts readily with $LiC_6H_3Me_2$-2,6 in diethyl ether to provide in situ $[Fe\{C(OLi)C_6H_3Me_2\text{-}2,6\}(CO)_4]$ (**1**) in high yield (Scheme 1). Soft electrophiles typically attack at the d^8 five-coordinate (and accordingly exposed) iron center of related iron acylates[4,5] and in the case of iodine as an electrophile, reductive elimination leads to the formation of acyl iodides.[4] The reaction of $Li[Fe\{\sigma\text{-}C(=O)C_6H_3Me_2\text{-}2,6\}(CO)_4]$ (**1**) with iodine in the presence of triphenylphosphine, however, provides the thermally stable aroyl complex $[Fe(\eta^2\text{-}OCC_6H_3Me_2\text{-}2,6)I(CO)_2(PPh_3)]$ (**2**), the formulation and stereochemistry (Scheme 1) of which follows from spectroscopic data. In addition to two infrared absorptions arising from the equatorial *cis*-$Fe(CO)_2$ group (CH_2Cl_2: 2028, 1960 cm^{-1}), a band at 1548 cm^{-1} can be assigned to the bidentate aroyl carbonyl. Despite the steric bulk of the xylyl group, this rotates freely on the NMR time scale, as indicated by the appearance of a single methyl resonance, in both the

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^{1}H (δ 2.73) and ^{13}C (22.4 ppm) NMR spectra. Most diagnostic for the presence of the acyl ligand, however, is the doublet ^{13}C resonance at 247.8 ppm (^2J(PC) =16 Hz) to low field of the two chemically distinct carbonyl resonances at 220.4 (^2J(PC) = 28.6 Hz) and 212.8 ppm (^2J(PC) = 17.8 Hz). The gross composition is confirmed by FAB mass spectrometry with the appearance of an isotopic distribution attributable to the molecular ion in addition to a range of assignable fragmentations.

The related compounds [Fe(η^2-OCC$_6$H$_2$Me$_3$-2,4,6)I(CO)(dippe)] (dippe = 1,2-bis(diisopropylphosphino)ethane) and [Fe(η^2-OC^{i}Pr)I(CO)(PEt$_3$)$_2$] have been described previously from alternative routes. The former results from carbonylation of [Fe(C$_6$H$_2$Me$_3$-2,4,6)I(dippe)],[6] while the latter is prepared via the oxidative addition of isopropyl iodide to [Fe(CO)$_3$(PEt$_3$)$_2$].[7] It therefore appears that the bidentate mode of aroyl or acyl ligand coordination for iron(II) is surprisingly favorable. The bidentate aroyl coordination mode is not, however, retained in the reaction of **2** with K[HB(pz)$_3$] (pz = pyrazol-1-yl). The product of the reaction is the monodentate aroyl complex [Fe{C(=O)C$_6$H$_3$Me$_2$-2,6}(CO)$_2${HB(pz)$_3$}] (**3**), resulting from loss of phosphine rather than one carbonyl ligand. Spectroscopic data of note for **3** include (i) an infrared absorption for the monodentate aroyl ligand (CH$_2$Cl$_2$: 1610 cm^{-1}) moved to higher frequency of that for the bidentate ligand in **2** and (ii) a singlet ^{13}C NMR resonance for the aroyl carbonyl (273.9 ppm) to lower field of both the related resonance in the precursor **2** and the two chemically equivalent terminal carbonyl ligands (211.9 ppm). The related acyl complex [Fe{C(=O)Me}(CO)$_2${HB(pz)$_3$}] has been reported to result in 8% yield from the reaction of K[HB(pz)$_3$] with [Fe$_2$(CO)$_9$] and methyl iodide.[8] In contrast to the formation of **3** from **2**, we note that the carbamoyl complex [Fe(η^2-OCN^{i}Pr$_2$)I(CO)$_2$(PPh$_3$)] reacts with K[HB(pz)$_3$] to provide the binuclear compound [Fe$_2$(μ−σ,σ'-OCN^{i}Pr$_2$)$_2$(CO)$_5$(PPh$_3$)][9] rather than the expected analogue of **3** viz. [Fe{C(=O)N^{i}Pr$_2$}(CO)$_2${HB(pz)$_3$}]. The FAB mass spectrum of [Fe{C(=O)C$_6$H$_3$Me$_2$-2,6}(CO)$_2${HB(pz)$_3$}] (**3**) shows a substantially abundant peak for [M − CO]$^+$ due to loss of one terminal carbonyl ligand. This transformation is not, however, reflected in the solution chemistry: all attempts to obtain the aryl complex [Fe(C$_6$H$_3$Me$_2$-2,6)(CO)$_2${HB(pz)$_3$}] by ejection of a carbonyl ligand and subsequent migration of the aryl group from the acyl carbon to iron have so far met with failure. The only characterizable product of thermolysis was identifed as the nonorganometallic complex [Fe{HB(pz)$_3$}$_2$].

The reaction of [Fe{C(OLi)N^{i}Pr$_2$}(CO)$_4$] with mercuric chloride and triphenylphosphine provides [Fe(CO)$_3$(PPh$_3$)$_2$] and [Fe$_2$(μ−σ,σ'-OCN^{i}Pr$_2$)$_2$(CO)$_5$(PPh$_3$)],[9] while the related bimetallic aroyl complex [Fe$_2$(μ−σ,σ'-OCC$_6$H$_3$Me$_2$-2,6)$_2$(CO)$_5$(PPh$_3$)] is obtained as a minor product from the reaction of **1** with trifluoroacetic anhydride and triphenylphosphine. Misguided by the superficial analogy between the aroyl and carbamoyl ferrates, we investigated the reaction of **1** with 0.5 equiv of mercuric chloride and triphenylphosphine, in an attempt to improve the yield of the bimetallic complex. Surprisingly, neither the formation of [Fe$_2$(μ−σ,σ'-OCC$_6$H$_3$Me$_2$-2,6)$_2$(CO)$_5$(PPh$_3$)] nor deposition of elemental mercury was observed. Rather, a trimetallic complex formulated as Hg[Fe{C(=O)C$_6$H$_3$Me$_2$-2,6}(CO)$_3$(PPh$_3$)]$_2$ (**4**) was obtained and yields of up to 94% could be obtained. The aroyl-associated infrared activity indicates η^1 coordination (CH$_2$Cl$_2$: 1597 cm^{-1}), as does the low-field doublet ^{13}C NMR resonance for the aroyl carbonyl at 265.2 ppm (^2J(PC) = 16 Hz). The single ^{31}P NMR resonance for the phosphine (51.3 ppm) shows satellites due to coupling to mercury, the magnitude of which (^2J(HgP) = 193 Hz) is consistent with a *cis*-Hg−Fe−P arrangement. The molecular structure of **4** was established by a single-crystal X-ray diffraction study (Figure 1, Tables 1 and 2). The complex has crystallographic C_2 symmetry with a nonlinear Fe(1)−Hg−Fe(1′) spine (166.77(4)°)[10] with the Hg−Fe(1) separation (2.5973(9) Å) reflecting single-bond character. The two approximately octahedral iron coordination polyhedra subtend

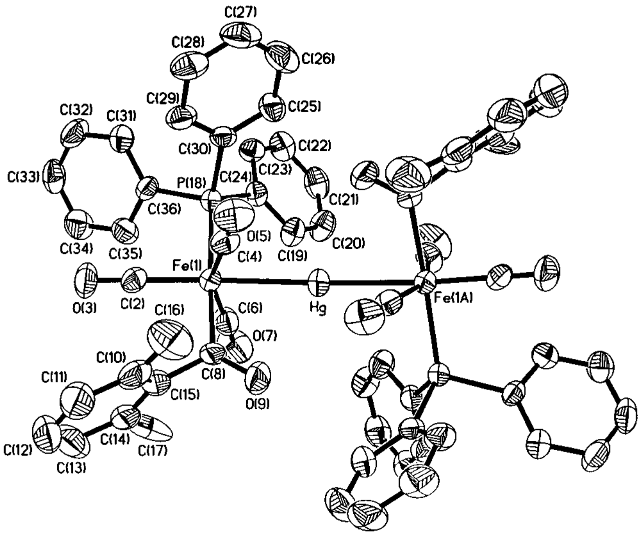

Figure 1. Molecular geometry for **4**. Phenyl groups are omitted for clarity.

Table 1. Crystallographic Data for Hg[Fe{C(=O)C$_6$H$_3$Me$_2$-2,6)(Co)$_3$(PPh$_3$)]$_2$ (4)

formula: C$_{60}$H$_{48}$Fe$_2$HgO$_8$P$_2$	fw = 1271.2
a = 27.844(4) Å	monoclinic
b = 10.138(1) Å	space group: $C2/c$ (No. 15)
c = 21.500(3) Å	λ = 0.710 73 Å
β = 118.73(1)°	μ(Mo Kα) = 35.3 cm^{-1}
V = 5322(1) Å^3	F(000) = 2536
Z = 4	ρ_{calc} = 1.587 g cm^{-3}
R1 = 0.048[a]	wR2 = 0.096[b]
T = 293(2) K	

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$; $w^{-1} = \sigma^2(F_o)^2 + (aP)^2 + bP$.

Table 2. Selected Bond Distances (Å) and Angles (deg) for 4 with Estimated Standard Deviations in Parentheses

Hg−Fe(1)	2.5973(9)	Fe(1)−C(4)	1.790(8)
Fe(1)−C(6)	1.796(8)	Fe(1)−C(2)	1.805(7)
Fe(1)−C(8)	2.051(6)	Fe(1)−P(18)	2.301(2)
C(8)−O(9)	1.208(8)	Hg···C(4)	2.713(7)
Fe(1)−Hg−Fe(1′)	166.77(4)	Hg−Fe(1)−C(4)	74.0(2)
Hg−Fe(1)−P(18)	94.49(5)	Fe(1)−C(8)−O(9)	121.8(5)
Fe(1)−C(8)−C(15)	119.6(5)	P(18)−Fe(1)−C(8)	177.6(2)

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a dihedral angle of 132° between symmetry-related phosphorus atoms on each iron. With no intermetallic multiple bonding, this angle can be assumed to derive from a minimization of steric and packing forces. There is a small degree of multiple bonding reflected in the iron−xyloyl separation (Fe(1)−C(8) = 2.051(6) Å), this being marginally shorter than those typical of alkyl- and aryliron separations and presumably enhanced by the aryl group being inclined by 86° and thus out of conjugation with the C(8) carbonyl group. The orientation of the aroyl carbonyl group is not, however, that which would be expected to maximize Fe−C(8) retrodonation, being aligned rather with an occupied retrodative orbital on iron which is already shared by two π-acidic carbonyl ligands. There is no noticeable trans influence by Hg upon the Fe(1)−C(2) bond length relative to the Fe(1)−C(4) and Fe(1)−C(6) bonds. Both of the mutually trans oriented CO groups are folded toward the bridging mercury atom such that the C(4)−Fe(1)−C(6) angle is contracted to 155.2(3)°. The bending is, however, asymmetric with one of the carbonyl carbons (C(4)) being significantly closer to the mercury center than the other. The associated Hg···C distances are 2.718(7) and 2.935(7) Å for C(4) and C(6), respectively. The reason for this asymmetry is not immediately apparent but probably reflects incipient semibridging character. There are no unusual intermolecular packing interactions.

Surprisingly, prolonged heating of **4** in refluxing toluene provides elemental mercury, $[Fe(CO)_3(PPh_3)_2]$, and $[Fe(CO)_4(PPh_3)]$ rather than $[Fe_2(\mu-\sigma,\sigma'-OCC_6H_3Me_2\text{-}2,6)_2(CO)_4(PPh_3)_2]$, an observation which would appear to exclude such complexes as intermediates in the formation of $[Fe_2(\mu:\sigma,\sigma'-OCC_6H_3Me_2\text{-}2,6)_2(CO)_5(PPh_3)]$. The complexes $Hg[Fe(CO_2R)(CO)_4]_2$ (R = Me, Et) have been described recently as resulting from the reaction of mercuric acetate with $[Fe(CO)_5]$ in alcohols (ROH),[11] and the isolation of **4** would appear to clarify the mechanism for the formation of these complexes.

Experimental Section

General Comments. All manipulations were carried out under an atmosphere of prepurified dinitrogen using conventional Schlenk-tube techniques. Solvents were purified by distillation from an appropriate drying agent (ethers and paraffins from sodium/potassium alloy with benzophenone as indicator; halocarbons from CaH_2). ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded on Bruker WH-400 NMR or JEOL JNM EX270 NMR spectrometers and calibrated against internal Me_4Si (^1H), internal $CDCl_3$ (^{13}C), or external H_3PO_4 (^{31}P). Infrared spectra were recorded using Perkin-Elmer 1720-X FT-IR or Mattson Research Series 1 spectrometers. FAB mass spectrometry was carried out with an Autospec Q mass spectrometer using nitrobenzyl alcohol as matrix. Light petroleum refers to that fraction with bp 40−60 °C. All reagents were commercially available and were used as received from commercial sources (Aldrich), with the exception of $LiC_6H_3Me_2$-2,6, which was prepared as a diethyl solution as described below.

Preparation of $LiC_6H_3Me_2$-2,6. Lithium wire (2.27 g, 0.32 mol, 1% sodium) was cut into a round-bottomed Schlenk flask containing sodium-dried diethyl ether (200 mL) and equipped with a reflux condenser and pressure-equalized dropping funnel. The flask was immersed in an ice bath and 2-xylyl bromide (20 g, 0.11 mol) added dropwise from the funnel over a period of 3 h. When addition was complete, the mixture was stirred at room temperature for a further 2 h to provide a solution approximately 0.40 mol dm^{-3} in $LiC_6H_3Me_2$-2,6.

Preparation of $[Fe(\eta^2\text{-}OCC_6H_3Me_2\text{-}2,6)I(CO)_2(PPh_3)]$ (2). $[Fe(CO)_5]$ (6.0 g, 31 mmol) was diluted in diethyl ether (50 mL) in a Schlenk tube and (2,6- dimethylphenyl)lithium (80 mL, 0.4 mol dm^{-3}, 31 mmol) added dropwise. On completion, the mixture was cooled (dry ice/propanone) and iodine (7.78 g, 31 mmol) added. On warming slightly with stirring, the iodine dissolved, at which point triphenylphosphine (12.2 g, 46 mmol) was added, and the mixture was warmed slowly to room temperature overnight. A dark red precipitate formed, which was isolated by decantation and washing with diethyl ether (2 × 10 mL). Lithium iodide was removed by extraction of the residue with a mixture of dichloromethane and light petroleum (2:1, 3 × 20 mL). The combined extracts were filtered through diatomaceous earth and concentrated to ca. 15 mL under reduced pressure. Cooling (−20 °C) resulted in crystallization of the crude product, which was further purified by column chromatography (silica gel, CH_2Cl_2/hexane eluant). Yield: 17.7 g (90%). IR (CH_2Cl_2) 2028, 1960 (ν_{CO}), 1548 cm^{-1} (ν_{RCO}). IR (Nujol): 2016, 1960 (ν_{CO}), 1571 cm^{-1} (ν_{RCO}). NMR ($CDCl_3$, 25 °C): ^1H, δ 2.73 (s, 6 H, CH_3), 7.11−7.61 ppm (m, 18 H, C_6H_5 and C_6H_3); $^{13}C\{^1H\}$, 247.8 (d, OCR, $^2J(PC) = 16$ Hz), 220.4 (d, FeCO, $^2J(PC) = 28.6$ Hz), 212.8 (d, FeCO, $^2J(PC) = 17.8$ Hz), 143.4 ($C^1(C_6H_3)$), 135.3−126.0 (C_6H_5 and $C^{2-6}(C_6H_3)$), 22.4 ppm (CH_3); $^{31}P\{^1H\}$, 78.8 ppm. FAB-MS (nba matrix): m/z 634 $[M]^+$, 578 $[M - 2CO]^+$, 550 $[M - 3CO]^+$, 507 $[M - I]^+$, 479 $[M - CO, I]^+$, 445 $[FePPh_3I]^+$, 423 $[FePPh_3C_6H_3Me_2]^+$. Anal. Found: C, 55.6; H, 4.0. Calcd for $C_{29}H_{24}FeO_3PI$: C, 54.9; H, 3.8.

Preparation of $[Fe\{C({=}O)C_6H_3Me_2\text{-}2,6\}(CO)_2\{HB(pz)_3\}]$ (3). $[Fe(\eta^2\text{-}OCC_6H_3Me_2\text{-}2,6)I(CO)_2(PPh_3)]$ (**2**; 10.0 g, 16 mmol) and potassium hydridotris(pyrazol-1-yl)borate (3.98 g, 16 mmol) were placed in a Schlenk tube. Tetrahydrofuran (50 mL) was added, and instantaneously the reaction mixture turned from purple to yellow. The mixture was stirred for 15 min, and then the solvent was removed under reduced pressure. The residue was extracted with a mixture of dichloromethane and light petroleum (2:1, 3 × 20 mL), and the combined extracts were filtered through diatomaceous earth. The filtrate was concentrated to ca. 15 mL and cooled (0 °C) to provide the desired product. Yield: 3.91 g (54%). IR (CH_2Cl_2): 2042, 1981 (ν_{CO}), 1610 cm^{-1} (ν_{RCO}). IR (Nujol): 2038, 1978 (ν_{CO}), 1604 cm^{-1} (ν_{RCO}). NMR ($CDCl_3$, 25 °C): ^1H, δ 1.54 (s, 6 H, CH_3), 6.78, 7.02 (d, t, 3 H, C_6H_3), 6.15 (t, 3 H, $H^4(pz)$), 7.31−7.71 ppm (m, 6 H, $H^{3,5}(pz)$); $^{13}C\{^1H\}$, 273.9 (OCR), 211.9 (FeCO), 150.0 ($C^1(C_6H_3)$), 144.5, 142.5 ($C^3(pz)$), 136.1−126.9 ($C^5(pz)$ and C_6H_3), 105.9, 105.7 ($C^4(pz)$), 17.7 ppm (CH_3). FAB-MS (nba matrix): 459 $[M + 1]^+$, 374 $[M - 3CO]^+$, 269 $[FeHB(pz)_3]^+$. Anal. Found: C, 52.1; H, 4.0; N, 18.4. Calcd for $C_{20}H_{19}BFeN_6O_3$: C, 52.4; H, 4.2; N, 18.4.

Preparation of $Hg[Fe\{C({=}O)C_6H_3Me_2\text{-}2,6\}(CO)_3(PPh_3)]_2$ (4). A solution of $[Fe(CO)_5]$ (1.00 g, 5.0 mmol) in diethyl ether (30 mL) was treated dropwise with a diethyl ether solution of (2,6-dimethylphenyl)lithium (13 mL, 0.40 mol dm^{-3}, prepared as above). The mixture was then cooled (dry ice/propanone) and treated with mercuric chloride (0.69 g, 2.5 mmol). The

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mixture was stirred at this temperature for 15 min, treated with triphenylphosphine (2.0 g, 7.5 mmol), and then warmed to room temperature overnight. The yellow precipitate was isolated by decantation and dried *in vacuo*. This was extracted with a mixture of dichloromethane and light petroleum (2:1, 3 × 20 mL), and the combined extracts were filtered through diatomaceous earth. The filtrate was concentrated to ca. 15 mL and stored at −30 °C to provide yellow crystals of the desired product. Yield: 3.0 g (94%). IR (CH_2Cl_2): 2000, 1945 (ν_{CO}), 1597 cm^{-1} (ν_{RCO}). IR (Nujol): 2000, 1937 (ν_{CO}), 1612 cm^{-1} (ν_{RCO}). NMR ($CDCl_3$, 25 °C): ^{1}H, δ 2.38 (s, 6 H, CH_3), 6.93 (m, 3 H, C_6H_3), 7.26−7.47 ppm (m, 15 H, C_6H_5); $^{13}C\{^1H\}$, 265.2 (d, OCR, ^2J(PC) = 16 Hz), 216.4 (d, FeCO, ^2J(PC) = 12.5 Hz), 213.6 (d, FeCO, ^2J(PC) = 14 Hz], 155.2 (d, $C^1(C_6H_3)$, ^2J(PC) = 10.7 Hz), 135.6−125.8 ppm (C_6H_5 and $C^{2-6}(C_6H_3)$), 19.8 ppm (CH_3); $^{31}P\{^1H\}$, 51.3 ppm (^2J(HgP) = 193 Hz). FAB-MS (nba matrix): m/z = 636 $[M]^{2+}$, 535 $[M\text{-}Hg]^{2+}$ or $[Fe(OCC_6H_3Me_2)(CO)_3(PPh_3)]^+$, 507 $[Fe(OCC_6H_3Me_2)(CO)_2(PPh_3)]^+$, 479 $[Fe(OCC_6H_3Me_2)(CO)(PPh_3)]^+$, 423 $[FePPh_3(C_6H_3Me_2)]^+$, 263 $[HPPh_3]^+$. The compound was also characterized crystallographically (vide infra).

Crystal Structure Determination of $Hg[Fe\{C(=O)C_6H_3Me_2\text{-}2,6\}(CO)_3(PPh_3)]_2$ (4). Yellow blocks were obtained by slow diffusion of hexane into a solution of the complex in dichloromethane at room temperature. A crystal of approximate dimensions 0.10 × 0.17 × 0.23 mm was used for the diffraction study. A total of 4688 independent reflections were collected in the ω-scan mode on a Siemens P4/PC diffractometer using Mo Kα radiation to a maximum 2θ value of 50°. Table 1 provides a summary of the crystal data and data collection and refinement parameters for **4**. The structure was solved by the heavy-atom method, and all the nonhydrogen atoms were refined anisotropically using absorption-corrected data (maximum/minimum transmission factors: 0.819/0.569) by full-matrix least squares based on F^2. The methyl hydrogen atoms were located from a ΔF map, optimized, assigned isotropic thermal parameters ($U(H) = 1.5U_{eq}(C)$), and allowed to ride on their parent carbon atoms. The remaining hydrogen atoms were placed in calculated positions, assigned isotropic thermal parameters ($U(H) = 1.2U_{eq}(C)$), and allowed to ride on their parent atoms. The phenyl rings were refined as idealized rigid bodies. Computations were carried out using the SHELXTL PC program system (version 5.03) to give R1 = 0.048, wR2 = 0.096 for 3452 independent, observed reflections ($|F_o| > 4\sigma(|F_o|)$) and 294 parameters. Selected bond lengths and angles are given in Table 2.

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Supporting Information Available: A figure giving an additional view and tables of crystallographic parameters, bond distances and angles, atom coordinates, and thermal parameters for **4** (6 pages). Ordering information is given on any current masthead page.

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