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Tandem acylation–complexation of a chlorophosphine by carbonylferrates

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Abstract

Chlorodiphenylphosphine reacts with lithium acyltetracarbonylferrates to give the corresponding mononuclear acylphosphine iron complexes.

Keywords: Iron; Mononuclear acylphosphine complexes

1. Introduction

Acylphosphines are the phospha analogs of the ubiquitous carboxamides, and the main routes for their preparation are the [2 + 2] addition of P–H bonds with ketenes [1], and the condensation of acyl chlorides with phosphides, especially with trimethylsilyl-phosphines (see for example Ref. [2]). The acylphosphine pattern is also found as a ligand of transition metals: in addition to binuclear complexes with bidentate α,β-unsaturated acylphosphine ligands [3], several mononuclear monodentate acylphosphine complexes have been prepared by simple ligand substitution [4], by sophisticated processes involving P–H bonds [5], or by CO insertion into P–C bonds of strained cyclic phosphine ligands [6]. We wish to report here a route to simple acylphosphine complexes, based on an analogy with Collman's sequence for converting alkyl halides to disymmetric ketones [7].

2. Experimental, results and discussion

We wondered whether chlorophosphines could react just as chloroalkanes RCl or R'Cl, where R or R' could therefore play the role of the ligand L in Scheme 1.

If both R and R' were phosphinyl groups, the products would be phospha analogs of urea derivatives, iron complexes of which have been studied by King and coworkers [8]. In the present approach, the R group is maintained as an alkyl group, whereas R' stands for the PPh_2 group.

The acylferrates **1a–c**, also described by their Fischer lithiumoxycarbene resonance forms, were generated from RLi and $Fe(CO)_5$ [9]. [IR data in THF. **1a**: 2017(m), 1927(m), 1902–1895(s), 1570(m). **1b**: 2015(m), 1925(m), 1901–1889(s), 1558(m). **1c**: 2020(m), 1932(m), 1914–1898(s).] At the very outset, both O- and Fe-phosphinylation of **1** by Ph_2PCl could be envisaged (Scheme 2).

The complexes **1a** and **1b** react overnight with an excess of Ph_2PCl (two equivalents) in THF between −50 and 20 °C, while the IR spectra display growing absorptions at 1694 and 1678 cm^{-1} respectively. Simultaneously, the ^{31}P NMR spectra display signals at +74.7 and +77.7 ppm which have been assigned to structures **4a** and **4b** respectively, and minor signals such as that of $Ph_2P–PPh_2$ at −15.4 ppm, coming from a reduction of the excess Ph_2PCl. [Two competitive processes, acylation–complexation and reduction, operate, but characterization of an oxidized iron product, formally "$Cl_2Fe(CO)_4$", has not been attempted.] The signal of traces of the known free acylphosphine **5b** is also observed [10]. After evaporation of THF and extraction in pentane, the oily product **4a** and the crystalline

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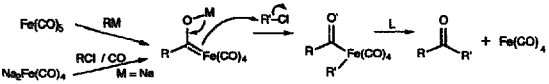
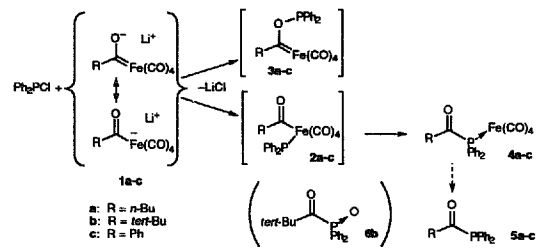


Scheme 1. Synthesis of disymmetrical ketones by carbonylation of alkyl halides.



Scheme 2. Possible reactions of chlorodiphenylphosphine with complexes **1a–c**.

Table 1
Main NMR and IR spectral data

	$\delta^{31}P$ (s)	$\delta^{13}C$ (PCO, d)	^1J(CO,P)	$\delta^{13}C$ (FeCO, d)	^2J(CO,P)	ν(PC=O)
4a	+74.7	214.1	10.9	212.5	13.1	1694
4b	+77.7	218.0	7.7	213.1	17.5	1678
5b	+5.8	225.4	52.5	—	—	1673

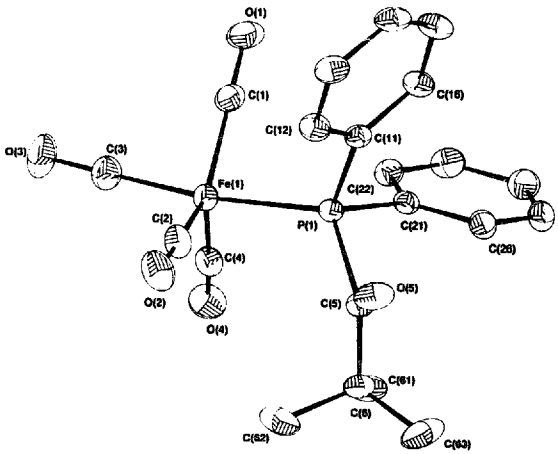


Fig. 1. Molecular structure for **4b** showing the atom labeling scheme and thermal ellipsoids at the 20% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (°): Fe(1)–P(1) = 2.247(1); Fe(1)–C(5) = 3.57; Fe(1)–O(5) = 4.30; P(1)–Fe(1)–C(3) = 169.4(2); Fe(1)–P(1)–C(5) = 117.5(1).

product **4b** are obtained in quantitative and 73% yield respectively.

Spectral data are summarized in Table 1. NMR spectra are recorded in $CDCl_3$ at 200 MHz for ^1H, 81 MHz for ^{31}P and 50 MHz for ^{13}C, with positive chemical shifts at low field given in parts per million. NMR coupling constants are in hertz. IR spectra are recorded in THF, with absorptions per centimeter. **4a**. IR: 2051(m), 1977(m), 1947(s), 1694(w). ^1H NMR: 0.87 (3H, t, CH_3), 1.30 (2H, m, CH_2Me), 1.65 (2H, m, CH_2), 2.83 (2H, m, CH_2CO), 7.41–7.68 (10H, aromatic CH). $^{13}C\{^1H\}$ NMR: 13.73 (s, CH_3), 21.98 (s, CH_2), 25.98 (s, CH_2), 42.47 (d, $^2J_{PC} = 41.7$, CH_2CO), 128.93 (d), 131.55 (s), 131.69 (d), 133.68 (d), 212.45 (d, $^2J_{PC} = 18.1$, $Fe(CO)_4$), 214.10 (d, $^1J_{PC} = 10.9$, PCO). **4b**. IR: 2051(m), 1980(m), 1949–1938(s), 1678(w). ^1H NMR: 1.18 (9H, s. $(CH_3)_3$), 7.30–7.70 (10H, aromatic C–H). $^{13}C\{^1H\}$ NMR: 28.22 (s, CH_3), 51.43 (d, $^1J_{PC} = 25.2$, *C*–CO), 128.81 (d), 131.35, 132.09 (d), 133.95 (d), 213.07 (d, $^2J_{PC} = 17.5$, $Fe(CO)_4$), 218.00 (d, $^1J_{PC} = 7.7$, PCO).

A $P \rightarrow O$ oxidation is reported to shift the C=O IR absorption from 1673 cm^{-1} in **5b** to 1725 cm^{-1} in the acylphosphine oxide **6b** (see Ref. [11]): it was therefore surprising that the $P \rightarrow Fe(CO)_4$ quaternization in **4b** did not affect the PC=O vibration from **5b**, but the structure of **4b** is confirmed by an X-ray diffraction study. To the best of our knowledge, this is the first reported structure of a mononuclear acylphosphine complex of iron (Fig. 1).

Crystal data for $C_{21}H_{19}O_5PFe$: triclinic, space group $P\bar{1}$, $Z = 2$, $a = 8.718(2)$, $b = 9.119(3)$, $c = 14.202(2)$ Å, $\alpha = 75.49(4)°$, $\beta = 76.20(1)°$, $\gamma = 79.43(3)°$, $V = 1052.4(5)$ Å^3, $M = 438.19$. Data collection was performed at $T = 293$ K (4404 reflections collected) on an Enraf–Nonius CAD-4 diffractometer using graphite monochromated Mo Kα radiation; the $\omega/2\theta$ scan mode was used. The structure was solved by direct methods (SHELXS-86) and refined by full direct-matrix least-squares techniques in the anisotropic approximation. 2420 unique reflections with $I > 3\sigma(I)$ were used in the refinement to $R = 0.0360$, $R_w = 0.0364$. Further details are available on request from the Director of the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, on quoting the full journal citation.

As expected from what is known of the carbon series, the above results are consistent with the putative iron phosphide **2** rather than the phosphinite **3**: the phosphide **2** undergoes a reductive elimination of the acyl and phosphide moities (stable complexes with both an acyl and a phosphide ligand can be characterized provided that the lone pair of the phosphide participates in a dative bond; see for example Ref. [12]). However, no acyl–phosphine complex **4c** could be detected in the reaction of Ph_2PCl with the phenyl derivative **1c** (only the phosphinite Ph_2P–OPh could be isolated hitherto). This is reminiscent of previously reported peculiar reactivities of **1c** [13], and efforts are in progress to clarify the scope and mechanism of the reaction. Optimization of a deprotection method to the free acylphosphine and study of the electrophilic reactivity of coordinated acylphosphines will be tackled.

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