ELSEVIER

Journal of Organometallic Chemistry 579 (1999) 198–205

Journal of Organometallic Chemistry

Synthesis and reactivity of acylphosphine tetracarbonyl–iron complexes

Jean-Jacques Brunet, Remi Chauvin *, Bruno Donnadieu, Erwan Thepaut

Laboratoire de Chimie de Coordination du CNRS,
UPR 8241 liée par conventions à l'Université Paul Sabatier et à l'Institut National Polytechnique, 205 route de Narbonne,
F-31077 Toulouse Cedex 4, France

Received 29 July 1998; received in revised form 3 December 1998

Abstract

A general method for the synthesis of $(CO)_4Fe[PPhX(C(O)R)]$ complexes from lithium acylferrates and PhXPCl is described (R = alkyl, phenyl, X = Ph, Cl). The X-ray crystal structure of $(CO)_4Fe[PPh_2(C(O)Me)]$ has been determined and compared with that of other mononuclear acylphosphine complexes, which all possess a long P–C(O) bond. The weakness of this bond is revealed in nucleophilic and basic media, where $(CO)_4Fe[PPh_2(C(O)R)]$ mostly leads to the $[(CO)_4FePPh_2]^-$ anion. In the presence of LDA, however, some deprotonation occurs for R = Me, *n*-Bu, and subsequent addition of Ph_2PCl leads to monodentate α-phosphinoxyvinyl phosphine carbonyliron complexes in moderate yield. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Acylphosphine; Acylchlorophosphine; (α-Phosphinoxyvinyl)phosphine; Tetracarbonyl–iron complex

1. Introduction

Whereas phosphites 'PO_3' [1], phosphines 'PC_3' [2] and phosphinites 'PC_2O' [3] can be coordinated to the iron atom of $[HFe(CO)_4]^-$ by CO substitution (Scheme 1, reactivity I), the more basic and cumbersome aminophosphines 'PN_3' [4] or chloroaminophosphines '$PClN_2$' [5] bind to the iron atom of $[HFe(CO)_4]^-$ by H-substitution and concomitant hydrogenolysis of one of the P–N or P–Cl bonds (Scheme 1, reactivity II) [6]. The reactivity II can be extended through the analogy E = H ⇒ E = RC(O): novel acylphosphine complexes have been prepared by tandem acylation-complexation of a monochlorophosphine [7]. We now report on the synthesis of new acylphosphine tetracarbonyl–iron complexes, on their reactivity with nucleophiles (binding with the substrate) or bases (deprotonation of the substrate and subsequent quenching with some electrophile) and on a further extension of the study to a dichlorophosphine substrate.

* Corresponding author. Fax: +33-561553113.
E-mail address: chauvin@lcc-toulouse.fr (R. Chauvin)

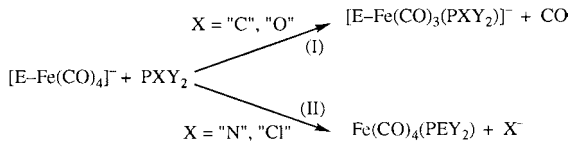
2. Results and discussion

2.1. New acyldiphenylphosphine ironcarbonyl complexes

Most acylphosphine ligands known to date occur in di- or trinuclear transition metal complexes [8], and surprisingly, (diacyl)phosphine $PR(C(O)R')_2$ [9] and carbonyl-diphosphines $(PR_2)_2CO$ [10] have received more attention than their simple models, (monoacyl)monophosphines. Whereas acylphosphine complexes can be prepared from metallic precursors and free acylphosphines [11], a one-pot procedure leads to acylphosphine complexes from chlorodiphenylphosphine and lithium acylferrates (Scheme 2), prepared from $Fe(CO)_5$ and alkyllithium reagents [12]. Although metallo–enolate resonance structures can be drawn from acylferrate structures, no *O*-phosphinylation products **2a**–**d** are observed (Scheme 2): by contrast, more electrophilic chlorophosphites have been recently reported to react with acyltungstates at the oxygen end [13].

An excess of $ClPPh_2$ has been needed for a complete conversion of the acylferrate reagent (IR monitoring):

0022-328X/99/$ - see front matter
PII: S0022-328X(98)01223-6



Scheme 1. Substitution reactivity of the hydridotetracarbonylferrate anion (E = H) by various phosphanes (Y = X or C_6H_5). The reactivity path II is now studied for acyltetracarbonylferrate anions (E = RC(O)).

in a competitive process, $ClPPh_2$ is reduced to Ph_2PPPh_2 (the concomitant oxidation process of the iron center, formally leading to '$FeCl_2$' derivatives, has not been studied). The procedure for the synthesis of **3b** described in a preliminary communication [7] has been optimized: only a one-and-one-tenth equivalent of $ClPPh_2$ is needed instead of the original two equivalents.

In contrast, the selectivity in the benzoylphosphine complex **3d** is low, and four equivalents of $ClPPh_2$ must be used for a complete conversion of **1d**. **3d** could not be isolated in a pure form (ca 60% selectivity with respect to Ph_2PPh_2 based on the integrated ^{31}P-NMR spectrum), but was spectroscopically characterized in a mixture with $ClPPh_2$ and Ph_2PPPh_2.

Whereas the *n*-Bu complex **3b** is an oil (even at −20°C), monocrystals of the new complex **3c** deposited from pentane and were subjected to X-ray diffraction analysis. The structural features of **3c** are similar to those of the *t*-Bu complex **3a** (Fig. 1, Table 2). A large P–C(O) bond length of ca 1.89 Å is measured, which is greater than the sum of the covalent radii of P and C ($r_C + r_P = 1.83$ Å). Owing to the steric bulk of the *t*-butyl substituent, an even longer P–C(O) bond of 1.93 Å was measured in **3a**. This structural feature is a common point of acylphosphine ligands in mononuclear carbonyl complexes (Table 3) [14–18] and of carbonyldiphosphine ligands in dinuclear carbonyl iron complexes [19]. Calculations showed that the P–C(O) bond is already stretched in free acylphosphines: the P–C=O ↔ $^{+}$P=C–O^{-} resonance (pπ conjugation) is less important than the N–C=O ↔ $^{+}$N=C–O^{-} resonance in analogous amides [11a, 20], but is enhanced in electron rich acylphosphines (e.g. in the η^3-acylphosphide $ClOs(CO)_2(PPh_3)_2\{P[C(O)t\text{-Bu}]H\}$ with an 18 electron count at the osmium atom, the P–C(O) length is only 1.79 Å [21]).

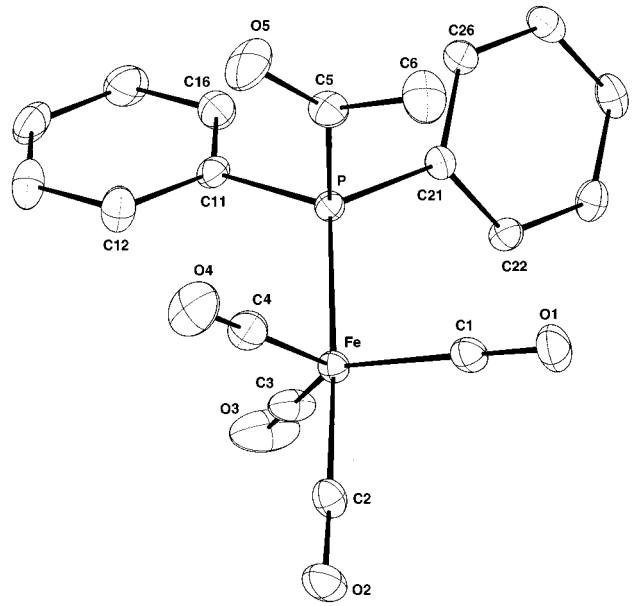
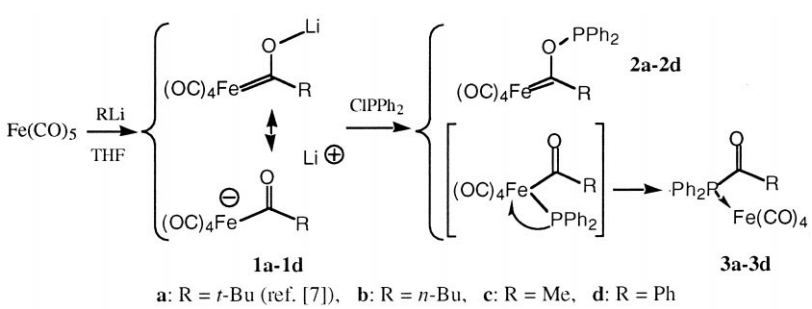


Fig. 1. CAMERON view of the X-ray crystal structure of **3c**. Molecular strucrure of **3c** showing the atom labelling scheme and thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity.

Regarding the reaction mechanism, the possibility of a reductive elimination to $RC(O)PPh_2 + Fe(CO)_4$ prior to the formation of the acylphosphine complex **3a**–**3d** (Scheme 1) is ruled out by the absence of $(ClPh_2P)Fe(CO)_4$ [22] and $(Ph_2PPh_2P)Fe(CO)_4$ [25] complexes which should result from a competitive trapping of the 16-electron species $Fe(CO)_4$ by the potential ligands $ClPPh_2$ or Ph_2PPPh_2 occurring in the reaction medium.

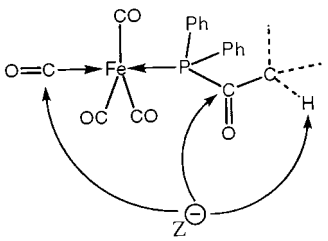


Scheme 2. One-step acylation-complexation of monochlorophosphines **3a**–**3d.** The phosphinoxy Fischer carbene isomers **2a**–**2d** were not observed.

Table 1
Spectral data for complexes **3a**–**3d**, **11b** and **11c** [a]

Complex (X, R)	NMR [b]					IR [c]
	δ ^{31}P (s)	δ ^{13}C (PCO, d)	$\lvert^1J_{C(O)-P}\rvert$ (Hz)	δ ^{13}C (FeCO, d)	$\lvert^2J_{C(O)-P}\rvert$ (Hz)	ν (PC=O) cm^{-1}
3a (Ph, *t*-Bu) [d]	77.7	218.0	7.7	213.1	17.5	1678
3b (Ph, *n*-Bu)	74.7	214.1	10.9	212.5	18.1	1694
3c (Ph, Me)	76.8	211.9	18.2	211.1	14.6	1697
3d (Ph, Ph)	77.9	212.6	17.7	202.6	16.9	1660
11b (Cl, *n*-Bu)	155.9	211.1 [a]	17	211.1 [a]	17	1704
11c (Cl, Me)	156.6	212.07	19.0	211.20	16.7	1686

[a] The signals of $(\underline{C}O)_4Fe$ and P$\underline{C}$O are interpreted as superimposed.
[b] In $CDCl_3$.
[c] In THF.
[d] See reference [7].



Scheme 3. Possible attacks of nucleophiles and bases (Z^-) on acylphosphine complexes.

2.2. Reactivity of acylphosphine carbonyliron complexes with nucleophiles and bases

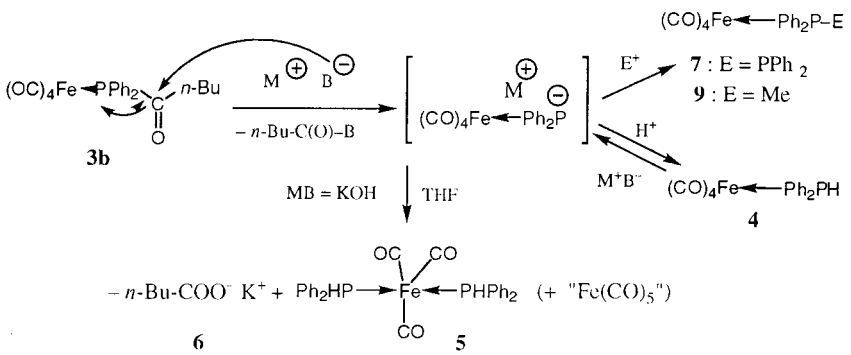
The acylation of $ClPPh_2$ can be regarded as a carbonylation step in the synthesis of phosphine derivatives, and might be followed by functionalization steps. Three electrophilic reaction sites can be distinguished (Scheme 3): the target of Z^- could be either: (i) the C atom of a carbonyl ligand (formation of an acylferrate derivative, or in the case of $Z = OH^-$, of a hydridoferrate after extrusion of CO_2), (ii) the C atom of the acyl group (with a subsequent cleavage of the P–C(O) bond), or (iii) an acidic H atom at the α position of the acyl group (formation of an enolate species which could be subsequently C- or O-functionalized by electrophiles).

2.2.1. Reactivity of *3b* with KOH

Complex **3b** is inert in methanol (and in CD_3OD), but is cleaved upon addition of KOH: potassium pentanoate **6** and complex **4** are the sole products identified by NMR analysis. The presence of **4** is due to the trapping of the intermediate phosphide anion $[(CO)_4FePPh_2]^-$ by methanolic protons (Scheme 4: in the presence of other electrophiles, other complexes such as **7** or **9** should form: see Sections 2.2.2 and 2.2.3). Evaporation of methanol and extraction in THF brings about a ligand redistribution between two molecules of **4**, and the final product is the *trans*-$(CO)_3Fe(PHPh_2)_2$ complex **5** (80% yield), which was previously obtained by reaction of $Fe(CO)_5$ with $NaBH_4$ in the presence of $PHPh_2$ (Scheme 4) [23].

2.2.2. Reactivity of *3b* with $NaBH_4$

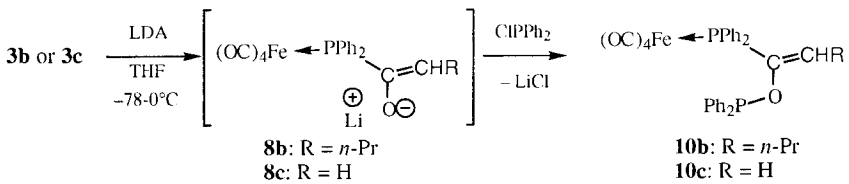
The weakness of the P–C(O) bond prevents a simple reduction of **3c** into the α-hydroxyalkylphosphine complex: complex **4** is isolated in 62% yield (non optimized) from **3c** and $NaBH_4$ in methanol. Curiously, no ligand redistribution to complex **5** is observed here upon extraction in diethylether: the formation of **5** which was mentionned in the preceeding section appears to be specific to the presence of KOH.



Scheme 4. Reaction of **3b** with nucleophiles or bases MB = KOH, NaBH4, *n*-BuLi, LDA.

Table 2
Selected bond lengths (Å) and bond angles (°) of complex **3c**, as determined from X-ray diffraction data

Bonds	Distances	Bonds	Distances	Bonds	Distances
Fe–P	2.2401(4)	O(3)–C(3)	1.146(2)	C(13)–C(14)	1.381(3)
Fe–C(2)	1.791(2)	O(5)–C(5)	1.203(2)	C(15)–C(16)	1.393(3)
Fe–C(4)	1.782(2)	C(6)–H(61)	0.81(3)	C(21)–C(26)	1.392(2)
P–C(11)	1.824(2)	C(6)–H(63)	0.88(3)	C(23)–C(24)	1.379(3)
O(1)–C(1)	1.138(2)	C(11)–H(16)	1.393(3)	C(25)–C(26)	1.386(2)
Fe–C(1)	1.806(2)	O(2)–C(2)	1.138(2)	C(12)–C(13)	1.383(3)
Fe–C(3)	1.793(2)	O(4)–C(4)	1.150(2)	C(14)–C(15)	1.374(3)
P–C(5)	1.894(2)	C(5)–C(6)	1.485(3)	C(21)–C(22)	1.395(2)
P–C(21)	1.820(1)	C(6)–H(62)	0.91(3)	C(22)–C(23)	1.392(2)
		C(11)–C(12)	1.387(3)	C(24)–C(25)	1.382(3)
P–Fe–C(1)	91.28(5)	C(2)–Fe–C(4)	90.81(7)	P–C(5)–O(5)	118.7(1)
C(1)–Fe–C(2)	92.40(7)	Fe–P–C(5)	110.70(6)	P–Fe–C(2)	175.64(5)
C(1)–Fe–C(3)	121.37(8)	C(5)–P–C(11)	102.71(7)	P–Fe–C(3)	86.36(5)
Fe–C(2)–O(2)	177.9(1)	C(5)–P–C(21)	102.24(7)	P–Fe–C(4)	89.81(6)



Scheme 5. Synthesis of α-(diphenylphosphinoxy)vinyl diphenylphosphine iron tetracarbonyl complexes **10b** and **10c**.

2.2.3. Reactivity of *3b* with n-BuLi

In an aprotic medium, the anion of **4**, $[(CO)_4FePPh_2]^-$ [24], can be generated by action of *n*-BuLi in THF, and then trapped by an electrophile other than a proton. Reaction of **3b** with *n*-BuLi in THF followed by treatment with Ph_2PCl leads to the known complex **7** ($\delta 31_P = 3.22$ (d), 62.0 (d) ppm, $^1J_{PP} = 324$ Hz [25]) which is further characterized by ^{13}C-NMR in $CDCl_3$: $\delta 13_C = 128.44–135.57$ and 213.07 ppm, dd, $^2J_{PC} = 16$ Hz, $^3J_{PC} = 4.4$ Hz.

2.2.4. Reactivity of *3b* with LDA

While *n*-BuLi acts as a nucleophile, LDA has a more basic character with respect to **3b**, and the enolate **8b** is detected by IR spectroscopy. The enolate **8b** reacts in situ with CH_3I and gives neither C- nor O-methylation products, but the P-methylation product $(CO)_4Fe(PPh_2Me)$ **9**, with $\delta 31_P = +56.7$ ppm [26]. By contrast, enolates **8b** and **8c** react with Ph_2PCl to give products whose IR and NMR spectra are compatible with phosphinyl enol ethers **10b** (30% crude yield) and **10c** (42% isolated yield) (Scheme 5).

The reaction is not highly selective since Ph_2PPPh_2 derivatives resulting from a cleavage of the P–C(O) are also observed in the NMR spectra of the crude reaction medium. To the best of our knowledge, however, these monodentate α-phosphinoxyvinyl phosphine ligands with a novel structural sequence $P^{III}–O–C_{sp}2–P$ are reminiscent of their bidentate β-phosphinoxyvinylphosphine isomers [27].

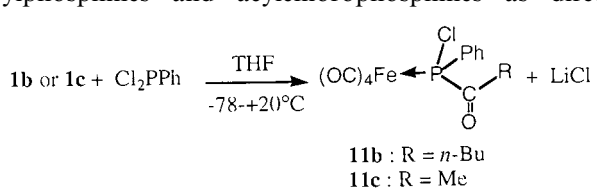
2.3. Synthesis of acylchlorophosphine ironcarbonyl complexes

Acylferrate **1b** reacts with $PhPCl_2$ to give the stable acylchlorophosphine complex **11b** in 79% yield. A similar sequence leads from **1c** to **11c**, which could not be completely purified, but which was spectroscopically characterized (Scheme 6, Table 1).

Finally, attempts to apply the synthetic principle to the reaction of lithium acylferrate **1b** with PCl_3 failed: the final dark crude oil gave no NMR information (paramagnetism).

3. Conclusions

This study paves the way to a broader use of acylphosphines and acylchlorophosphines as direct



Scheme 6. Synthesis of acylchlorophosphine complexes by a tandem acylation-complexation process.

reagents for the synthesis of phosphane transition metal complexes. Owing to the weakness of the FeP–C(O) bond, already indicated by X-ray diffraction data, the chemistry of acylphosphine tetracarbonyl–iron complexes in basic medium often boils down to that of the $[(CO)_4FePPh_2]^-$ anion. Nonetheless a new type of α-phosphinoxyvinyl phosphine complexes has been described, and their use in selective bimetallic coordination chemistry can be envisioned: the phosphinite end does not displace the phosphine end at the iron center.

An extension of the strategy is underway, aimed at the synthesis of formylphosphine complex **3e** or its phosphinoxy Fischer carbene isomer **2e** (R = H, in Scheme 2) from $Na[(CO)_4FeCHO]$ [28]. Efforts are intended to elaborate a simple way to remove the $Fe(CO)_4$ moiety from the acylphosphine: this would allow us for tackling a study of the steric and electronic effects of acylphosphine ligands in transition metal catalysis [10, 29].

4. Experimental

4.1. Materials

All experiments were performed under an argon atmosphere using standard Schlenk techniques. THF and diethylether were distilled over Na/benzophenone be-fore use. Commercial synthesis grade pentane and methanol were degassed by bubbling argon before use. Potassium hydroxide (Technical 86%, Prolabo), pentacarbonyliron (Fluka), *n*-butyllithium (1.6 M in hexane, Aldrich), phenyllithium (1.6 M in cyclohexane/ether, Aldrich), methyllithium (1.6 M in diethylether, Fluka), and lithium diisopropylamide (LDA, 2 M in THF/heptane/ethylbenzene, Aldrich) were used without further purification. Ph_2PCl (Aldrich) and $PhPCl_2$ (Aldrich) were distilled before use.

4.2. Measurements

IR spectra were recorded in the 1500–2500 cm^{-1} region on a Perkin–Elmer 1725X FT-IR spectrometer using CaF_2 windows. NMR spectra were recorded on a Brucker AC 200 spectrometer: at 200 MHz for ^1H, 81 MHz for ^{31}P and 50 MHz for ^{13}C, with positive chemical shifts at low field expressed in ppm by internal reference to TMS for ^1H and ^{13}C and by external reference to 85% H_3PO_4 in D_2O for ^{31}P. X-ray diffraction experiments were carried out on a STOE IPDS (imaging plate diffraction system) equipped with an Oxford cryosystem cooler device using Mo–K_α radiation ($\lambda = 0.71073$ Å).

4.3. Preparations

4.3.1. Lithium acyltetracarbonylferrates *1b–d*

A solution of of $Fe(CO)_5$ (0.68 ml, 5 mmol) in 15 ml of THF was cooled to −78°C. A total of 3.1 ml of a 1.6 M solution of RLi (5 mmol, R = *n*-Bu, Me, Ph) were syringed in. The temperature was allowed to rise to 20°C over a 2.5 h period. Completion of the reaction was checked by IR analysis in the 1500–2500 cm^{-1} region and compared with data from the literature [12].

1b R = *n*-Bu: $\nu CO = 2017$ (m), 1927 (m), 1902–1895 (s), 1570 (m) cm^{-1}

1c R = Me: $\nu CO = 2019$ (m), 1929 (m), 1904–1896 (s), 1569 (m) cm^{-1}

1d R = Ph: $\nu CO = 2020$ (m), 1931 (m), 1912–1896 (s), 1596 (m) cm^{-1}

4.3.2. Acyldiphenylphosphine tetracarbonyl–iron *3b–d*

Ph_2PCl (1.0 ml, 0.55 mmol for **3b**, 1.8 ml, 10 mmol for **3c**, 3.6 ml, 20 mmol for **3d**) was added to the solution of the lithium acylferrates **1b–d** (ca 5 mmol in 15 ml of THF) at −78°C. After stirring for 12 h between −78 and +20°C, the solvent was evaporated, and the residue extracted in pentane (3 × 15 ml).

After evaporation of pentane, spectroscopically pure **3b** was obtained as a brown oil (1.90 g, 87%). IR (THF): $\nu = 2051$ (m), 1977 (m), 1947 (s), 1694 (w) cm^{-1}. ^1H-NMR ($CDCl_3$): $\delta = 0.87$ (t, 2 H, $C\underline{H}_3CH_2$); 1.30 (m, 2 H, $CH_3C\underline{H}_2CH_2$); 1.65 (m, 2 H, $CH_2C\underline{H}_2CH_2$); 2.83 (t, 2 H, $CH_2C\underline{H}_2CO$); 7.41–7.68 (10 H, aromatic C$\underline{H}$). ^{31}P-NMR ($CDCl_3$): $\delta = 74.8$ ($Ph_2\underline{P}$). ^{13}C-NMR ($CDCl_3$): $\delta = 13.73$ (s, $\underline{C}H_3$); 21.98 (s, $CH_3\underline{C}H_2CH_2$); 25.98 (s, $CH_2\underline{C}H_2CH_2$); 42.47 (d, $CH_2\underline{C}H_2CO$, $^2J_{PC} = 41.7$ Hz); 128.93–133.68 (aromatic $\underline{C}$); 212.45 (d, $Fe(\underline{C}O)_4$, $^2J_{PC} = 18.1$ Hz); 214.10 (d, $P\underline{C}O$, $^1J_{PC} = 10.9$ Hz).

Crystallization from pentane afforded **3c** as a yellow solid (1.08 g, 55%). M.p. = 89–91°C. Microanalysis: $C_{18}H_{13}O_5PFe$ (396.12): Anal. Calc. C 54.58, H 3.31; Found C 55.82, H 3.36. IR (THF): $\nu = 2052$ (m), 1978 (m), 1945 (s), 1697 (w) cm^{-1}. ^1H-NMR ($CDCl_3$): $\delta = 2.46$ (d, 3 H, $C\underline{H}_3$, $^3J_{PH} = 4.5$ Hz); 7.40–7.65 (10H, aromatic C$\underline{H}$). ^{31}P-NMR ($CDCl_3$): $\delta = 76.8$ ($Ph_2\underline{P}$). ^{13}C-NMR ($CDCl_3$): $\delta = 29.69$ (d, $\underline{C}H_3$, $^2J_{PC} = 46.5$ Hz); 128.18–133.27 (aromatic $\underline{C}$); 211.09 (d, $Fe(\underline{C}O)_4$, $^2J_{PC} = 14.6$ Hz); 211.93 (d, $P\underline{C}O$, $^1J_{PC} = 18.2$ Hz).

After evaporation of pentane, **3d** was obtained as a mixture with Ph_2PPPh_2 (60% **3d**, 40% Ph_2PPh_2) and excess $ClPPh_2$. IR (THF): $\nu = 2051$ (m), 1977 (m), 1948 (s), 1660 (w) cm^{-1}. ^1H-NMR ($CDCl_3$): $\delta = 7.37–7.83$ (15 H, aromatic C$\underline{H}$). ^{31}P-NMR

($CDCl_3$): $\delta = 77.9$ (s, $Ph_2\underline{P}$) ppm. ^{13}C-NMR ($CDCl_3$): $\delta = 126.79–138.79$ (aromatic $\underline{C}$), 202.60 (d, $Fe(\underline{C}O)_4$, $^2J_{PC} = 16.9$ Hz), 212.60 (d, $P\underline{C}O$, $^1J_{PC} = 17.7$ Hz).

4.3.3. Acylchlorodiphenylphosphine tetracarbonyl–iron **11b**

$PhPCl_2$ (0.68 ml, 5 mmol) was added to a solution of the lithium acylferrate **1b** (ca 5 mmol) in THF (15 ml) at −78°C. After stirring for 12 h between −78 and +20°C, the solvent was evaporated. The residue was extracted in pentane (3 × 15 ml) and the solvent evaporated to dryness to give **11b** as a brown oil (1.57 g, 79%). IR (THF): $\nu = 2064$ (m), 1999 (m), 1969 (s), 1704 (w) cm^{-1}. ^{1}H-NMR ($CDCl_3$): $\delta = 0.87$ (t, 3 H, $C\underline{H}_3CH_2$); 1.30 (m, 2 H, $CH_3C\underline{H}_2CH_2$); 1.64 (m, 2 H, $CH_2C\underline{H}_2CH_2$); 2.88 (m, 1 H, $^2J_{HH} = 18.2$ Hz, $^3J_{PH} = 2$ Hz) and 2.97 (m, 1 H, $^2J_{HH} = 18.1$ Hz): (2 diastereotopic H in $CH_2C\underline{H}_2CO$) 7.79–7.86 (5 H, aromatic C$\underline{H}$). ^{31}P-NMR ($CDCl_3$): $\delta = 155.9$ (Ph$\underline{P}$Cl). ^{13}C-NMR ($CDCl_3$): $\delta = 13.64$ (s, $\underline{C}H_3CH_2$); 21.92 (s, $CH_3\underline{C}H_2$); 25.81 (s, $CH_2\underline{C}H_2CH_2$); 39.92 (d, $CH_2\underline{C}H_2CO$, $^2J_{PC} = 46.9$ Hz); 127.38–133.02 (aromatic $\underline{C}$); 211.11 (2 d, $Fe(\underline{C}O)_4$ and $P\underline{C}O$, $^2J_{PC}$ ca $^1J_{PC}$ ca 17 Hz).

A similar procedure leads from **1c** to **11c** (sensitive compound which could not be purified on silica gel column, but which was spectroscopically identified). IR (THF): $\nu = 2057$ (m), 1988 (m), 1951(s), 1686 (w) cm^{-1}. ^{1}H-NMR ($CDCl_3$): $\delta = 2.58$ (d, 3 H, $C\underline{H}_3CO$, $^3J_{PH} = 4.8$ Hz); 7.47–7.59 (5 H, aromatic C$\underline{H}$). ^{31}P-NMR ($CDCl_3$): $\delta = 156.6$ (Ph$\underline{P}$Cl). ^{13}C-NMR ($CDCl_3$): $\delta = 129.31–137.20$ (aromatic $\underline{C}$); 211.20 (d, $Fe(\underline{C}O)_4$, $^2J_{PC} = 16.7$ Hz); 212.07 (d, $P\underline{C}O$, $^1J_{PC} = 19.0$ Hz).

4.3.4. $(CO)_4Fe(PHPh_2)$ **4**

A sample of 0.053 g (1.5 mmol) of $NaBH_4$ was added to a solution of 0.200 g (0.5 mmol) of **3c** in 10 ml of methanol at 0°C. After stirring for 20 min at 0°C and then 30 min at 20°C, the solvent was evaporated. The residue was treated with 10 ml of water and 10 ml of diethylether under stirring. The organic layer was separated, dried over $MgSO_4$, filtered and evaporated to dryness to give **4** (0.110 g, 62%). IR (THF): $\nu = 2053$ (w), 1972 (m), 1943 (s) cm^{-1}. ^{1}H-NMR ($CDCl_3$): $\delta = 6.95$ (d, 1 H, P$\underline{H}$, $^1J_{PH} = 374$ Hz); 7.60–7.66 (aromatic C$\underline{H}$). ^{31}P-NMR ($CDCl_3$): $\delta = 42.7$ (d, $\underline{P}H$, $^1J_{PH} = 377$ Hz). ^{13}C-NMR ($CDCl_3$): $\delta = 129.12–132.77$ (aromatic $\underline{C}$); 212.77 (d, $\underline{C}O$, $^2J_{PC} = 20.2$ Hz).

4.3.5. trans-$(CO)_3Fe(PHPh_2)_2$ **5**

A solution of KOH (0.111 g, 1.7 mmol) in methanol (8 ml) was pourred into a solution of **3b** (0.373 g, 0.85 mmol) in methanol (2 ml) at 0°C. After 0.5 h, the temperature rose to 20°C and the solvent was evaporated. The green-brown residue was extracted in THF (2 × 20 ml): the solution was filtered and evaporated to dryness, giving **5** as an oil (0.180 g, 80% = traces of **4**). IR (THF): $\nu = 2016$ (w), 1896 (s) cm^{-1}. ^{31}P-NMR ($CDCl_3$): $\delta = 53.7$ (d, $^1J_{PH} = 365.3$ Hz). ^{13}C-NMR ($CDCl_3$): $\delta = 128.82–132.66$ (aromatic $\underline{C}$); 212.69 (t, $\underline{C}O$, $^2J_{PC} = 30$ Hz). The insoluble solid was identified as pure potassium pentanoate **6**: ^{1}H-NMR (CD_3OD): $\delta = 1.01$ (t, 3 H,$C\underline{H}_3CH_2$); 1.44 (m, 2 H, $CH_3C\underline{H}_2CH_2$); 1.67 (m, 2 H, $CH_2C\underline{H}_2CH_2$); 2.49 (t, 2 H, $CH_2C\underline{H}_2COO^-$). ^{13}C-NMR ($CD_3OD$): $\delta = 14.64$ ($\underline{C}H_3CH_2$); 24.18 ($CH_3\underline{C}H_2CH_2$); 30.36 ($CH_2\underline{C}H_2CH_2$); 39.43 ($CH_2\underline{C}H_2COO^-$); 183.55 ($\underline{C}OO^-$).

4.3.6. α-Phosphinoxyvinyl phosphine tetracarbonyl–iron complxes **10c** and **10b**

A solution of 2 M LDA (0.70 ml 1.4 mmol) was synringed into a solution of **3c** (1.0 mmol) in THF (10 ml) at −78°C. The solution was stirred for 45 min between −78 and −50°C: the enolate **8c** was detected by IR in THF ($\nu = 2036$, 1933, 1593 cm^{-1}). The solution was cooled back to −78°C, and $ClPPh_2$ (0.25 ml, 1.4 mmol) was added. After stirring overnight between −78 and 20°C, the solution was filtered and evaporated to dryness. The oily residue was extracted in pentane (2 × 10 ml), and the solution was kept at −15°C until an oil deposited. The supernatant was separated and evaporated to give the *O*-phosphinylation product **10c** Scheme 5 (0.363 g, 42%): IR (THF): $\nu = 2049$ (m), 1981 (m), 1948 (s), 1598 (w) cm^{-1}. ^{1}H-NMR ($CDCl_3$): $\delta = 4.99$ (ddd,$^2J_{HH} = 3.4$ Hz, $^3J_{PH} = 9.6$ Hz, $^4J_{PH} = 2.5$ Hz); 5.50 (ddd,$^2J_{HH} = 3.4$ Hz, $^3J_{PH} = 30.0$ Hz, $^4J_{PH} = 3.2$ Hz); 7.25–7.50 (aromatic $\underline{H}$). ^{31}P-NMR ($CDCl_3$): $\delta = 76.2$ (s, $(CO)_4Fe$-$\underline{P}Ph_2$-C); 114.9 (s, O-$\underline{P}Ph_2$). ^{13}C-NMR ($CDCl_3$): $\delta = 108.14$ (dd, $=\underline{C}H_2$, $^2J_{CP}$ ca $^3J_{CP}$ ca 17 Hz); 128.59–134.33 (aromatic $\underline{C}$); 157.26 (dd, PPh_2-$\underline{C}$(O-PPh_2), $^2J_{CP} < 5$ Hz, $^1J_{CP} = 63.9$ Hz); 213.39 (d, $(\underline{C}O)_4Fe$, $^2J_{CP} = 19.5$ Hz).

A similar procedure leads from **3b** to **8b** (IR (THF): $\nu = 2037$, 1940, 1588 cm^{-1}) and **10b** Scheme 5 (30% crude yield). IR (THF): $\nu = 2052$ (m), 1979 (m), 1943

Table 3
Crystal data of mononuclear (monoacyl)phosphine carbonyl complexes

Complexes	P–C(O) (Å)	Ref.
3a	1.93	[7]
3b	1.89	This work
$BrMn(CO)_4\{P[C(O)CCl_3]PhMe\}$	1.90	[14]
$BrMn(CO)_4\{P[C(O)CH_2CHMeCl]Ph_2\}$	1.89	[15]
$AcMoCp(CO)_2\{P[COMe]Ph_2\}$	1.89	[16]
$IWCp(CO)\{P[C(O)CH_2p\text{-tol}][o\text{-}PH_2C_6H_4][(CH_2)_4I]\}$	1.90	[17]
$IWCp(CO)\{P[C(O)CH_2p\text{-tol}][o\text{-}PH_2C_6H_4]Me\}$	1.91	[17]
$W(CO)_5\{P[C(O)PhC{=}CPh]PhMe\}$	1.93	[18]

(s), 1587 (w) cm^{-1}. ^{1}H-NMR ($CDCl_3$): $\delta = 0.71$ (t, 3 H, $C\underline{H}_3$); 1,28 (m, 2 H, $CH_3C\underline{H}_2$); 2.09 (m, 2 H, $CH_3CH_2C\underline{H}_2$); 6.11 (m, 1 H, C<u>H</u>, $^3J_{PH} = 11.4$ Hz, $^4J_{PH} < 2$ Hz); 7.23–7.35 (aromatic <u>H</u>). ^{31}P-NMR ($CDCl_3$): $\delta = 76.8$ (s, $(CO)_4$Fe-<u>P</u>Ph_2-C); 122.9 (s, O-<u>P</u>Ph_2). ^{13}C-NMR ($CDCl_3$): $\delta = 13.50$ (q, $\underline{C}H_3$-CH_2, $^1J_{CH} = 125$ Hz); 22.60 (t, $CH_3\underline{C}H_2CH_2$, $^1J_{CH} = 126$ Hz); 29.65 (t, $CH_3CH_2\underline{C}H_2$, $^1J_{CH} = 126$ Hz); 149.10 (dd, PPh_2-<u>C</u>(O-PPh_2), $^2J_{CP} = 5.2$ Hz, $^1J_{CP} = 59.9$ Hz); 128.02–133.25 (=<u>C</u>H and aromatic <u>C</u>); 213.21 (d, $(\underline{C}O)_4$Fe, $^2J_{CP} = 18.8$ Hz).

4.4. Experimental data for the X-ray crystal structure determination of **3c**

Crystal data for $C_{18}H_{13}O_5PFe$: $M = 396.12$, triclinic crystal of dimensions: $0.50 \times 0.40 \times 0.30$ mm^3 (space group $P\bar{1}$ with unit cell $a = 8.872(1)$ Å, $b = 8.6078(1)$ Å, $c = 12.606(2)$ Å, $\alpha = 84.20(2)°$, $\beta = 83.19(2)°$, $\gamma = 69.23(2)°$, $V = 892$ (2) Å^3, $Z = 2$, $\rho_{calc.} = 1.47$ g cm^{-3}, $\mu = 9.55$ cm^{-1}, $F(000) = 404.88$. A total of 6863 reflections were measured (2544 independent) with $R_{average} = 0.035$. The structure was solved by direct methods (SIR92) [30] and refined by least-squares procedures on F_{obs}. All hydrogen atoms were located on a difference Fourier map, but they were introduced in calculation in idealized positions (d(C–H) = 0.96 Å), and their coordinates were recalculated after each cycle of refinement. They were given isotropic thermal parameters 20% higher than those of the carbon to which they are attached. Excepted concerning the H atoms of the methyl group, which have been isotropically refined. All non-hydrogen atoms were refined anisotropically.

Least-squares refinements were carried out by minimizing the function $\Sigma w\|F_o| - |F_c\|^2$, where F_o and F_c are the observed and calculated structures. A weighting scheme was used:

$$\text{weight} = 1/\sum_{r=1}^{n} A_r T_r(X)$$

where A_r are the coefficients for the Chebyshev polynomials $T_r(X)$ with $X = F_c/F_{cmax}$. The model reached convergence with $R = \Sigma\|F_o| - |Fc\|/\Sigma|F_o|$, $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$. A total of 2398 reflections were used with the criterion $I = \sigma(I)$. This unrestrictive criterion lead to 239 variables refined (reflections/variables ratio ca 10) for a good quality of structure: the final $R(R_w)$ value was 0.026 (0.028). The calculations were carried out with the aid of the CRYSTALS package programs [31a] running an a PC. The drawing of the molecule was realized with CAMERON (Fig. 1) [31b]. The atomic scattering factors were taken from the International Tables for X-Ray Crystallography [31c].

5. Supplementary material

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 115134 for **3c**. Copies of the information can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk). Details of the X-ray structure determination of complex **3c** are also available from the author.

Acknowledgements

This work was supported by the Centre National de la Recherche Scientifique. The authors wish to thank Ms L. Noé for performing microanalyses.

References

[1] J.-J. Brunet, G. Commenges, F.-B. Kindela, D. Neibecker, Organometallics 11 (1992) 3023.
[2] J.-J. Brunet, G. Commenges, F.-B. Kindela, D. Neibecker, Organometallics 11 (1992) 1343.
[3] J.-J. Brunet, R. Chauvin, B. Donnadieu, P. Leglaye, D. Neibecker, J. Organomet. Chem. 571 (1998) 7.
[4] J.-J. Brunet, R. Chauvin, D. Neibecker, Synthetic Commun. 27 (1997) 1433.
[5] J.-J. Brunet, R. Chauvin, O. Diallo, B. Donnadieu, J. Jaffart, D. Neibecker, J. Organomet. Chem. 570 (1998) 195.
[6] (a) A.-M. Caminade, J.P. Majoral, M. Sanchez, R. Mathieu, S. Attali, A. Grand, Organometallics 6 (1987) 1459. (b) A.-M. Caminade, J.P. Majoral, A. Igau, New J. Chem. 11 (1987) 457.
[7] J.-J. Brunet, A. Capperucci, R. Chauvin, B. Donnadieu, J. Organomet. Chem. 533 (1997) 79.
[8] (a) N. Carleton, J.F. Corrigan, S. Doherty, R. Pixner, Y. Sun, N.J. Taylor, A.J. Carty, Organometallics 13 (1994) 4179.(b) L. Weber, O. Kaminski, B. Quasdorff, H.G. Stammler, B. Neumann, J. Organomet. Chem. 529 (1997) 329.
[9] L. Weber, K. Reizig, R. Boese, Organometallics 4 (1985) 1890.
[10] R.B. King, J. Organomet. Chem. 557 (1998) 29.
[11] (a) G. Becker, W. Becker, O. Mundt, Phosphorus Sulfur 14 (1983) 267. (b) E. Lindner, R.D. Merkle, H.A. Mayer Chem. Ber. 119 (1986) 645.
[12] (a) M. Ryang, Organometal. Chem. Rev. A 5 (1970) 67. (b) E.O. Fischer, V. Kiener, J. Organomet. Chem. 23 (1970) 215.
[13] J. Barluenga, J.A. Revelli, F.J. Fananas, B. Sanni, S. Garcia-Granda, Organometallics 16 (1997) 3732.
[14] E. Lindner, R.D. Merkle, W. Hiller, R. Fawzi, Chem. Ber. 119 (1986) 659.
[15] E. Lindner, M. Steinwand, S. Hoehne, Chem. Ber. 115 (1982) 2478.
[16] H. Adams, N.A. Bailey, P. Blenkiron, M.J. Morris, J. Chem. Soc. Dalton Trans. (1997) 3589.
[17] J.E. Denison, J.C. Jeffery, S. Harvey, K.D.V. Weerasuria, J. Chem. Soc. Dalton Trans. (1991) 2677.

[18] A. Marinetti , J. Fischer, F. Mathey, J. Am. Chem. Soc. 107 (1985) 5001.
[19] R.B. King, F.-J. Wu, N.D. Sadanami, Inorg. Chem. 24 (1985) 4449.
[20] Y. Xie, J.E. Boggs, L.S. Khainkin, J.Mol. Struct. 139 (1986) 255.
[21] D.S. Bohle, G.R. Clarke, C.E.F. Rickard, W.R. Roper, J. Organomet. Chem. 353 (1988) 355.
[22] (a) R.J. Haines, C.R. Nolte, J. Organomet. Chem. 36 (1972) 163. (b) W. Ehrl, H. Wahrenkamp, J. Organomet. Chem. 63 (1973) 389.
[23] R.L. Keiter, E.A. Keiter, K.H. Ecker, C.A. Boecker, Organometallics 7 (1988) 2466.
[24] (a) P.M. Treichel , W.M. Douglas, W.K. Dean, Inorg. Chem. 11 (1972) 1615. (b) W. Petz, F. Weller, Z. Naturforsch. 51b (1996) 715.
[25] J.P. Collman, R.G. Komoto, W.O. Siegl, J. Am. Chem. Soc. 95 (1977) 2389.
[26] M.O. Albers, N.J. Coville, T.V. Ashworth, E. Singleton, J. Organomet. Chem. 217 (1981) 385.
[27] S. Al-Jibori, M. Hall, A.T. Hutton, B.L. Shaw, J. Chem. Soc. Dalton Trans. (1984) 863.
[28] R.L. Keiter, E.A. Keiter, K.H. Ecker, C.A. Boecker, Organometallics 7 (1988) 2466.
[29] E. Lindner, A. Thasitis, Chem. Ber. 107 (1974) 2418.
[30] A. Altomare, G. Cascarano, G. Giacovazzo, A. Guargliardi, M.C. Burla, G. Polidori, M. Camalli, J. Appl. Crystalogr. 27 (1994) 435.
[31] (a) D.J. Watkin, J.R. Carruthers, P.W. Betteridge, CRYSTALS User Guide, Chemical Crystallography Laboratory, University of Oxford, Oxford (1985). (b) D.J. Watkin, C.K. Prout, L.J. Pearce, CAMERON, Chemical Crystallography Laboratory, University of Oxford, Oxford, 1996. (c) International Tables for X-Ray Crystallography, vol. IV, Kynoch Press, Birmingham, UK, 1974.