Expedient synthesis of $(Ph_3P)_2Fe(CO)_3$

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(Received December 23rd, 1988)

Abstract

A one-step, high yield synthesis of highly pure $(Ph_3P)_2Fe(CO)_3$ from $KHFe(CO)_4$ and Ph_3P in ethanol is described.

Introduction

The replacement of one or two carbon monoxide ligands of $Fe(CO)_5$ by phosphines or arsines has attracted much attention, both from a synthetic and from a mechanistic point of view [1–9]. Indeed, although $(Ph_3P)Fe(CO)_4$ and $(Ph_3P)_2Fe(CO)_3$ were mentioned by Reppe as early as in 1948 [1], no selective synthesis has been described up to now, and there have been many attempts to prepare the separate complexes in good yields. Selective formation of only one substitution product is important, since there are separation difficulties, especially of the mono- from the di-substituted product, as well as of the excess of the free ligand from the products [6,7].
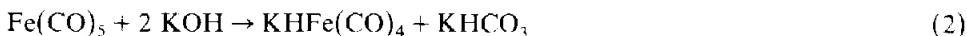
The monosubstituted complexes $Fe(CO)_4(L)$ can now be readily made from $Fe(CO)_5$ either by a combined photochemical-thermal procedure [6], or by use of metal hydrides [7] or of catalysts such as iron carbonyl anions [8] or Co^{II} salts [9]. The direct synthesis of the disubstituted complexes, however, is more difficult and, to the best of our knowledge, the most efficient (71% yield), one-step way to $(Ph_3P)_2Fe(CO)_3$ is a time-consuming (50 h) reaction of $Fe(CO)_5$ with $LiAlH_4$ in the presence of an excess of PPh_3 in refluxing THF [7]. Moreover, reactions involving the presence of an excess of triphenylphosphine often necessitate a purification step, e.g. by column chromatography ($CoCl_2 \cdot 6H_2O$/neutral alumina/silica gel column) [9].

During work aimed at developing the use of $KHFe(CO)_4$ in organic synthesis and catalysis [10,11], we observed that this complex reacts with PPh_3 in ethanol. This was quite unexpected, since an earlier report indicated that $HFe(CO)_4^-$ (as the PPN^+ or Li^+ salt) does not react with phosphines in refluxing THF for 2.5 days [7].

We were thus prompted to examine this new reaction more fully, and we report below a very simple and efficient method for the one-step synthesis of $(Ph_3P)_2Fe(CO)_3$.
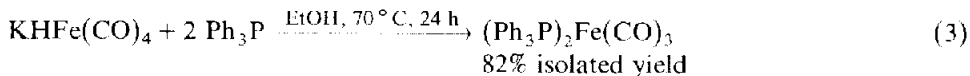
Results and discussion

The usual way of preparing ethanolic solutions of $KHFe(CO)_4$ involves reaction of $Fe(CO)_5$ with 3 equiv. KOH in ethanol for 1 h at room temperature (see eq. 1) [12]. However, this complex can also be obtained by use of 2 equiv. KOH (see eq. 2):

$$Fe(CO)_5 + 3 \, KOH \rightarrow KHFe(CO)_4 + K_2CO_3 + H_2O \qquad (1)$$

$$Fe(CO)_5 + 2 \, KOH \rightarrow KHFe(CO)_4 + KHCO_3 \qquad (2)$$

The IR spectra of solutions prepared by the reactions shown in equations 1 and 2 are superposable (carbonyl region) and show no traces of residual $Fe(CO)_5$ [13].

When PPh_3 (22 mmol) is added to an ethanolic $KHFe(CO)_4$ solution (prepared from 11 mmol $Fe(CO)_5$ and 22 mmol KOH in 60 ml ethanol) at $70 \degree C$ under argon, the solution, which is initially pale pink, rapidly deposits yellow crystals. Evaporation of the solvent after 24 h stirring at $70 \degree C$ and IR analysis of the crude residue in $CHCl_3$ indicates the formation of the disubstituted iron carbonyl complex, $(Ph_3P)_2Fe(CO)_3$, contaminated by small amounts of the monosubstituted derivative. A very simple work-up (see Experimental section) gives pure $(Ph_3P)_2Fe(CO)_3$ in 82% yield. The purity was checked by elemental analysis, IR spectroscopy (absence of the monosubstituted derivative) and ^{31}P NMR spectroscopy (absence of free triphenylphosphine and of the monosubstituted derivative). The ^{13}C NMR spectrum is also in agreement with literature data [14], and is unambiguously different from that of the monosubstituted derivative prepared as described in ref. 9, as shown by $^{13}C\{^1H,^{31}P\}$ NMR spectroscopy (see Experimental). Reaction 3 thus

$$KHFe(CO)_4 + 2 \, Ph_3P \xrightarrow{\text{EtOH, } 70 \degree C, \, 24 \, h} (Ph_3P)_2Fe(CO)_3 \qquad (3)$$
$$\text{82\% isolated yield}$$

appears to provide the best procedure reported so far for the synthesis of $(Ph_3P)_2Fe(CO)_3$.

Further experiments showed that use of larger amounts of triphenylphosphine $(Ph_3P/Fe(CO)_5 = 3)$ did not improve the yield, and that the reaction was not

Table 1

Influence of the amount of potassium hydroxide [a]

Run	KOH (mmol)	$Fe(CO)_5$ (mmol)	$(Ph_3P)_2Fe(CO)_3$ [b] (yield%)
1	33	11	55
2	22	11	82
3	11	11	60
4	5.5	11	37

[a] Reactions conducted for 24 h at $70 \degree C$ in 60 ml ethanol with 22 mmol triphenylphosphine. [b] Isolated yields; No effort has been made to determine the yield of the monosubstituted derivative.

inhibited by a carbon monoxide atmosphere. As expected from earlier reports [7], control experiments showed that $Fe(CO)_5$ itself does not react with Ph_3P (2 equiv.) during 24 h at $70\,°C$ in ethanol. As the presence of potassium hydroxide appeared to be necessary to promote the transformation of $Fe(CO)_5$ into a more reactive species, the influence of the amount of KOH was briefly studied (Table 1).

As can be seen from Table 1, the presence of an excess of base has an inhibitory effect (run 1), and the best yields are obtained with 2 equiv. of $KOH/Fe(CO)_5$ (run 2). Interestingly, the result of run 4 shows that the reaction does not require a stoichiometric amount of potassium hydroxide,which thus acts to some extent as a catalyst.

Studies are in progress to gain insight into the reaction mechanism and to extend the scope of this reaction to the synthesis of other $Fe(CO)_3(L)_2$ complexes.

Experimental

All solvents were degassed under argon immediately before use. ^{31}P and ^{13}C NMR spectra, were recorded on Bruker WH 90 and WM 250 FT spectrometer, respectively. The IR spectra were recorded on a Perkin–Elmer 597 spectrometer.

Iron pentacarbonyl (Aldrich) (1.5 ml, 11 mmol) was added to a solution of potassium hydroxide (Prolabo, 86%) (1.47 g, 22 mmol) in absolute ethanol (60 ml) previously degassed under argon for 0.5 h. After 1 h stirring at room temperature, the IR spectrum of the pale pink reaction medium exhibited absorption bands at 2000 (vw), 1920 (sh) and 1900 (s) cm^{-1}, as expected for $KHFe(CO)_4$ [15]. Triphenylphosphine (5.78 g, 22 mmol) was then added, and the closed reaction flask kept at $70\,°C$ for 24 h with stirring under argon then cooled and filtered through on sintered glass disc. The yellow solid isolated was washed with ethanol (4×50 ml), then with water (6×50 ml) and finally with ethanol (2×50 ml), and then dissolved in CH_2Cl_2 (400 ml). The solution was filtered, dried over sodium sulfate for 2 h and evaporated under reduced pressure to gave 6 g (82% yield) of yellow crystals of $(Ph_3P)_2Fe(CO)_3$. This complex is soluble in dichloromethane, chloroform and acetone, but slowly decomposes in these solvents. Analysis: Found: C, 70.68; H, 4.66. $C_{39}H_{30}O_2P_2Fe$ calc.: C, 70.50; H, 4.55%. IR $(CHCl_3)$: 1887 cm^{-1}. $^{31}P\{^1H\}$-NMR (36.43 MHz, CD_3COCD_3): 87.8, relative to external H_3PO_4. $^{13}C\{^1H\}$ and $^{13}C\{^1H,^{31}P\}$ NMR (62.89 MHz, CD_2Cl_2)(CO only): 214.70, t, $^2J(C-P)$ 29 Hz, relative to CD_2Cl_2 at 53.6 ppm.

By comparison, the complex $Fe(CO)_4(PPh_3)$ under the same conditions gives the following data: $^{31}P\{^1H\}$ NMR: 75.9; $^{13}C\{^1H\}$ and $^{13}C\{^1H,^{31}P\}$ NMR: 213.75, d, $^2J(C-P)$ 20 Hz.

Note added in proof. Since this paper was submitted, Keiter et al. [16] have reported a similarly high yield synthesis of $(Ph_3P)_2Fe(CO)_3$ by treating PPh_3 (3 equiv.) with $Fe(CO)_5$ (1 equiv.) in the presence of $NaBH_4$ (1 equiv.) in refluxing n-butanol. They also found that $NaHFe(CO)_4$ reacts with PPh_3 in refluxing n-butanol to yield $(Ph_3P)_2Fe(CO)_3$, and noted that this complex "may be prepared in high yield from the reaction of $Fe(CO)_5$, PPh_3 and NaOH".

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