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Reactions of undecacarbonyltriferrate with α,β-unsaturated acyl halides. Decomposition of $[\mu_3\text{-RCH=CHCOOCFe}_3(\text{CO})_{10}]^-$ to $[\eta^2\text{-RCH=CHFe}_2(\text{CO})_7]$ involving transfer of the acyl group from oxygen to iron

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Abstract

$[\text{PPN}]_2[\text{Fe}_3(\text{CO})_{11}]$ (PPN = bis(triphenylphosphine)iminium) (**1**) reacts with α,β-unsaturated acyl halides in CH_2Cl_2 at 25°C during 15 min to give $[\text{PPN}][\mu_3\text{-RCH=CHCOOCFe}_3(\text{CO})_{10}]$ (**2a, 2b**) (**2a**: $R = CH_3$, **2b**: R = Ph), which slowly decomposes to give $[\text{PPN}][\eta^2\text{-RCH=CHFe}_2(\text{CO})_7]$ (**4a, 4b**) (**4a**: $R = CH_3$, **4b**: R = Ph) and $Fe(CO)_5$ in CH_2Cl_2 at room temperature. Complex **1** also reacts with alkyl halides in tetrahydrofuran at 25°C to give $[\text{PPN}][\mu_3\text{-RCOFe}_3(\text{CO})_9]$ (**6a–6c**) (**6a**: $R = CH_3$, **6b**: $R = PhCH_2$, **6c**: $R = C_2H_5$) in high yields.

Introduction

Reactions of metal carbonyl anions with alkylating or acylating agents provide a convenient route to metal σ-alkyl or -acyl complexes [1–6]. For example, reactions of the mononuclear anion $[\text{Fe(CO)}_4]^{2-}$ with alkyl halides (RX) or acyl halides (RCOX) give the corresponding mononuclear complexes, $[\text{RF(CO)}_4]^-$ or $[\text{RC(O)Fe(CO)}_4]^-$ [5,7–9]. A dinuclear anion $[\text{Fe}_2(\text{CO})_8]^{2-}$ reacts with CH_3I and CH_2I_2 to give $[\text{Fe}_3(\mu_3\text{-CH}_3\text{CO})(\text{CO})_9]^-$ [10*] and $CH_2Fe_2(CO)_8$ [11], respectively. The trinuclear dianion $[\text{Fe}_3(\text{CO})_{11}]^{2-}$ is expected to react with carboelectrophiles to give either $[\mu_3\text{-ROCFe}_3(\text{CO})_{10}]^-$ or $[\text{RFe}_3(\text{CO})_{11}]^-$ (eq. 1). Shriver reported that electrophilic attack of $ROSO_2F$ or CH_3COCl on $[\text{PPN}]_2[\text{Fe}_3(\text{CO})_{11}]$ [PPN = bis(triphenylphosphine)iminium] occurs selectively at the oxygen atom of the bridging carbonyl to give $[\text{PPN}][\mu_3\text{-ROCFe}_3(\text{CO})_{10}]$ ($R = CH_3$, C_2H_5 or CH_3CO) [12]; however, no electrophilic attack by carboelectrophiles on the iron atom of $[\text{Fe}_3(\text{CO})_{11}]^{2-}$ has so far been reported.

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* Reference number with asterisk indicates a note in the list of references.

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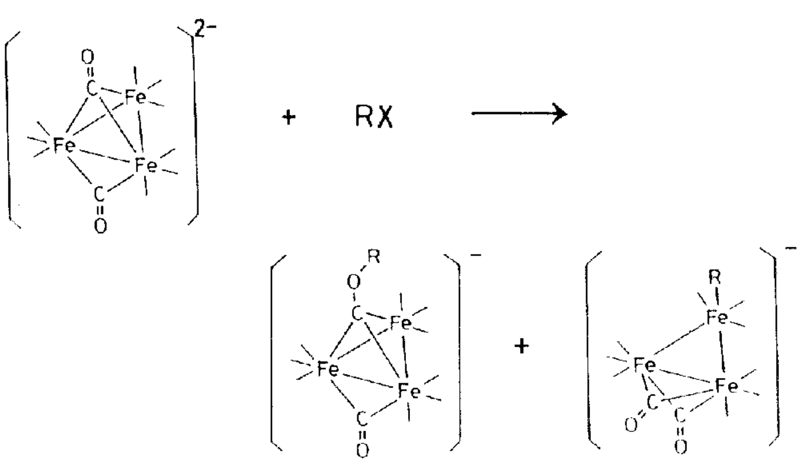


(1)

In the course of our studies on the chemistry of acyl carbonyl ferrates [13–16], we have been interested in preparing trinuclear α,β-unsaturated acyl iron complexes. This paper deals with the reaction of $[Fe_3(CO)_{11}]^{2-}$ with α,β-unsaturated acyl halides, which involves the unusual transfer of α,β-unsaturated acyl group from an oxygen atom to the iron atom. The reactions with alkyl halides are also described here.

Results and discussion

Reaction of $[PPN]_2[Fe_3(CO)_{11}]$ with α,β-unsaturated acyl halides. When trinuclear dianion complex $[PPN]_2[Fe_3(CO)_{11}]$ (**1**) was treated with crotonoyl chloride in CH_2Cl_2 at 25 °C for 15 min, **1** reacted completely and the IR spectrum of the reaction mixture [2054(w), 2000(vs), 1971(s) (ν(C≡O)), 1734(w,ν(C=O)), 1655 cm^{-1} (w,ν(C=C))] showed the formation of $[PPN][\mu_3\text{-}CH_3CH{=}CHCOOCFe_3(CO)_{10}]$ (**2a**). Work-up of the reaction mixture, however, resulted in the decomposition of a large amount of **2a** and the regeneration of **1**, as confirmed by the IR spectrum; pure 2a was isolated only in 8% yield after repeated recrystallization. When the reaction time was prolonged to 48 h, IR absorptions of **2a** could no longer be detected and only those for $[PPN][\eta^2\text{-}CH_3CH{=}CHFe_2(CO)_7]$ (**4a**) (for the structure for **2a** and **4a**, see below) and $Fe(CO)_5$ were observed. The complex **4a** was isolated in 14% yield by column chromatography on silica gel followed by recrystallization. $Fe(CO)_5$ was formed in 80% yield which was confirmed by the characteristic absorption at 243 nm of the volatiles above the reaction mixture. The conversion of **2a** into **4a** and $Fe(CO)_5$ was monitored by NMR spectroscopy. Complex **2a** in CD_2Cl_2 under an atmosphere of argon was subjected to ^{13}C NMR spectroscopy at 24 °C. After several hours the intensities of the signals of **2a** decreased and signals of **4a** and $Fe(CO)_5$ appeared without broadening of the signals; this suggests that no paramagnetic intermediate is formed during the decomposition. After 48 h only the signals for **4a** and $Fe(CO)_5$ were detected.

When treated with cinnamoyl chloride in CH_2Cl_2 at 25 °C during 15 min, **1** reacted completely and the IR spectrum of the reaction mixture [2058(w), 1985(vs), 1962(sh), 1946(s) (ν(C≡O)), 1734(w,ν(C=O)) and 1636 cm^{-1} (w,ν(C=C))] showed the formation of an analogue of **2a**. However, work-up of the reaction mixture regenerated a significant amount of **1**, to give a mixture of **1** and **2b**; but pure **2b** could not be obtained. When the reaction was carried out for 48 h, IR absorptions of **2b** could no longer be detected and only those for [PPN][η^2-PhCH=CHFe$_2$(CO)$_7$] [17] (**4b**) and Fe(CO)$_5$ were observed. **4b** was isolated from the reaction mixture in 20% yield and Fe(CO)$_5$ was obtained in 70% yield.

A reasonable deduction is that **2a** is bis(triphenylphosphine)iminium μ-carbonyl-nonacarbonyl-μ_3-cinnamoyloxymethylidyne-triangulo-triferrate on the basis of the spectral data, which are compared with those of [PPN][μ_3-CH$_3$COOCFe$_3$(CO)$_{10}$] [12] and [NEt$_4$][μ_3-CH$_3$OCH$_2$OCFe$_3$(CO)$_{10}$] [10*].

The IR spectra of **2a** in KBr disks exhibited the absorptions of the terminal ν(C≡O) vibrations in the 1914–2054 cm^{-1} region and the ν(C=O) of an acyl group at 1752 cm^{-1} as well as ν(C=C) of an olefin at 1651 cm^{-1}. The ^{13}C NMR spectrum exhibited a characteristic signal from the μ_3-carbyne carbon at 307.5 ppm and a metal carbonyl signal at 219.7 ppm. The ratio of the intensities of the signals at 307.5 and 219.7 ppm was 10 : 1 at 24 °C as previously observed in the ^{13}C NMR spectrum of [PPN][μ_3-ROCFe$_3$(CO)$_{10}$] [7]. The ^{1}H NMR signals of **2a** at 6.21 and 7.31 ppm (d, J = 15.7 Hz) and the ^{13}C NMR signals at 123.2 ppm (d, J = 158.6 Hz) and 145.4 ppm (d, J = 153.8 Hz) revealed the presence of an uncoordinated olefinic group.

Compound **4a** was identified as bis(triphenylphosphine)iminium μ-carbonyl-hexacarbonyl-μ, η^2-1-propenyldiferrate on the basis of the spectral data, in analogy with those of [PPh$_4$][η^2-CH$_2$=CHFe$_2$(CO)$_7$] [18].

The IR spectrum of **4a** exhibited characteristic absorptions due to terminal ν(C≡O) at 2025(m), 1971(vs), 1929(vs) and 1921(vs) cm^{-1} and due to bridging ν(C=O) vibrations at 1732(m) cm^{-1}. The ^{1}H NMR exhibited two olefinic signals, one at high field (2.98 ppm) and the other at low field (7.84 ppm); the spectrum is characteristic of the vinyl group σ-bonded to one iron atom while the olefinic double bond is coordinated to the other iron atom. The variable-temperature ^{13}C NMR spectra for the carbonyl ligands of [PPN][η^2-PhCH=CHFe$_2$(CO)$_7$] (**4b**) are shown in Fig. 1. At 0 °C complete exchange among the terminal carbonyls occurs so that the signals coalesce into one broad signal centered at 217.6 ppm. The signal of the bridging carbonyls, which might be affected by the exchange of terminal carbonyls, was no detected. At −20 °C, the signal of the bridging carbonyl was observed at 274.3 ppm, but the signal of the terminal carbonyls remained broad.At −30 °C, four slightly broad signals from the terminal carbonyls appeared at 214.7, 215.7, 217.4 and 218.4 ppm. These signals became sharper below −50 °C, thus indicating cessation of the exchange.

Mechanisms of the formation of **2** and **4** by the reaction of **1** with α,β-unsaturated acyl halides may be rationalized by assuming that there is an equilibrium between **1** and **2** (Scheme 1). The acylation of [PPN]$_2$[Fe$_3$(CO)$_{11}$] by α,β-unsaturated acyl halides occurs at an oxygen atom of the bridging carbonyl, giving the kinetically controlled product **2** which would be rather unstable. The unstable complex **2** would regenerate the original complex **1** and the acylation of **1** would alternatively occur at the iron atom to give the unstable trinuclear η^1-acyliron complex **3** as an intermediate which decomposes into a dinuclear η^2-vinyliron complex **4** and iron pentacarbonyl via decarbonylation. Noteworthy is that the

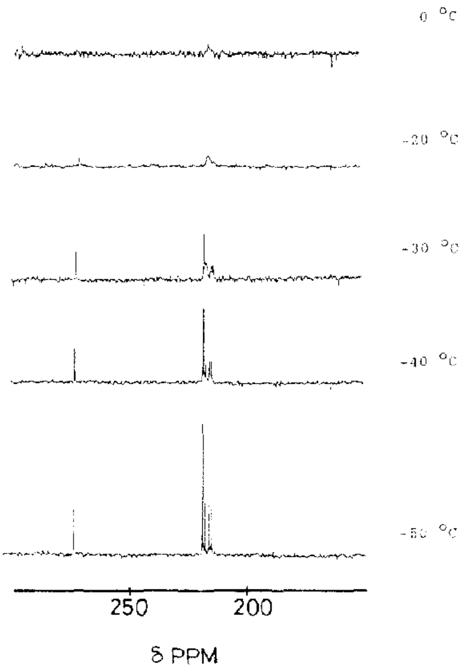
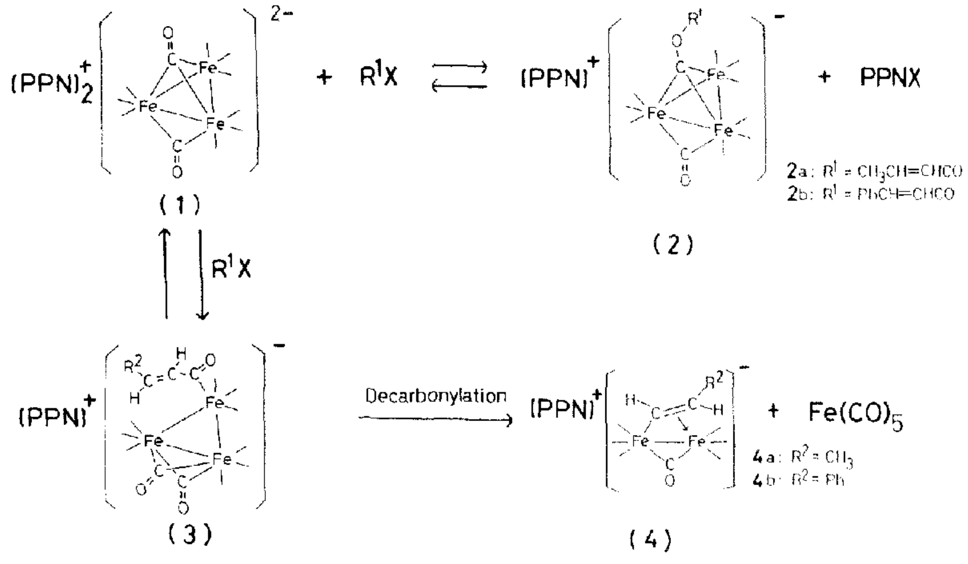


Fig. 1. Variable-temperature ^{13}C NMR spectra for the metal carbonyls of [PPN][η^2-PhCH=CHFe$_2$(CO)$_7$].

α,β-unsaturated acyl group transfers from the oxygen atom of the bridging carbonyl to the iron atom since complex **2** gives the complex **4** and Fe(CO)$_5$.

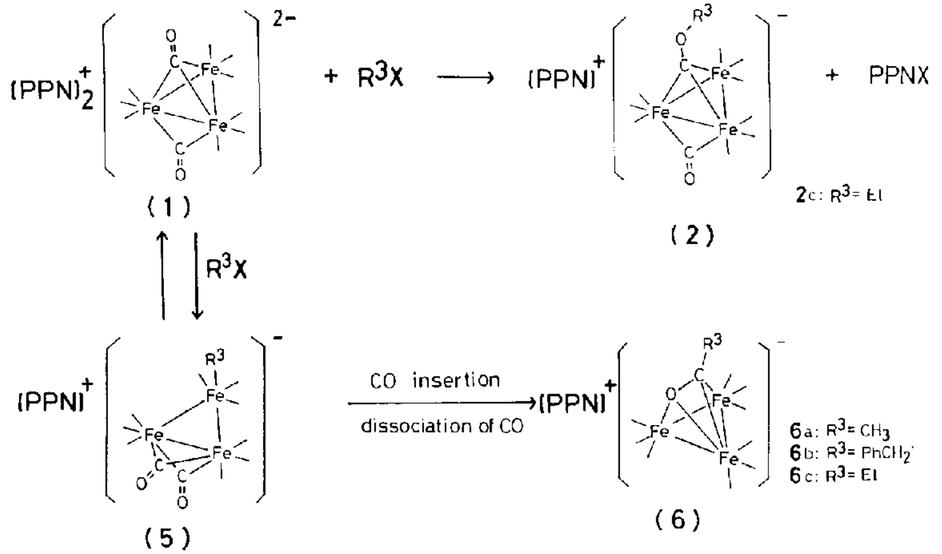
Reaction of [PPN]$_2$[Fe$_3$(CO)$_{11}$] (1) with alkyl halides. We were interested to find out whether the transfer of alkyl group in [μ_3-ROCFe$_3$(CO)$_{10}$]$^-$ could took



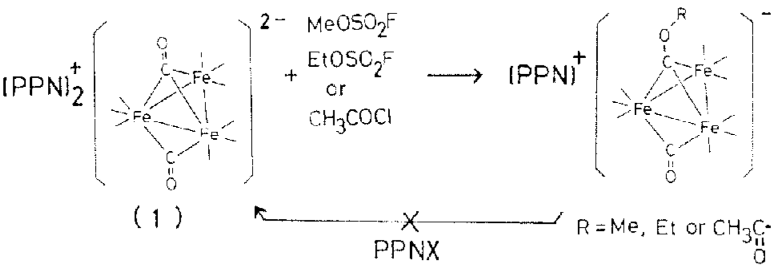
Scheme 1

place. First, the reaction of $[PPN]_2[Fe_3(CO)_{11}]$ with alkyl halides was re-examined. Wilkinson has pointed out that the alkylation (an *O*-alkylation) of $[Fe_3(CO)_{11}]^{2-}$ invariably leads to the formation of complexes containing a bridging μ-COR ligand [10*]. $[PPN]_2[Fe_3(CO)_{11}]$ (**1**) reacts with methyl iodide in tetrahydrofuran (THF) at 25°C to give $[PPN][\mu_3\text{-}CH_3COFe_3(CO)_9]$ (**6a**) in 88% yield (Scheme 2). This complex has been identified as bis(triphenylphosphine)iminium μ_3-acetyl-$C^1(Fe^1Fe^2)O(Fe^1Fe^3)$-nonacarbonyl-triangulo-triferrate by comparing its spectral data with those of an authentic sample prepared by cation exchange reaction of $[NEt_4][\mu_3\text{-}CH_3COFe_3(CO)_9]$ [10] with [PPN]Cl. When methylene chloride or acetone are used in place of THF as the solvent, **6a** is also formed in 82 and 59% yields, respectively. When this reaction was performed in an atmosphere of carbon monoxide, the mononuclear complex $[PPN][CH_3COFe(CO)_4]$ was formed instead of the trinuclear **6a**. Complex **1** also reacts with one molar equiv. of benzyl bromide in THF at 25°C during 24 h to give a trinuclear acyl iron complex $[PPN][\mu_3\text{-}PhCH_2COFe_3(CO)_9]$ (6b) in 71% yield. When an excess amount of benzyl bromide is used, $[PPN]_2[Fe_3(CO)_{11}]$ is completely converted after 5 h and the formation of **6b** can be confirmed by IR spectroscopy. However, when the reaction mixture was stirred for a further 10 h, **6b** was not detected by IR, but several unidentified organic products were detected by GLC. The ^1H NMR and ^{13}C NMR spectra of **6b** exhibited signals at δ 4.00 and 63.9 ppm, respectively, (from the methylene group of the benzyl group), which are found at rather low fields because of the substituent effect by an electronwithdrawing phenyl group. Since all the spectral data for **6b** are similar to those for **6a** (see, Experimental), **6b** should be a derivative of **6a**.

The reaction of **1** with ethyl iodide in THF affords a mixture of $[PPN][\mu_3\text{-}EtOCFe_3(CO)_{10}]$ **2c** [12] and $[PPN][\mu_3\text{-}EtCOFe_3(CO)_9]$ **6c** [19] in a ratio of 38:62 as determined from the ^1H NMR data. The yield of the mixture of **2c** and **6c** was 76%. The same reaction in CH_2Cl_2 gives **2c** and **6c** in 67% yield (**2c**:**6c** = 57:43).



Scheme 2



Scheme 3

The reaction of **1** with ethyl bromide gives $[PPN][HFe_3(CO)_{11}]$ in addition to **2c** and **6c**; the total yield was 72% ($[HFe_3(CO)_{11}]$: **2c** : **6c** = 26 : 35 : 39).

The mechanism of the reaction of $[PPN]_2[Fe_3(CO)_{11}]$ with alkyl halides can be outlined as follows. When methyl iodide and benzyl bromide are used, the alkylation occurs at the iron atom to give the unstable trinuclear alkyl iron complex [20*] **5**, which in turn undergoes insertion of carbon monoxide into the metal–alkyl bond and the dissociation of one terminal carbonyl (Scheme 2). The coordination of the C=O double bond of the acyl group and the lone pair electrons of its oxygen atom to each vacant site of two iron atoms would then afford complex **6** by the stabilization of the trinuclear iron cluster. In the reaction with methyl iodide, no *O*-alkylated product was obtained. In the case of ethyl iodide and ethyl bromide excess amounts of these halides were required to complete the reaction and gives simultaneously the *O*-alkylated product **2c** and the iron-alkylated product **6c**. The larger size of ethyl group may cause the *O*-alkylation.

However, in contrast to the reactions with α,β-unsaturated acyl halides, the reaction with alkyl halides, did not regenerate $[PPN]_2[Fe_3(CO)_{11}]$ from **2c** and thus this reaction is irreversible. As shown in Scheme 3, neither $[PPN][\mu_3\text{-}ROCFe_3(CO)_{10}]$ (R = Me and Et) nor $[PPN][\mu_3\text{-}CH_3COOCFe_3(CO)_{10}]$ [12] regenerated $[PPN]_2[Fe_3(CO)_{11}]$ even in the presence of [PPN]I or [PPN]Cl (Scheme 3). Thus the transfer of the acyl groups as shown in Scheme 1 would be characteristic of **2a** and **2b** which he the α,β-unsaturated acyl groups.

Conclusion

$[PPN]_2[Fe_3(CO)_{11}]$ reacts with α,β-unsaturated acyl halides to give $[PPN][\mu_3\text{-}RCH{=}CHCOOCFe_3(CO)_{11}]$, whose acyl group transfer from the oxygen atom to the iron atom to give $[PPN][\eta^2\text{-}RCH_2{=}CHFe_2(CO)_7]$ and $Fe(CO)_5$. $[PPN]_2[Fe_3(CO)_{11}]$ also reacts with alkyl halides to give $[PPN][\mu_3\text{-}CH_3COFe_3(CO)_9]$ in high yields. To our knowledge these reactions are the first examples of an acylation and an alkylation that can occur at the iron atom of the trinuclear iron dianion complex $[PPN]_2[Fe_3(CO)_{11}]$.

Shriver et al. have reported that $[PPN]_2[Fe_3(CO)_{11}]$ reacts with CH_3OSO_2F, $C_2H_5OSO_2F$ or CH_3COCl to give $[PPN][\mu_3\text{-}ROCFe_3(CO)_{11}]$ [12] (R = CH_3, C_2H_5 or CH_3CO) which was formed as the result of an attack on the oxygen atom of the bridging carbonyls. It was always thought that the acylation and alkylation of a trinuclear iron dianion complex could not occur at the iron atom [12]; however, when softer alkyl halides were used, even the iron atom of the trinuclear complex was attacked. Furthermore, when softer α,β-unsaturated acyl halides were used, the transfer of the acyl group from oxygen atom to iron atom occurred.

Experimental

Unless otherwise indicated, all experiments were performed under argon. Infrared spectra were recorded on a Nicolet Model 5MX Fourier transform infrared spectrometer and the NMR spectra on JEOL JNM-FX-90, JEOL JNM-FX-100 and JEOL GSX-270 spectrometers. Elemental analyses were performed at the Micro Analytical Center of Kyoto University. Solvents were dried by use of previously published techniques and were distilled under argon before use. $[PPN]_2[Fe_3(CO)_{11}]$ [21], $[NEt_4][\mu_3\text{-}CH_3COFe_3(CO)_9]$ [10] and $[PPN][\mu_3\text{-}ROCFe_3(CO)_9]$ (R = CH_3, C_2H_5 or CH_3CO) [12] were prepared as described in the literature.

Reaction of $[PPN]_2[Fe_3(CO)_{11}]$ *with crotonoyl chloride to give* $[PPN][\mu_3\text{-}CH_3CH{=}CHCOOCFe_3(CO)_{10}]$ *(2a).* To a solution of $[PPN]_2[Fe_3(CO)_{11}]$ (0.84 g, 0.54 mmol) in CH_2Cl_2 (5 ml) was added 0.11 g (1.1 mmol) of crotonoyl chloride and the mixture was stirred at 25 °C for 4 h to give a dark brown solution. To this solution was added 40 ml of diethyl ether and the precipitate of [PPN]Cl that formed was filtered off. The filtrate was concentrated to 5 ml and 30 ml of pentane was added to give a dark brown oil of **2a** and **4a** in a 1 : 1 ratio. The supernatant was removed and the residual oil was dried in vacuo. The dark brown solid was recrystallized repeatedly from MeOH to give 44 mg (8%) of the dark brown crystals of **2a**; mp. 91 °C (dec.) Found: C, 56.77; H, 3.07; N, 1.29. $C_{51}H_{35}Fe_3NO_{12}P_2$ calcd.: C, 56.54; H, 3.26; N, 1.29%. IR (KBr) $\nu(C{\equiv}O)$: 2054(w), 1985(vs), 1954(s), 1939(sh), 1927(sh) and 1914(m); $\nu(C{=}O)$ acyl: 1752(m); $\nu(C{=}C)$: 1651(w). (CH_2Cl_2) $\nu(C{\equiv}O)$: 2054(w), 2000(vs), 1971(s); $\nu(C{=}O)$ acyl: 1734(w); $\nu(C{=}C)$: 1655(w) cm^{-1}. NMR (δ, $SiMe_4$, J Hz), at 24 °C, abbreviations: s = singlet; d = doublet; quartet; m = multiplet; sh = shoulder). ^1H NMR (CD_2Cl_2): 1.99 (dd, J = 6.9, J = 2.0, 3H, CH_3), 6.21 (dq, J = 15.7, 2.0 Hz, 1H, =CHCO), 7.31 (dq, J = 15.7, J = 6.9, 1H, CH_3CH=), 7.45–7.58 (m, 30H, PPN) ppm. ^{13}C NMR (25.0 MHz, CD_2Cl_2) 18.4 (q, ^1J(C–H = 127.8, CH_3), 123.2 (dq, ^1J(C–H) = 158.6, ^3J(C–H) = 5.7, =CHCO), 145.4 (dq, ^1J(C–H) = 153.8, ^2J(C–H) = 7.3, CH_3*C*H=), 163.6 (s, CH_3CH=CH*C*O), 219.7 (s, metal carbonyls), 307.5 (s, μ_3-*C*OOCCH=$CHCH_3$), 124–134 (m, PPN) ppm.

Reaction of $[PPN]_2[Fe_3(CO)_{11}]$ *with crotonoyl chloride to give* $[PPN][\eta^2\text{-}CH_3CH{=}CHFe_2(CO)_7]$ *(4a).* To a solution of $[PPN]_2[Fe_3(CO)_{11}]$ (2.85 g, 1.84 mmol) in CH_2Cl_2 (20 ml) was added 0.35 ml (0.38 g, 3.67 mmol) of crotonoyl chloride, and the mixture was stirred at 25 °C for 48 h to give a brown solution. To this solution was added 80 ml of diethyl ether. The precipitate of [PPN]Cl that formed was filtered off and washed with 10 ml of diethyl ether. Volatiles were removed in vacuo into a trap at −78 °C and the UV absorption at 243 nm indicated the formation of $Fe(CO)_5$ in 80% yield. The residual oil was chromatographed on silica gel (Merck 0.063–0.200 mm, deactivated by 10% of water; eluent, ether/CH_2Cl_2 (1 : 1)). Recrystallization of the dark orange solid from MeOH gave the orange crystals of **4a** (228 mg, yield 14%); mp. 90 °C (dec.). Found: C, 61.47; H, 3.90; N, 1.54. $C_{46}H_{35}Fe_2NO_7P_2$ calcd.: C, 62.26; H, 3.98; N, 1.58%. IR (KBr) $\nu(C{\equiv}O)$: 2025(m), 1991(sh), 1971(vs), 1929(vs), 1921(vs) and 1917(sh); bridging carbonyl: 1732(m) cm^{-1}. ^1H NMR (CD_2Cl_2): 1.51(d, J = 5.9, 3H, CH_3), 2.98(dq, J = 10.7, J = 5.9, 1H, CH_3C*H*), 7.84(d, J = 10.7, 1H, CH_3CH=C*H*), 7.46, 7.51 and

7.60(30H, PPN) ppm. ^{13}C NMR (67.8 MHz, CD_2Cl_2, at −70 °C) 25.8(q, ^1J(C–H) = 128.7, CH_3), 82.6(d, ^1J(C–H) = 159.9, CH_3CH), 148.1(d, ^1J(C–H) = 150.9, $CH_3CH{=}CH$), 215.0(s), 216.4(s), 217.7(s), 219.2(s) (terminal carbonyls), 278.0(s, bridging carbonyl), 126.4(d, ^1J(C–P) = 108.5, $=\overset{|}{C}-P$), 129.1(d, ^1J(C–H) = 169.1, PPN), 13.17(d, ^1J(C–H) = 167.3, PPN), and 133.3(d, ^1J(C–H) = 163.6, PPN) ppm.

Reaction of [PPN]$_2$[Fe$_3$(CO)$_{11}$] with cinnamoyl chloride. To a solution of $[PPN]_2[Fe_3(CO)_{11}]$ (2.46 g, 1.58 mmol) in CH_2Cl_2 (20 ml) was added a solution of cinnamoyl chloride (0.527 g, 3.17 mmol) in CH_2Cl_2 (5 ml) and the mixture was stirred at 25 °C for 48 h to give a deep brown solution. To this solution was added 80 ml of diethyl ether. The precipitate of [PPN]Cl that formed was filtered off and washed with 10 ml of diethyl ether. Volatiles were removed in vacuo into a trap at −78 °C. Their UV spectrum indicated the formation of $Fe(CO)_5$ in 70% yield. The residue was chromatographed on silica gel (Merck 0.063–0.200 mm, deactivated by 10% of water, eluent ether/CH_2Cl_2 (1 : 1)). Recrystallization of the dark orange solid from MeOH solution gave orange crystals of **4b** (0.31 g, yield 20%) mp. 121 °C (dec.). Found C, 64.27; H, 3.94; N, 1.52. $C_{51}H_{37}Fe_2NO_7P_2$ calcd.: C, 64.51: H, 3.93; N, 1.48%. IR (KBr) $\nu(C{\equiv}O)$: 2027(m), 1979(s), 1944(sh) and 1923(vs); bridging carbonyl: 1757(m) cm^{-1}. ^{1}H NMR (CD_2Cl_2): 3.78(d, J = 11.6, 1H, PhCH), 8.70(d, J = 11.6, 1H, PhCH=CH), 7.0–7.59(m, 35H, Ph and PPN) ppm. ^{13}C NMR (25.0 MHz, CD_2Cl_2, at −70 °C): 81.7(d, ^1J(C–H) = 158.7, PhCH=), 141.1(d, ^1J(C–H) = 148.9, PhCH=CH), 214.4(s), 215.3(d, ^3J(C–H) = 4.9), 217.0(s), 218.0(s,br) (terminal carbonyls), 275.5(s, bridging carbonyl), 124.6(d, ^1J(C–H) = 158.5, Ph), 127.9(d, Ph), 141.0(d, ^1J(C–H) = 148.9, Ph), 143.3(s, Ph), 126.1(d, ^1J(C–P) = 107.0, PPN), 128.8(m, PPN), 131.6(m, PPN), 133.2(m, PPN) ppm.

Reaction of [PPN]$_2$[Fe$_3$(CO)$_{11}$] with methyl iodide. To a suspension of $[PPN]_2[Fe_3(CO)_{11}]$ (0.93 g, 0.60 mmol) in THF (10 ml) was added 0.17 g (1.20 mmol) of methyl iodide and the mixture was stirred at 25 °C for 1.5 h to give a dark brown solution with white precipitates of [PPN]I. To this mixture was added 20 ml of diethyl ether, and the [PPN]I was filtered off and washed with 5 ml of diethyl ether. The filtrate was concentrated to 10 ml, and 20 ml of n-pentane was added to give dark brown crystals of 6a (0.54 g, yield 88%).

This reaction was also performed in CH_2Cl_2 and acetone in place of THF to give **6a** in 82% and 59% yield, respectively; mp. 121 °C (dec.). Found: C, 56.12; H, 3.25; N, 1.38. $C_{47}H_{33}Fe_3NO_{10}P_2$ calcd.: C, 56.38; H, 3.32; N, 1.40%. IR (KBr) $\nu(C{\equiv}O)$: 2039(m), 1968(vs), 1946(s), 1923(s), 1902(sh) and 1869(m); (CH_2Cl_2) $\nu(C{\equiv}O)$: 2039(m), 1981(vs), 1973(vs), 1950(s) and 1927(s) cm^{-1}. ^{1}H NMR (CD_2Cl_2): 2.71(s, 3H, CH_3), 7.53, 7.62(m, 30H, PPN) ppm. ^{13}C NMR (67.8 MHz, acetone-d_6, −60 °C): 43.0(q, ^1J(C–H) = 126.9, CH_3), 213.1(s, br), 215.4(s, br), 216.3(s) (terminal carbonyls), 234.2 (q, ^2J(C–H) = 5.5, μ_3-CH_3CO), 128.1(d, J(C–P) = 106.6, PPN), 130.4(m, PPN), 133.2(m, PPN), 134.6(d, PPN) ppm.

Reaction of [PPN]$_2$[Fe$_3$(CO)$_{11}$] with benzyl bromide. To a suspension of $[PPN]_2[Fe_3(CO)_{11}]$ (0.46 g, 0.29 mmol) in THF (5 ml) was added 0.055 g (0.32 mmol) of benzyl bromide and the mixture was stirred at 25 °C for 24 h to give a dark brown solution and white precipitates of [PPN]Br. To this mixture was added 10 ml of diethyl ether and [PPN]Br was filtered off and washed with 5 ml of diethyl ether. Volatiles were removed from the filtrate under vacuum. The weight of the crude product was 0.23 g (71%, yield). Analytically pure **6b** could not be obtained.

IR (KBr) $\nu(C{\equiv}O)$: 2039(m), 1979(vs), 1970(vs), 1948(s), 1925(s) and 1869(m) cm^{-1}. ^1H NMR (CD_2Cl_2): 4.00(s, 2H, $PhCH_2$), 7.09–7.82(m, Ph and PPN, 35 H) ppm. ^{13}C NMR (25.0 MHz, CD_2Cl_2): 63.9(t, J = 129.4, $PhCH_2$), 213.1(s) and 215.7(s) (metal carbonyls), 234.6(s, μ_3-$PhCH_2CO$), 126.9(d, Ph), 128.8(d, Ph), 134.3(d, Ph), 140.0(s, Ph), 128.0(d, ^1J(C–P) = 108.0 Hz, PPN), 130.1(m, PPN), 132.9(m, PPN), 134.3(d, PPN) ppm.

Reaction of $[PPN]_2[Fe_3(CO)_{11}]$ with ethyl iodide. To a suspension of $[PPN]_2[Fe_3(CO)_{11}]$ (0.92 g, 0.59 mmol) in THF (7.5 ml) was added 0.56 g (3.57 mmol) of ethyl iodide and the mixture was stirred at 25 °C for 48 h to give a dark brown solution and white precipitates of [PPN]I. To this mixture was added 15 ml of diethyl ether, and [PPN]I was filtered off and washed with 5 ml of diethyl ether. Volatiles were removed from the filtrate under vacuum, and the residue was extracted with three 5-ml portions of diethyl ether. To the extract was added 10 ml of pentane to give a mixture of **2c** and **6c** as dark brown crystals (0.46 g, total yield 76%, **2c** : **6c** = 38 : 62).

Spectral data of $[PPN][\mu_3\text{-}EtCOFe_3(CO)_9]$ (**6c**): IR (KBr) $\nu(C{\equiv}O)$: 2039(w), 1977(vs), 1971(vs), 1944(s), 1923(sh), 1912(sh) and 1869(w). (CH_2Cl_2) $\nu(C{\equiv}O)$: 2039(w), 1983(vs) and 1948(s) cm^{-1}. ^1H NMR (acetone-d_6): 1.21(t, J = 7.6, 3H, CH_3), 2.81(q, J = 7.5, 2H, CH_2), 7.52 and 7.78(m, 30H, PPN) ppm. ^{13}C NMR (25.0 MHz, acetone-d_6): 13.7(q, ^1J(C–H) = 124.5, CH_3), 50.7(t, ^1J(C–H) = 127.0, CH_2), 214.3(s) and 215.4(s) (metal carbonyls), 239.3(s, μ_3-EtCO), 127.9(d, ^1J(C–P) = 107.5 Hz, PPN), 129.9(m, PPN), 132.8(m, PPN), 134.2(d, PPN) ppm.

The reaction was also performed in CH_2Cl_2 in place of THF to give a mixture of **2c** (39%) and **6c** (28%). When ethyl bromide in THF, instead of ethyl iodide, was used, a mixture of **2c** (25%), 6c (28%) and $[PPN][HFe_3(CO)_{11}]$ (19%) was obtained.

Cation exchange of $[NEt_4][\mu_3\text{-}CH_3COFe_3(CO)_9]$ with [PPN]Cl. To a solution of $[NEt_4][\mu_3\text{-}CH_3COFe_3(CO)_9]$ (0.32 g, 0.54 mmol) in CH_2Cl_2 (3 ml) was added a solution of [PPN]Cl (0.31 g, 0.54 mmol) in CH_2Cl_2 (2 ml) and the mixture was stirred for 5 min. To this solution was added 20 ml of diethyl ether, and the precipitate of $[NEt_4]Cl$ was filtered off and washed with 10 ml of diethyl ether. Volatiles were removed from the filtrate under vacuum, and the residue was extracted with 15 ml of diethyl ether. The extract was concentrated to 5 ml, and 10 ml of pentane was added to give dark brown crystals (0.31 g, 57%). The spectral and analytical data were perfectly consistent with those of **6a**.

Reaction of $[PPN][\mu_3\text{-}ROCFe_3(CO)_{10}]$ (R=CH_3, C_2H_5 or CH_3CO) with [PPN]I or [PPN]Cl. To a solution of $[PPN][\mu_3\text{-}CH_3OCFe_3(CO)_{10}]$ (0.15 g, 0.14 mmol) (or $[PPN][\mu_3\text{-}C_2H_5OCFe_3(CO)_{10}]$ (0.097 g, 0.093 mmol)) in CH_2Cl_2 (1 ml) was added a solution of [PPN]I in CH_2Cl_2 (1 ml) and the mixture was stirred at 25 °C. The reaction was monitored by IR spectroscopy. After stirring for 5 days no change was detected.

The reaction of $[PPN][\mu_3\text{-}CH_3COOCFe_3(CO)_{10}]$ with [PPN]Cl was performed similarly but no change was detected.

Reaction of $[PPN]_2[Fe_3(CO)_{11}]$ with methyl iodide under CO. To a solution of $[PPN]_2[Fe_3(CO)_{11}]$ (0.68 g, 0.44 mmol) in CH_2Cl_2 (5 ml) was added 0.12 g (0.85 mmol) of methyl iodide and and the mixture was stirred at 0 °C under carbon monoxide for 3.5 h to give a deep brown solution. To this solution was added 10 ml of diethyl ether, and the [PPN]I that formed, was filtered off and washed with 5 ml of diethyl ether. Volatiles were removed under vacuum. The residue was dissolved in

1 ml of CH_2Cl_2. To this solution was added 10 ml of diethyl ether to give pale yellow crystals (0.31 g) including $[PPN][CH_3COFe(CO)_4]$ and an unidentified iron complex.

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