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Synthesis and X-ray Crystal Structures of an Analogous Pair of Iron Formyl and Iron Acetyl Complexes[†]

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The reaction of $K^+HB(O\text{-}i\text{-}Pr)_3^-$ with $Fe(CO)_4[P(OC_6H_5)_3]$ (**9**) and with $Re_2(CO)_{10}$ produced the isolated metal formyl complexes $N(CH_2CH_3)_4^+[trans\text{-}(CO)_3[(C_6H_5O)_3P]FeCHO]^-$ (**1**) and $N(CH_2CH_3)_4^+[cis\text{-}(CO)_9Re_2CHO]^-$ (**3**). Similarly reaction of CH_3Li with **9** gave the analogous acetyl complex $N(CH_2CH_3)_4^+[trans\text{-}(CO)_3[(C_6H_5O)_3P]FeCOCH_3]^-$, **4**. The structures of the closely analogous formyl **1** and acetyl **4** complexes were determined by X-ray crystallography. **1** crystallizes in space group $P2_1/n$ with four molecules in the unit cell of dimensions a = 10.037 (2) Å, b = 18.588 (3) Å, c = 16.292 (4) Å, β = 90.05 (2)°, V = 3039.5 Å^3, R = 0.047, and R_w = 0.057. **4** crystallizes in space group $P2_1/n$ with four molecules in the unit cell of dimensions a = 9.956 (2) Å, b = 19.374 (4) Å, c = 16.180 (3) Å, β = 96.35 (2)°, V = 3101.8 Å^3, R = 0.062, and R_w = 0.082. The structure of formyl complex **1** and acetyl complex **4** are remarkably similar with the exception that the 1.166 (4) Å C=O bond length of the formyl ligand of **1** is substantially shorter than the 1.226 (5) Å C=O bond length of the acetyl ligand of **4**.

The increased cost and decreasing reserves of petroleum have caused renewed interest in the conversion of CO and H_2, derived from coal, into liquid hydrocarbon fuels and into oxygenated chemicals.[1] Metal formyl complexes[2] have been suggested as important intermediates in the hydrogenation of carbon monoxide. Pichler and Schulz suggested that the initial step in the Fischer–Tropsch reaction is migration of a surface metal hydride to a surface-bound CO to give a metal formyl intermediate.[3] While more recent studies indicate that the initial step in the heterogeneously catalyzed Fischer–Tropsch reaction is dissociative CO chemisorption to give surface-bound carbide groups[4] and that surface-bound methylene groups are key intermediates,[1d,5] metal formyl compounds continue to be considered as important intermediates in the homogenously catalyzed hydrogenation of carbon monoxide particularly to oxygenated products.[6]

In 1975, when we began our studies of the synthesis and reactions of metal formyl compounds, the intramolecular migration of hydride from a transition metal to a coordinated CO had never been observed, even under high CO pressure. This seemed very unusual since the corresponding migration of alkyl groups from a transition metal to coordinated CO were well-known to be kinetically rapid and thermodynamically favorable.[7] Even today, $(C_5Me_5)_2Th[\eta^2\text{-}CH{=}O]OR$[8] and (OEP)Rh(CHO)[9] are the only two examples of metal formyl compounds prepared from the corresponding metal hydrides and CO.[10,11]

To gain an understanding of the differences between metal formyl and metal acyl complexes, access to metal formyl compounds was required and synthetic routes other than hydride migration to CO had to be developed. Collman reported the first successful synthesis of a metal formyl compound in 1973 via addition of $Fe(CO)_4^{2-}$ to acetic formic anhydride which produced $(CO)_4Fe(CHO)^-$.[14] However, our early attempts to extend this synthetic procedure to the preparation of metal formyl complexes from $(C_5H_5)Fe(CO)_2^-$, $Cr(CO)_5^{2-}$, $(C_6H_5)_3PMn(CO)_4^-$, and $[(C_6H_5)_3P]_2Mn(CO)_3^-$ were uniformly unsuccessful.[15] More recently, Fiato et al. employed the reaction of $CH_3COO^{13}COH$ with $Mn(CO)_5^-$ to produce $(CO)_5Mn^{13}CHO$ that was too unstable to detect directly but was inferred to be an intermediate which decomposed in situ to produce $(CO)_4(^{13}CO)MnH$.[16a] The anhydride procedure was also used to synthesize $[(MeO)_3P]_2(CO)_3MnCHO$ that is unstable above −30 °C.[16b]

In 1976, we reported that trialkoxyborohydrides react with a range of metal carbonyls to produce metal formyl compounds.[15] Similar observations by Winter[17] and by Gladysz[18] at approximately the same time indicated that

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[†] Dedicated to the memory of Professor Earl Muetterties.

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a wide range of boron and aluminum hydrides could be used to synthesize metal formyl compounds. Hydride addition to metal carbonyl compounds remains the most general synthesis of metal formyl compounds.[2,19] Several cases of intermolecular transfer of hydride from one transition metal to a CO ligand bonded to a second transition metal have now been observed. For example, Labinger reported the formation of an iron formyl intermediate in the reaction of Cp_2NbH_3 with $Fe(CO)_5$;[20] Bercaw reported the reaction of $(C_5Me_5)_2ZrH_2$ with a variety of metal carbonyls;[21] and Dombek has observed hydride transfer from $(CO)_4RuH^-$ to $(C_5H_5)Re(CO)_2NO^+$.[22] Other synthetic routes to metal formyl compounds include reaction of formaldehyde with metal complexes and rearrangement of formaldehyde complexes to metal formyl hydrides.[23,24]

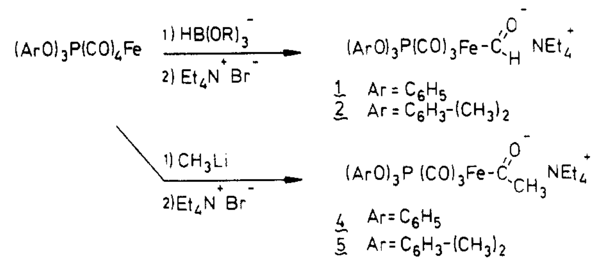
In order to compare the structures, kinetic reactivity, and thermodynamic stability of metal formyl and metal acyl complexes,[25] we set out to prepare a pair of acetyl and formyl complexes in which all other ligands and counterions were identical. Here we report an improved synthesis of metal formyl complexes and the X-ray crystal structures of a precisely analogous pair of formyl and acetyl complexes.

Results

Synthesis of Metal Formyl Compounds. Organolithium reagents react with an extremely wide range of metal carbonyl compounds to produce acyl metal anions. By analogy with these reactions (which are the basis of Fischer's general route to metal–carbene complexes), we decided to investigate hydride addition to metal carbonyls as a new route to metal formyl compounds. Trialkoxyborohydrides were initially chosen since these reagents are powerful hydride donors and the resulting trialkylborates are volatile neutral compounds easily removed from anionic formyl compounds either by washing with solvent or by high vacuum evaporation. Moreover, the trialkoxyborohydrides have only a single active hydride group and we did not have to contend with relative reactivities of a series of hydridic species produced in the course of a reduction. For example, Graham has shown that $(C_5H_5)Re(CO)_2(NO)^+$ can be reduced by BH_4^- under varying conditions to either a formyl-, a (hydroxymethyl)-, or a methylrhenium complex,[26] these results are undoubtedly due to various reducing agents including BH_4^- and BH_3 present in the reaction mixtures.

Initially we employed trimethoxyborohydride for the preparation of metal formyl complexes. Later we found that more rapid rates and higher yields could be obtained by using potassium triisopropoxyborohydride.[15] We obtained NMR evidence for the formation of anionic formyl compounds in the reaction of $K^+HB(O\text{-}i\text{-}Pr)_3^-$ with many metal carbonyls including $Cr(CO)_6$, $W(CO)_6$, $Fe(CO)_5$, $Fe(CO)_4[P(C_6H_5)_3]$, $(CO)_5Cr[P(C_6H_5)_3]$, and $(CO)_5W[P(C_6H_5)_3]$.[15] Gladysz has found that triethylborohydride is another versatile reagent for the synthesis of formyl compounds.[2,9,18]

We have found that iron tetracarbonyl phosphite complexes react with $K^+HB(O\text{-}i\text{-}Pr)_3^-$ to give stable formyl complexes that are readily isolated as tetraethylammonium salts. These formyl complexes are ideal candidates for structural studies and for studies of the kinetic and thermodynamic stability of metal formyl complexes. Reaction of $Fe(CO)_4[P(OC_6H_5)_3]$ with 4 equiv of $K^+HB(O\text{-}i\text{-}Pr)_3^-$ and 2 equiv of $N(CH_2CH_3)_4^+Br^-$ in THF at room temperature led to the isolation of $N(CH_2CH_3)_4^+[trans\text{-}(CO)_3[(C_6H_5O)_3P]FeCHO]^-$ (**1**) as a light tan powder in 90% yield. Solid **1** is extremely air sensitive and is somewhat light sensitive. The thermal decomposition of **1** in THF at 65 °C gave a 3:1 mixture of $(CO)_4FeH^-$ formed by loss of phosphite and hydride migration and $[(C_6H_5O)_3P](CO)_3FeH^-$ formed by loss of CO and hydride migration.[25,30]



In an effort to find a metal formyl compound that would decompose more cleanly and be more amenable to kinetic investigations, we synthesized the related 3,5-dimethylphenyl phosphite complex **2** in the hope that the bulkier phosphite ligand would be a better leaving group in the thermal decomposition of the formyl complex. Reaction of $Fe(CO)_4[(3,5\text{-}(CH_3)_2C_6H_3O)_3P]$ with 4 equiv of $K^+HB(O\text{-}i\text{-}Pr)_3^-$ and 2.5 equiv of $N(CH_2CH_3)_4^+Br^-$ in THF at room temperature led to the isolation of $N(CH_2CH_3)_4^+[trans\text{-}(CO)_3[(3,5\text{-}(CH_3)_2C_6H_3O)_3P]FeCHO]^-$ (**2**) in 90% yield. **2** is extremely air sensitive, and its solutions are unstable under fluorescent lights. This complex with a bulkier phosphite decomposes via selective loss of phosphite and hydride migration.[25a]

Reaction of $Re_2(CO)_{10}$ with $K^+HB(O\text{-}i\text{-}Pr)_3^-$ and $N(CH_2CH_3)_4^+Br^-$ in THF led to the isolation of $N(CH_2CH_3)_4^+[cis\text{-}(CO)_9Re_2CHO]^-$ (**3**). Solid **3** is stable in air but decomposes via a radical chain pathway in the presence of fluorescent lights[27] or free radical initiators.[28]

Spectral Characterization of Metal Formyl Complexes. The far downfield ^1H NMR chemical shifts of the formyl protons of **1** at δ 14.82, **2** at δ 14.88, and **3** at δ 16.04 allowed ready characterization of these metal formyl complexes. In the ^{13}C NMR spectra, the formyl carbon resonance is also seen far downfield at δ 267.5 (d, J_{PC} = 31.7 Hz) for **1**, δ 268.7 (d, J_{PC} = 31.6 Hz) for **2**, and δ 264.2 for **3**. To obtain narrow line widths in the ^{13}C NMR spectrum of **3**, we had to obtain the spectrum at −53 °C where quadrupole broadening by rhenium was diminished.

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Table I. Bond Lengths and Angles of Formyl and Acetyl Groups

	1	2[31]	4	6[9]	7[34]	8[35]
C=O, Å	1.166 (4)	1.166 (6)	1.226 (5)	1.175 (5)	1.181 (11)	1.220 (12)
∠M-C-O, deg	133.0 (3)	133.7 (5)	125.7 (3)	129.6 (5)	130.7 (27)	128.1 (8)
M-COR, Å	1.976 (3)	1.949 (6)	2.006 (4)	1.896 (6)	2.155 (28)	2.055 (10)
ν(C=O), cm^{-1}	1580	1578	1588	1700	1558	1566

As expected for the cis configuration of **3**, five MCO resonances were seen at δ 188.8, 194.4, 199.0 (with shoulder), and 203.2 with relative intensities 0.9:0.8:4.7 (including shoulder):2.5.

The C=O stretch of the formyl ligand in the infrared spectrum was difficult to assign directly due to interferences from aromatic stretches of the phosphite ligand. Bands were seen at 1580 cm^{-1} for **1** and **2** and at 1559 cm^{-1} for **3**. To aid in the assignment of the C=O stretch of the formyl compounds, a randomly ^{13}C-labeled sample of **1** was prepared from 48% ^{13}CO labeled Fe(CO)$_4$[(C$_6$H$_5$O)$_3$P]. This sample had a new band at 1545 cm^{-1} for the H^{13}C=O group (corresponding to 1580 cm^{-1} for H^{12}C=O) and at 1590 cm^{-1} for aromatic C=C.

Synthesis of Metal Acetyl Compounds. Metal acetyl compounds closely analogous to the formyl compounds described above were synthesized so that their structures and thermal stabilities could be directly compared. Reaction of CH$_3$Li with Fe(CO)$_4$[P(OC$_6$H$_5$)$_3$] followed by workup with aqueous basic N(CH$_2$CH$_3$)$_4$$^+Br^-$ gave an 80% yield of N(CH$_2$CH$_3$)$_4$$^+$[*trans*-[(C$_6H_5$O)$_3$P](CO)$_3$FeCOCH$_3$]$^-$ (**4**), which is a light tan, air-sensitive solid. The ^{13}CO stretch of the acetyl ligand of a sample of **4** prepared from 48% ^{13}CO labeled [(C$_6$H$_5$O)$_3$P]Fe(CO)$_4$ was at 1552 cm^{-1} (corresponding to 1588 cm^{-1} for CH$_3$^{12}C=O). The tris(3,5-dimethylphenyl) phosphite analogue N(CH$_2$CH$_3$)$_4$$^+$[*trans*-[(3,5-(CH$_3$)$_2$-C$_6H_3$O)$_3$P](CO)$_3$FeCOCH$_3$]$^-$ (**5**) was prepared in 74% yield by a similar procedure.

X-ray Structural Comparison of Acetyl and Formyl Complexes. We experienced considerable difficulty in obtaining crystal structures of a closely analogous pair of acetyl and formyl complexes. A crystal structure determination of the 3,5-dimethylphenyl phosphite formyl complex **2** was completed in 1978,[25a] but details of the structure were not immediately published[31] because we wanted to compare the structure of **2** with that of the closely analogous acetyl complex **5**. However, although all the atoms were found in the X-ray structure of **5**, disorder problems associated with the N(CH$_2$CH$_3$)$_4$$^+$ ion precluded structural refinement beyond R$_1$ = 0.19 and reliable structural information was not obtained. Attempts to determine the structure of the related compound N(CH$_3$)$_4$$^+$[[(3,5-(CH$_3$)$_2C_6H_3$O)P](CO)$_3$FeCOCH$_3$]$^-$·THF were similarly thwarted by disorder problems. Consequently, we were forced to determine the X-ray structures of the triphenyl phosphite substituted formyl **1** and acetyl **4** complexes to have reliable structural comparisons.

The molecular structures of both the formyl and acetyl complexes consist of discrete tetraethylammonium cations and trigonal-bipyramidal iron anions with axial acyl and phosphite ligands and equatorial carbonyl ligands (Figures 1 and 2). The gross structural features of the formyl and acetyl complexes are remarkably similar. In each structure, the triphenyl phosphite ligand has two phenyl groups roughly in the same plane as the three phosphite oxygens and one phenyl group extended down from the plane of the oxygens. Newman projections down the iron–phosphorus bond show that the three equatorial carbonyl groups in each structure are staggered relative to the oxygens on phosphorus (Figure 3). The plane of the formyl group of **1** is roughly perpendicular (75°) to the unique carbonyl group [(C(5)O(5)] of **1** that is anti to the phosphite oxygen bonded to the phenyl group extending down from the plane of the three phosphite oxygens. The plane of the acetyl group of **4** is roughly perpendicular (84°) to one of two carbonyl groups [C(3)O(3)] of **5** anti to a phosphite oxygen bonded to a phenyl group in the plane of the three phosphite oxygens.

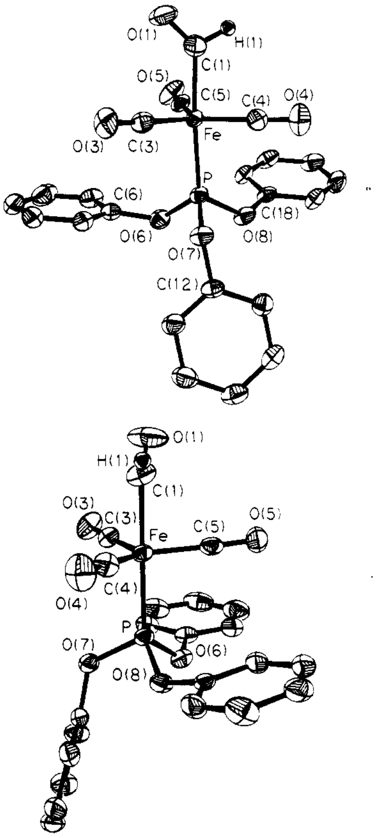

Figure 1. ORTEP drawings of two views of formyl complex **1** with 50% thermal ellipsoids.

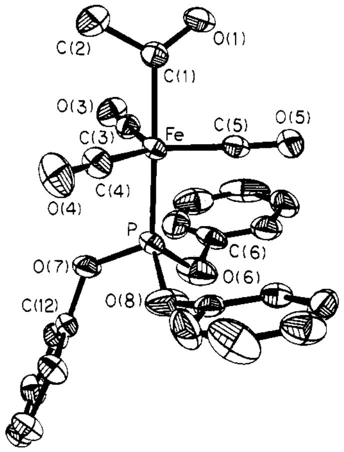

Figure 2. ORTEP drawing of acetyl complex **4** with 50% thermal ellipsoids.

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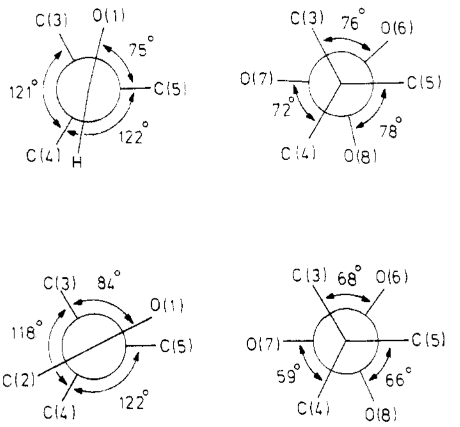

Figure 3. Newman Projections of formyl complex 1 and acetyl complex 4. The upper two are views down the C(1)–Fe and Fe–P bonds, respectively, of formyl complex 1. The lower two are the analogous views for acetyl complex 4.

Table II. Bond Lengths (Å) of 1 and 4

	formyl 1	acetyl 4
C(1)-H,C(2)	1.02 (6)	1.518 (6)
Fe-P	2.124 (1)	2.117 (1)
Fe-C(3)	1.774 (3)	1.765 (4)
Fe-C(4)	1.769 (3)	1.777 (4)
Fe-C(5)	1.756 (3)	1.773 (4)
C(3)-O(3)	1.153 (3)	1.163 (5)
C(4)-O(4)	1.161 (3)	1.158 (5)
C(5)-O(5)	1.166 (3)	1.159 (5)
P-O(6)	1.635 (1)	1.639 (1)
P-O(7)	1.617 (1)	1.597 (1)
P-O(8)	1.623 (1)	1.639 (1)
O(6)-C(6)	1.404 (3)	1.434 (6)
O(7)-C(12)	1.409 (3)	1.390 (5)
O(8)-C(18)	1.382 (3)	1.365 (6)
mean phenyl C-C	1.381	1.369
mean N-C for NEt$_4^+$	1.517	1.518
mean C-C for NEt$_4^+$	1.508	1.509

Bond lengths and angles for 1 and 4 are listed in Tables I–III. Other than for the acyl groups, the bond lengths (Å) and angles (deg) are remarkably similar: the average CO bond length for the carbonyl groups of both 1 and 4 are 1.160; the average Fe–CO bond lengths are 1.766 for 1 and 1.771 for 4; the average P–O bond lengths are 1.624 for 1 and 1.625 for 4; the Fe–P distances are 2.124 for 1 and 2.117 for 4.

Differences between bond lengths and angles in the acyl ligands of 1 and 4 (Table I) should be related to intrinsic differences between the formyl and acetyl groups since the structures of the remainder of these molecules is so similar. The Fe–C–O angle of the formyl group of 1 is 133.0 (3)°, this is 7.3° wider than the Fe–C–O angle of the acetyl ligand of 4 which is 125.7 (3)°. While the C–O bond of the acetyl group of 4 is 1.226 (5) Å and is similar to that of other acyl C–O bonds,[32] the C–O bond of the formyl group of 1 is surprisingly a full 0.06 Å shorter than that of the acetyl group. As seen in Figure 1, the thermal parameter of the oxygen atom of the formyl ligand is largest in the direction approximately perpendicular to the FeC(1)O(1) plane. (For O(1), B_{11} = 4.77, B_{22} = 3.97, and B_{33} = 8.41; for C(1), B_{11} = 3.17, B_{22} = 2.72, and B_{33} = 4.42.) The possibility that the apparently short formyl CO bond length is caused by thermal motion was considered. With use of a riding model[33] for the formyl oxygen atom of 1, a 0.038 Å longer carbon–oxygen bond length of 1.204 Å was calculated; for comparison, a riding model calculation for the acetyl oxygen of 4 gave a 0.021 Å longer carbon oxygen bond of 1.247 Å. Even with use of these riding model corrections, the formyl C–O bond is 0.043 Å shorter than the acetyl C–O bond. Short formyl C=O bond lengths have been found in at least three other crystal structures of metal formyl complexes. We found a 1.166 (6) Å formyl C=O bond length for the related tris(3,5-dimethylphenyl) phosphite substituted formyl complex 2.[25a,31] Wayland reported a 1.175 (5) Å formyl C=O bond length for the (octaethylporphyrin)rhodium formyl complex 6.[9] Cole-Hamilton found a 1.181 (11) Å formyl C=O bond length for $[Os(CHO)(CO)(Ph_2PCH_2CH_2PPh_2)_2]^+SbF_6^-$ (7).[34]

Table III. Bond Angles of 1 and 4

	formyl 1	acetyl 4
Fe-C(1)-H,C(2)	117 (3)	118.5 (3)
O(1)-C(1)-H,C(2)	109 (3)	115.8 (4)
P-Fe-C(1)	176.2 (1)	177.3 (1)
P-Fe-C(3)	96.2 (1)	94.2 (1)
P-Fe-C(4)	89.7 (1)	88.5 (1)
P-Fe-C(5)	94.6 (1)	94.9 (1)
C(1)-Fe-C(3)	87.2 (1)	83.2 (2)
C(1)-Fe-C(4)	87.0 (1)	92.2 (2)
C(1)-Fe-C(5)	85.4 (1)	86.9 (2)
C(3)-Fe-C(4)	120.6 (1)	118.3 (2)
C(3)-Fe-C(5)	116.2 (1)	119.5 (2)
C(4)-Fe-C(5)	122.1 (1)	121.6 (2)
Fe-C(3)-O(3)	176.9 (3)	178.1 (2)
Fe-C(4)-O(4)	179.0 (3)	177.6 (2)
Fe-C(5)-O(5)	178.2 (2)	178.3 (2)
Fe-P-O(6)	120.9 (1)	123.1 (1)
Fe-P-O(7)	116.2 (1)	114.1 (1)
Fe-P-O(8)	120.9 (1)	122.3 (1)
P-O(6)-C(6)	123.8 (2)	120.1 (3)
P-O(7)-C(12)	125.6 (2)	130.1 (3)
P-O(8)-C(18)	128.3 (2)	128.6 (3)
O(6)-P-O(7)	102.7 (1)	105.7 (1)
O(7)-P-O(8)	96.2 (1)	95.6 (1)
O(6)-P-O(8)	95.1 (1)	90.7 (1)

The shortness of the formyl CO bonds in 1, 2, 6, and 7 needs to be interpreted cautiously. Gladysz has found a somewhat longer 1.220 (12) Å formyl C=O length in $(C_5H_5)(NO)(PPh_3)ReCHO$ (8).[35] Moreover, the low stretching frequency of the formyl group of 1 at 1580 cm^{-1} is unexpected for such a short C–O bond and is approximately the same as the 1587 cm^{-1} frequency for the longer C–O bond of the acetyl group of 4. Interestingly the (porphyrin)rhodium formyl complex 6 has a short formyl C—O bond length but a higher frequency C=O stretch at 1700 cm^{-1}. Apparently, there is little correlation between metal acyl CO bond lengths and stretching frequencies.

The differences in the CO bond lengths between X–C(O)–H and X–C(O)–CH_3 is large when X = Fe, but for organic molecules where X = H or even π-electron donor groups such as X = NH_2 or OH, there is little difference in the CO bond lengths of the formyl and acetyl moieties.[36]

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[36] Bond lengths (Å) determined in the gas phase by electron diffraction or microwave spectroscopy are as follows: CH_2=O, 1.208 (3);[37] CH_3CHO, 1.216 (2);[38] $HCONH_2$, 1.212 (3);[39] CH_3CONH_2, 1.220 (3);[40] HCO_2H, 1.217 (3);[41] CH_3CO_2H, 1.214 (3).[42]

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In considering reasons for the relatively short formyl C–O bond and for the relatively wide formyl Fe–C–O angle, we note that anionic iron formyl complexes are excellent hydride donors capable of transferring hydride to ketones, alkyl halides, and metal carbonyl compounds.[2,30] In these reactions the formyl ligand is converted to a linear carbonyl ligand with a shortened C–O bond. We suggest that the short formyl C–O bond length and the wide Fe–C–O angle may be indicative of the hydride donor ability of the formyl ligand.

While the C–O bond of the formyl group is apparently shorter than that of the acetyl ligand, we do not wish to overemphasize the small structural differences between the two ligands. The structures of formyl complex 1 and acetyl complex 4 are strikingly similar, and structural differences cannot account for the reluctance of metal hydrides to undergo CO insertion reactions. The greater strength of M–H bonds compared to $M-CH_3$ bonds is the major factor that makes CO insertion into an M–H bond substantially less thermodynamically favored than insertion into an $M-CH_3$ bond.[2,25]

Experimental Section

General Data. All reactions were carried out in flame-dried glassware under nitrogen, and transfers of solutions were made under positive nitrogen pressure by using either syringes or hypodermic stainless steel tubing (cannula). Iron formyl complexes 1 and 2 are particularly air sensitive and were handled only in Schlenk glassware on a vacuum line or in an inert-atmosphere glovebox. Solvents were distilled from sodium and benzophenone prior to use. Infrared spectra were recorded on Perkin-Elmer 267, Beckman 4230, or Digilab FTS-20 instruments using NaCl solution cells. ^1H NMR spectra were recorded on either a JEOL MH-100 (100-MHz) or a Bruker WH-270 (270-MHz) spectrometer. ^{13}C NMR spectra were recorded on either a JEOL FX-200 (50.10-MHz) or a Varian XL-100 (25.16-MHz) spectrometer. Proton-decoupled ^{31}P NMR (80.76 MHz) spectra were obtained on a JEOL FX-200 spectrometer. ^{31}P chemical shifts are referenced in parts per million from 85% H_3PO_4; downfield chemical shifts are recorded as positive.

Tris(3,5-dimethylphenyl) phosphite (8) was prepared by a modification of a procedure for the preparation of $P(OC_6H_5)_3$.[43] PCl_3 (8.75 mL, 0.10 mol) in 40 mL of hexane was added slowly to a stirred suspension of 3,5-dimethylphenol (36.7 g, 0.30 mol) and *N,N*-diethylaniline (47.7 mL, 0.30 mol) in 200 mL of hexane at 0 °C. After the addition was completed, the mixture was refluxed for 1 h, cooled, and filtered to remove *N,N*-diethylaniline hydrochloride. The solution was concentrated, filtered through a short plug of alumina, and cooled to −22 °C to produce white crystals of 8 (29.1 g, 74%): mp 50–52 °C; ^1H NMR (CS_2) δ 2.24 (s, 6 H), 6.66 (s, 3 H); ^{31}P NMR (THF) δ 130.1; IR (hexane) ν(C=C) 1614 (m), 1591 (m) cm^{-1}; mass spectrum calcd for $C_{22}H_{27}O_3P$ 394.1698, found 394.1692.

$Fe(CO)_4[P(OC_6H_5)_3]$ was prepared as described by Shriver:[44] mp 67–68 °C (lit. 66–69 °C); IR (hexane) (relative intensity) 2061 (0.51), 1998 (0.46), 1965 cm^{-1} (1.00).

^{13}CO-Labeled $Fe(CO)_4[P(OC_6H_5)_3]$. ^{13}CO (375 mL, 660 mmHg, 90% ^{13}C, 13.4 mmol, Mound Laboratories) was added to a 400-mL quartz flask containing a degassed solution of $Fe(CO)_4[P(OC_6H_5)_3]$ (1.45 g, 3.0 mmol) in 25 mL of THF. The solution was irradiated for 20 h in a Rayonet photochemical reactor equipped with both 254- and 350-nm lamps. Labeled $Fe(CO)_4[P(OC_6H_5)_3]$ (0.46 g, 31%) was isolated by column chromatography (alumina–hexane): IR (hexane) (relative intensity): 2056 (0.13), 2047 (0.21), 2041 (0.19), 2027 (0.13), 2014 (0.10), 1987 (0.19), 1984 (0.17), 1966 (0.95), 1955 (0.25), 1942 (0.68), 1920 m^{-1} (1.00); mass spectrum for natural abundance $Fe(CO)[P(OC_6H_5)_3]^+$, *m/e* (intensity) 395 (0.25), 394 (1.00), labeled $Fe(CO)[P(OC_6H_5)_3]^+$, 396 (0.28), 395 (1.00), 394 (0.84) (this corresponds to 48% probability that any CO in $Fe(CO)_4[P(OC_6H_5)_3]$ is ^{13}C labeled); mass spectrum for natural abundance $Fe(CO)_3[P(OC_6H_5)_3]^+$, *m/e* (relative intensity) 451 (0.26), 450 (1.00), labeled $Fe(CO)_3[P(OC_6H_5)_3]^+$, 453 (0.63), 452 (1.00), 451 (0.84), 450 (0.42) (this corresponds to a 50% probability that any CO in $Fe(CO)_4[P(OC_6H_5)_3]$ is ^{13}C labeled).

$Fe(CO)_4\{P[OC_6H_3\text{-}3,5\text{-}(CH_3)_2]_3\}$ (10). Following a procedure similar to that of Siegel,[45] $Fe(CO)_5$ (10.4 mL, 77.3 mmol), 8 (20.6 g, 52.3 mmol), and $LiAlH_4$ (1.3 g, 33.4 mmol) were refluxed in 200 mL of THF for 5 days. Filtration through a short plug of alumina followed by column chromatography (alumina, hexane) and crystallization from hexane at −20 °C gave 10 (15.28 g, 52%); mp 90–94 °C; ^1H NMR ($CDCl_3$) δ 2.30 (s, 6 H), 6.90 (s, 3 H); IR (THF) 2060 (m), 1991 (m), 1958 (s), 1617 (m), 1589 (m) cm^{-1}; $^{31}P\{^1H\}$ NMR (THF-d_8) δ 173.0; mass spectrum calcd for $C_{28}H_{27}FeO_7P$ 562.0843, found 562.0839.

$N(CH_2CH_3)_4^+$[*trans*-$(CO)_3[(C_6H_5O)_3P]Fe(COCH_3)]^-$ (4). CH_3Li (1.78 mL, 1.5 M, 2.67 mmol) was added via syringe to a solution of $Fe(CO)_4[P(OC_6H_5)_3]$ (0.96 g, 2.0 mmol) in 20 mL of ether at −72 °C. The solution was stirred for 30 min at 0 °C, and then a solution of $N(CH_2CH_3)_4^+Br^-$ (0.84 g, 4.0 mmol) in aqueous NaOH (8.0 mL, 0.5 M, 4 mmol) was added. The light tan solid that precipitated was collected by filtration, washed with H_2O (2 × 10 mL) and hexane (2 × 15 mL), and dried in vacuo to give 4 (1.00 g, 80%): mp 109–112 °C dec (sealed tube); ^1H NMR (270 MHz, THF-d_8) δ 6.8–7.4 (m, 15 H), 3.42 (q, J = 7.2 Hz, 8 H), 2.36 (s, 3 H), 1.33 (tt, J = 7.2 Hz, J_{NH} = 1.8 Hz, 12 H, NCH_2CH_3); ^{13}C NMR (50.1 MHz, THF-d_8, 0.07 M $Cr(acac)_3$) δ 268.9 (d, J_{PC} = 33.0 Hz, $FeCOCH_3$), 229.7 (d, J_{PC} = 25.6 Hz, CO), 153.8 (d, J_{PC} = 6.6 Hz, ipso), 129.4 (s, meta), 123.9 (s, para), 122.8 (d, J_{PC} = 3.3 Hz, ortho), 53.2 (s, NCH_2), 51.2 (d, J_{PC} = 25.7 Hz, $FeCOCH_3$), 7.8 (s, NCH_2CH_3); ^{31}P NMR (80.8 MHz, THF-d_8) δ 189.9; IR (THF) 1958 (w), 1870 (s), 1858 (s) cm^{-1}. Anal. Calcd for $C_{31}H_{38}NO_7PFe$: C, 59.72; H, 6.14; N, 2.25; Fe, 8.96. Found: C, 59.98; H, 6.30; N, 2.42; Fe, 8.82.

^{13}C-labeled 4 was prepared from ^{13}C-labeled $Fe(CO)_4[P(OC_6H_5)_3]$: IR (THF) 1968 (m), 1935 (w), 1808 (2), 1861 (m), 1846 (s), 1827 (vs), 1779 (w), 1727 (w), 1590 (m, aromatic C=C), 1552 (w, CH_3C=O) cm^{-1}.

$N(CH_2CH_3)_4^+$[*trans*-$(CO)_3[(3,5\text{-}(CH_3)_2C_6H_3O)_3P]FeCOCH_3]^-$ (5). Addition of CH_3Li (2.7 mL, 1.5 M, 4.05 mmol) to **10** (1.34 g, 2.38 mmol) followed by workup with $N(CH_2CH_3)_4^+Br^-$ as described for **4** gave **5** (1.24 g, 74%): mp 117–119 °C dec (sealed tube); ^1H NMR (acetone-d_6) δ 1.28 (tt, J = 7.7 Hz, J_{NH} = 1.5 Hz, 12 H, NCH_2CH_3), 2.25 (s, 18 H, $(CH_3)_2C_6H_3$), 2.39 (s, 3 H, $FeC(O)CH_3$), 3.37 (q, J = 7.7 Hz, 8 H, NCH_2CH_3), 6.74 (s, 3 H, para), 6.94 (s, 6 H, ortho); IR (THF); 1955 (w), 1868 (s), 1855 (s), 1589 (m, CH_3CO) cm^{-1}; ^{13}C NMR (CD_3CN; 0.07 M $Cr(acac)_3$) δ 7.8 (s, NCH_2CH_3), 21.6 (s, $(CH_3)_2C_6H_3$)), 51.9 (d, J_{PC} = 24.2 Hz, $FeC(O)CH_3$), 53.5 (s, NCH_2CH_3), 121.2 (d, J_{PC} = 4.4 Hz, ortho), 127.0 (s, para), 140.7 (s, meta), 154.4 (d, J_{PC} = 5.5 Hz, ipso), 222.7 (d, J_{PC} = 26.4 Hz, FeCO), 272.3 (d, J_{PC} = 33.2 Hz, $FeC(O)CH_3$); ^{31}P NMR (acetone-d_6) δ 187.8.

Anal. Calcd for $C_{37}H_{50}FeNO_7P$: C, 62.81; H, 7.12; N, 1.97. Found: C, 62.27; H, 7.26; N, 2.00.

$N(CH_2CH_3)_4^+$[*trans*-$(CO)_3[(C_6H_5O)_3P]Fe(CHO)]^-$ (1). $K^+HB(OCH(CH_3)_2)_3^-$ (8 mL, 1.0 M in THF, 8.00 mmol) was added to a 50 mL-flask equipped with a sidearm and stopcock. The flask was connected to a vacuum line, and the solvent was evaporated under high vacuum, leaving an oily residue. The flask was taken into an inert-atmosphere glovebox, and **9** (0.96 g, 2 mmol), $N(CH_2CH_3)_4^+Br^-$ (0.84 g, 4 mmol) and 15 mL of THF were added. The heterogeneous mixture was stirred under nitrogen for 40 min, and then degassed NaOH (8 mL, 1 N, 8 mmol) was syringed into the golden suspension, which led to evolution of gas and formation of two distinct layers. THF was slowly evaporated under high vacuum to give an oily brown solid and an aqueous layer. Diethyl

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Table IV. Summary of Crystal Data and Intensity Collection

parameter	acetyl 4	formyl 1
empirical formula	$FePO_7NC_{31}H_{38}$	$FePO_7NC_{30}H_{36}$
cryst dimens, mm	0.20 × 0.25 × 0.80	0.25 × 0.30 × 0.55
temp, °C	−70 ± 5	−105 ± 5
cell parameters		
a, Å	9.956 (2)	10.037 (2)
b, Å	19.374 (4)	18.588 (3)
c, Å	16.180 (3)	16.292 (4)
β, deg	96.35 (2)	90.05 (2)
V, Å^3	3101.8	3039.5
space group	$P2_1/n$	$P2_1/n$
Z	4	4
D(calcd), g/cm^3	1.34	1.33
radiatn	graphite-monochromated Mo Kα ($\bar{\lambda}$ = 0.710 73 Å)	
abs coeff, μ, mm^{-1}	0.532	0.543
scan range, deg below $2\theta_{K\alpha_1}$	0.7	0.8
deg above $2\theta_{K\alpha_2}$	0.7	0.8
scan rate, deg/min	2.0–24.0	2.0–24.0
2θ limits, deg	3.5–54.9	3.5–54.9
$(\sin\theta)/\lambda_{max}$, Å^{-1}	0.649	0.649
unique data, theor	7109	6966
obsd, $F_o > 3\sigma(F_o)$	4693	4842

ether (10 mL) was distilled into the flask, and the mixture was stirred rapidly to give a light tan solid together with the ether and aqueous layers. The H_2O and ether were removed via cannula. The remaining solid was washed twice with ether and dried in vacuo to give 1 (1.10 g, 90%), mp 90–94 °C dec. (sealed tube). 1 is a light tan powder that decomposes rapidly in air and slowly in light: ^{1}H NMR (THF-d_8) δ 14.77 (d, J_{PH} = 44.9 Hz, 1 H), 6.4–7.3 (m, 15 H), 3.21 (q, J = 7.2 Hz, 8 H), 1.18 (tt, J = 7.2 Hz, J_{NH} = 1.8 Hz, 12 H); ^{13}C NMR (THF-d_8) δ 7.6 (s, NCH_2CH_3), 53.0 (s, NCH_2CH_3), 122.6 (d, J_{PC} = 4.9 Hz, ortho), 124.3 (s, para), 129.6 (s, meta), 153.5 (d, J_{PC} = 6.1 Hz, ipso), 220.3 (d, J_{PC} = 24.4 Hz, FeCO), 267.5 (d, J_{PC} = 31.7 Hz, Fe*C*HO); ^{31}P NMR (THF-d_8) δ 189.4 (d, J_{PH} = 44 Hz); IR (THF) 1964 (w), 1876 (vs), 1580 (m, C_6H_5, and formyl CH=O), 2515 (w, formyl CH) cm^{-1}.

Anal. Calcd for $C_{30}H_{36}FeNO_7P$: C, 59.12; H, 5.95; Fe, 9.16; N, 2.30; P, 5.08. Found: C, 58.37; H, 6.05; Fe, 9.66; N, 2.02; P, 4.90.

^{13}C-labeled 1 was prepared from ^{13}C-labeled $Fe(CO)_4(P(OC_6H_5)_3)$: IR (THF) 1958 (w), 1937 (w), 1913 (w), 1866 (m), 1854 (s), 1832 (vs), 1590 (m, aromatic C=C), 1545 (m, (H^{13}C=O)) cm^{-1}.

$N(CH_2CH_3)_4^+[$*trans*-$(CO)_3[(3,5-(CH_3)_2C_6H_3O)_3P]Fe(CHO)]^-$ (2) was prepared from $K^+HB(OCH(CH_3)_2)_3^-$ (8 mL, 1.0 M in THF, 8 mmol), 10 (1.16 g, 2.06 mmol), and $N(CH_2CH_3)_4^+Br^-$ (1.14 g, 5.42 mmol) as described for 1 above. 2 (1.29 g, 90%) was isolated as a light tan, air- and light-sensitive powder: mp 84–87 °C dec (sealed tube); ^{1}H NMR (THF-d_8) δ 1.10 (tt, J = 7.7 Hz, J_{NH} = 1.52 Hz, 12 H), 2.26 (s, 18 H) 3.14 (q, J = 7.7 Hz, 8 H), 6.71 (s, 3 H, para), 6.92 (s, 6 H, ortho), 14.88 (d, J_{PH} = 44.4 Hz, 1 H, FeCHO); ^{13}C NMR (THF-d_8, 0.08 M $Cr(acac)_3$) δ 8.0 (s), 21.4 (s, $CH_3C_6H_3$), 53.5 (s), 120.4 (d, J_{PC} = 3.61 Hz, ortho), 125.4 (s, para), 138.7 (s, meta), 153.5 (d, J_{PC} = 6.4 Hz, ipso), 220.7 (d, J_{PC} = 24.4 Hz, FeCO), 268.7 (d, J_{PC} = 31.6 Hz, FeCHO); IR (THF) 1958 (w), 1872 (vs), 1617 (w), 1588 (m, aromatic C=C), 1578 (m, CH=O), 2510 (w, formyl CH) cm^{-1}.

$N(CH_2CH_3)_4^+[$*cis*-$(CO)_9Re_2(CHO)]^-$ (3). Since 3 was found to be very sensitive to fluorescent light, it was prepared in a dark room. A solution of $K^+HB[OCH(CH_3)_2]_3^-$ (3 mL, 0.48 M in THF, 1.44 mmol) was slowly added to a suspension of $Re_2(CO)_{10}$ (0.65 g, 1.0 mmol) and $N(CH_2CH_3)_4^+Br^-$ (0.21 g, 1.01 mmol) in 1 mL of THF at 0 °C. The mixture was stirred for 20 min at 0 °C, 5 mL of 1 N aqueous NaOH was added, and THF was evaporated under vacuum to give a light yellow solid and an aqueous solution. The resulting air-stable solid was collected by filtration and washed with water and hexane to give 0.73 g of a yellow solid that contained 20% $N(CH_2CH_3)_4^+[$*cis*-$(CO)_9ReH]^-$ in addition to 3 (^{1}H NMR analysis). Recrystallization from 0.6 mL of THF and 0.6 mL of hexane at −20 °C gave 3 (0.25 g, 32%) as a yellow solid that decomposed at 86–135 °C without melting: ^{1}H NMR (THF-d_8) δ 1.32 (tt, J = 7.2 Hz, J_{NH} = 1.5 Ha, 12 H, NCH_2CH_3), 3.40 (q, J = 7.2 Hz, 8 H, NCH_2CH_3), 16.04 (s, 1 H, ReCHO); IR (THF) 2084 (w), 2066 (m), 2015 (s), 1979 (s), 1949 (wm), 1899 (wm), 1559 (w, HC=O) cm^{-1}; ^{13}C NMR (THF-d_8, −53 °C, 0.07 M $Cr(acac)_3$) δ 7.6 (NCH_2CH_3), 52.1 (NCH_2CH_3), 188.8, 194.4, 199.0, 203.2 (relative intensity 0.9, 0.8, 4.7, 2.5 ReCO); 264.2 (ReCHO). Higher-resolution ^{13}C NMR spectra (−57 °C) of this sample resolved the signal at δ 199.0 into two resonances separated by 3.6 Hz.

Anal. Calcd for $C_{18}H_{21}NO_{10}Re_2$: C, 27.58; H, 2.70; N, 1.79; Re, 47.51. Found: C, 26.34; H, 2.49; N, 1.40; Re, 48.66.

X-ray Data Collection. Single crystals of $N(CH_2CH_3)_4^+[$*trans*-$(CO)_3[(C_6H_5O)_3P]Fe(COCH_3)]^-$ (4) and $N(CH_2CH_3)_4^+[$*trans*-$(CO)_3[(C_6H_5O)_3P]Fe(CHO)]^-$ (1) were grown by vapor diffusion of hexane into tetrahydrofuran solutions. Single crystals of both compounds were mounted in thin-walled glass capillaries for the diffraction studies. The data sets were collected on a Syntex-Nicolet P$\bar{1}$ four-circle diffractometer equipped with a modified LT-1 low-temperature device. Unit cell parameters were obtained from least-squares refinements based on the setting angles of 60 relections collected at $\pm 2\theta$ ($|2\theta| \approx 28°$) at the same temperature as the data collection. The dimensions of the crystals, the unit cell parameters, and other crystal data are listed in Table IV. Delauney cell reductions did not reveal any hidden symmetry.

Intensity data were collected with the crystals used for the preliminary examinations. Details of the intensity measurements are given in Table IV. Four standard reflections from diverse regions of reciprocal space were measured every 50 reflections throughout data collection to monitor long-term stability. There were no significant trends for either compound. Structure amplitudes and their standard deviations were calculated from the intensity data by procedures similar to those described previously.[46] Absorption corrections were applied by using a psi curve method.

The structures were solved by direct methods using the MULTAN package.[47] The positions of the iron, phosphorus and some of the carbon and oxygen atoms were revealed by the E maps, and the rest of the non-hydrogen atoms were located by subsequent electron density difference maps. The segmented full-matrix least-squares refinements of the structures were based on F_o and used the reflections with $F_o > 3\sigma(F_o)$. Both structures were initially refined to convergence by using isotropic thermal parameters for the non-hydrogen atoms. Difference electron density maps revealed plausible positions for nearly all the hydrogen atoms. All hydrogen atoms (except the formyl hydrogen) were included as fixed contributors in idealized positions [d(C–H) = 0.95 Å; $B_H = B_C + 1.0$]. Atomic form factors for the non-hydrogen atoms were taken from Cromer and Waber,[48] anomalous dispersion corrections for iron and phosphorus from Cromer and

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Liberman,[49] and the form factor for hydrogen from Stewart, Davidson, and Simpson.[50] In the final cycles of refinement all non-hydrogen atoms were assumed to vibrate anisotropically.

The formyl hydrogen atom parameters were refined in the final cycles of refinement of the formyl complex 1. The final values of the discrepancy indices were $R_1 = \sum||F_o| - |F_c||/\sum|F_o| = 0.047$ and $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2} = 0.057$ for 1. The estimated standard deviation of an observation of unit weight was 1.61, with a final data/variable ratio of 13.3. The final difference electron density map was featureless. The final values of the discrepancy indices for 4 were $R_1 = 0.062$, $R_2 = 0.082$, and the estimated standard deviation of an observation of unit weight = 2.31. The final data/variable ratio was 12.7. There were no significant features on the final difference electron density map.

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Registry No. 1, 60606-70-4; 2, 70459-98-2; 3, 92641-73-1; 4, 92641-75-3; 5, 92641-77-5; 8, 36432-47-0; 9, 18475-06-4; 10, 92641-78-6; $N(CH_2CH_3)_4{}^+[cis\text{-}(CO)_9ReH]^-$, 92669-26-6; PCl_3, 7719-12-2; $Fe(CO)_5$, 13463-40-6; $Re_2(CO)_{10}$, 14285-68-8; (3,5-dimethylphenyl)phenol, 108-68-9.

Supplementary Material Available: Tables of final atomic coordinates, listings of the observed and calculated structure factors (×10), the coordinates and thermal parameters for the fixed hydrogen atoms, and the anisotropic thermal parameters for both compounds (51 pages). Ordering information is given on any current masthead page.

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Crystal and Molecular Structure of the $[\{(C_6H_5)_3P\}_2N]^+$ Salt of $[Fe_4(CO)_{13}]^{2-}$. A Structural Isomer of the Anion along a Valence Tautomeric Coordinate[1]

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The complex $[Et_4N]_2[Fe_4(CO)_{13}]$, 1, is synthesized in 74% yield by thermolysis of $[Et_4N][HFe_3(CO)_{11}]$ for 48 h in tetrahydrofuran solution. The [PPN] salt, $[PPN]^+ = [\{(C_6H_5)_3P\}_2N]^+$, is isolated by precipitation with [PPN][Cl]. Due to differences in the carbonyl absorptions between these materials and salts containing other cations isolated in the past, a structure determination was undertaken on a single crystal of the title compound at 115 K. Data were collected on a Syntex P$\bar{1}$ automated diffractometer using graphite-monochromatized Mo Kα radiation. The salt crystallizes in space group $R\bar{3}$ with $a = b = c = 18.039$ (7) Å, $\alpha = \beta = \gamma = 81.51$ (3)°, $V = 5694$ (4) Å^3, $Z = 3$, $\rho_{obsd}(298\ K) = 1.48$ (1) g cm^{-3}, and $\rho_{calcd}(115\ K) = 1.46$ g cm^{-3}. Phenyl group atoms of the cation were refined as rigid bodies. All nongroup atoms were located by using standard direct methods, Fourier, and least-squares techniques. The final discrepancy indices are $R_F = 5.94\%$ and $R_{wF} = 5.29\%$ for 2369 independent reflections having $I > 3\sigma(I)$ in the range $0° < 2\theta < 50°$. Two tetrahedra of iron atoms each face capped by one carbonyl group are symmetry related and ordered; the third tetrahedron of iron atoms similarly capped is disordered, lying on the crystallographic center of symmetry. The iron interactions are all bonding, ranging from 2.545 (2) to 2.610 (2) Å. The principal features of the molecular structure are the (symmetry related) M–C–O angles of 172.1 (9)° in the basal plane of the iron tetrahedron and the long nonbonded Fe–C(O) contacts in the range 2.62–2.82 (1) Å. These parameters denote a significant departure from the semibridging observed in the structure of the $[Fe(py)_6]^{2+}$ (py = pyridine) salt of the title anion determined earlier. The occurrence of a new conformer in the solid must be due to a rather shallow and perhaps flat barrier in the coordinate involving fluxional processes of the basal carbonyl groups in the cluster anion. Appropriately, at –90 °C the ^{13}C NMR of 1 shows rapid equilibration of all but one (presumably the face capping) carbonyl groups.

Introduction

Recent studies with salts of the $[HFe_3(CO)_{11}]^-$ anion[2] in refluxing tetrahydrofuran revealed its conversion within 48 h, in approximately 75% yield, to a species with a relatively simple absorption pattern in the infrared; for the $[Et_4N]^+$ salt, in acetonitrile solution (cm^{-1}): 2020 (w), 1949 (vsbr), 1896 (sh), 1772 (vvw), 1635 (vw). Further heating beyond this period leads (after another 48 h) to $[Fe_6C(CO)_{16}]^{2-}$ as the only anion in solution, evidenced by a single broad carbonyl infrared absorption at 1968 cm^{-1} (CH_3CN).[3] We reasoned that the principal species after 48 h of heating would be one of intermediate nuclearity, i.e., Fe_4 or Fe_5,[4] but the carbonyl IR pattern cited above corresponded to no published spectrum for a carbonylferrate anion.[5] We were thus led to determine its structure.

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[5] Among the various references perused are those containing spectra of tetra- and pentanuclear cations.[4,5a–e] Comparisons between spectra of salts of air-sensitive anions that cannot be purified by chromatographic means is very tenuous. Low-yield preparations are thus susceptible to contamination by impurities, hence the advantage of a high-yield route for spectroscopic characterization. An even better synthesis has become known since the completion of the present work; see ref 10. (a) Hsieh, A. T. T.; Mays, M. J. *J. Organomet. Chem.* **1972**, *37*, C53. (b) Hieber, W.; Lipp, A. *Chem. Ber.* **1959**, *92*, 2075. (c) Edgell, W. F.; Yang, M. T. B.; Bulkin, J.; Bayer, R.; Koizumi, N. *J. Am. Chem. Soc.* **1965**, *87*, 3080. (d) Razuvaev, G. A.; Petukhov, G. G.; Ermolaev, V. I.; Beketov, V. P. *Zh. Obshch. Khim.* **1967**, *37*, 672. (e) Farmery, K.; Kilner, M.; Greatrex, R.; Greenwood, N. N. *J. Chem. Soc. A* **1969**, 2339.

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