Journal of Organometallic Chemistry, *461* (1993) 169–172

JOM 23753

The reaction of [PPN][HFe(CO)$_4$] with styrene in THF: an unexpected and facile synthesis of [PPN]$_2$[Fe$_2$(CO)$_8$]

Jean-Jacques Brunet, Denis Neibecker and Radhey Shyam Srivastava

Laboratoire de Chimie de Coordination du CNRS, Unité No. 8241, liée par conventions à l'Université Paul Sabatier et à l'Institut National Polytechnique de Toulouse, 205 route de Narbonne, 31077 Toulouse Cedex (France)

(Received March 26, 1993)

Abstract

The reaction of [PPN][HFe(CO)$_4$] (PPN = bis(triphenylphosphine)iminium) with styrene in refluxing tetrahydrofuran leads to the formation of [PPN]$_2$[Fe$_2$(CO)$_8$] which can be easily isolated (85% yield). The reaction mechanism is discussed.

---

1. Introduction

As part of our interest in developing new synthetic applications of tetracarbonylhydridoferrates M[HFe(CO)$_4$] [1] in both organic [2] and coordination [3] chemistry, we have recently described [3a] a simple, one-pot preparation of the dianionic mononuclear ferrate K$_2$[Fe(CO)$_4$] according to eqn. (1).

$$2\mathrm{K[HFe(CO)_4]} + 2\mathrm{PPh_3} \xrightarrow[\text{reflux}]{\text{THF}} \downarrow \mathrm{K_2[Fe(CO)_4]} + \mathrm{[Fe(CO)_3(PPh_3)_2]} + \mathrm{CO} + \mathrm{H_2} \quad (1)$$

According to the stoichiometry of eqn. (1), the yield is only 50% but this reaction appears as the best way, at least on a laboratory scale, to prepare K$_2$[Fe(CO)$_4$], a non-pyrophoric analogue of the Collman reagent [4].

We have now found that [PPN][HFe(CO)$_4$] (PPN = bis(triphenylphosphine)iminium) (**1**) is a good precursor for the facile preparation of the dinuclear ferrate [PPN]$_2$[Fe$_2$(CO)$_8$] (**2**) in good yield.

2. Results

As recently stated [5], the known procedures for preparation of [Fe$_2$(CO)$_8$]$^{2-}$ rely either on the reaction of [Fe(CO)$_4$]$^{2-}$ with pentacarbonyliron (eqn. (2)) [6], or on the reaction of the dinuclear [Fe$_2$(CO)$_9$] with hydroxides (eqns. (3), (4)) [7].

$$\mathrm{[Fe(CO)_4]^{2-}} + \mathrm{[Fe(CO)_5]} \longrightarrow \mathrm{[Fe_2(CO)_8]^{2-}} + \mathrm{CO} \quad (2)$$

$$\mathrm{[Fe_2(CO)_9]} + 3\mathrm{[OH]^-} \longrightarrow \mathrm{[Fe_2(CO)_8]^{2-}} + \mathrm{HCO_3^-} \quad (3)$$

$$\mathrm{[Fe_2(CO)_9]} + 4\mathrm{[OH]^-} \longrightarrow \mathrm{[Fe_2(CO)_8]^{2-}} + \mathrm{CO_3^{2-}} + 2\mathrm{H_2O} \quad (4)$$

Although reaction (2) can be conducted in one pot by *in situ* generation of [Fe(CO)$_4$]$^{2-}$ from [Fe(CO)$_5$], these preparations involve the manipulation of sodium (or sodium dispersion) to generate the reducing agents, namely benzophenone-sodium [5] or naphthalene-sodium [8,9]. On the other hand, reactions (3) and (4) suffer from the need for [Fe$_2$(CO)$_9$], a rather expensive iron carbonyl.

We have now discovered that the reaction of **1** (easily prepared from the inexpensive [Fe(CO)$_5$] [3b]) with styrene in refluxing THF under argon leads to the precipitation of **2** (eqn. (5)).

$$\underset{\mathbf{1}}{\mathrm{[PPN][HFe(CO)_4]}} + \underset{\text{2 equiv}}{\mathrm{C_6H_5{-}CH{=}CH_2}} \xrightarrow[\text{reflux}]{\text{THF}} \downarrow \underset{\mathbf{2}}{\mathrm{[PPN]_2[Fe_2(CO)_8]}} + \ldots \quad (5)$$

The air-sensitive brick-red complex **2** was isolated in 85% yield. It was identified by comparison of its spec-

---

Correspondence to: Professor J.-J. Brunet.

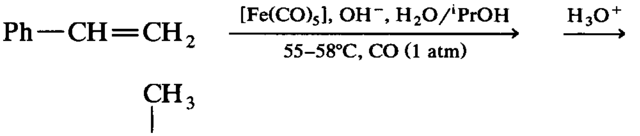
0022-328X/93/$6.00

troscopic properties (IR in various solvents, ^{13}C NMR, see experimental section) with those of an authentic sample prepared according to eqn. (4) [10]. Its purity was checked by elemental analysis and the absence of any hydridocarbonylferrate complex was verified by ^1H NMR spectroscopy. This new reaction thus appears to be a very easy and safe route for the preparation of very pure $[PPN]_2[Fe_2(CO)_8]$.

GC analysis of the THF solution indicated the presence of unreacted styrene and the formation of ethylbenzene in nearly 50% yield with respect to iron. No traces of either 2- or 3-phenylpropionaldehydes (or the corresponding alcohols) could be detected. Furthermore, GC analysis of the gas above the solution indicated that neither carbon monoxide nor hydrogen had been evolved.

3. Discussion

The reaction of $M[HFe(CO)_4]$ (M = Na or K) with styrene *in protic media* has been studied by several workers [11]. Under carbon monoxide (1 atm or higher pressure) these reactions lead to mixtures of 2- and 3-phenylpropionaldehydes (or the corresponding alcohols) together with reduction products (ethylbenzene, 1,3-diphenylbutane). We showed recently that, under strongly basic conditions, $[HFe(CO)_4]^-$ promotes a slow but highly regioselective hydrocarboxylation of styrene to 2-phenylpropionic acid under 1 atm carbon monoxide pressure (eqn. (6)) [12].



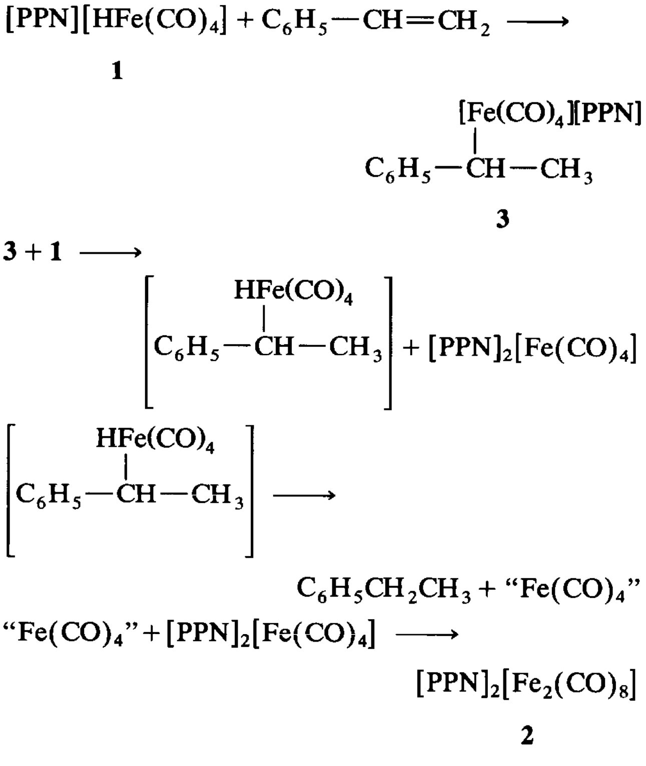
$$Ph—CH=CH_2 \xrightarrow[55–58°C,\ CO\ (1\ atm)]{[Fe(CO)_5],\ OH^-,\ H_2O/^iPrOH} \xrightarrow{H_3O^+} PH—\overset{CH_3}{\overset{|}{CH}}—CO_2H + Ph—CH_2CH_2CO_2H \quad (6)$$

$$>97\% \quad / \quad <3\%$$

To the best of our knowledge, the reaction of $M[HFe(CO)_4]$ with styrene *in aprotic media* is reported here for the first time.

Based on our experimental observations (*vide supra*), an overall reaction pathway can be proposed for the reaction of **1** with styrene (Scheme 1).

The key step of Scheme 1 is the protonation of the alkyltetracarbonylferrate **3** by **1** to generate an unstable alkyltetracarbonylhydridoferrate, which rapidly gives ethylbenzene and an unsaturated "$Fe(CO)_4$" species by reductive elimination [13]. The latter, in turn, would be quenched by the dianionic $[Fe(CO)_4]^{2-}$ (possibly via a $[(styrene)Fe(CO)_4]$ to give the dinuclear $[Fe_2(CO)_8]^{2-}$, which precipitates.



$$[PPN][HFe(CO)_4] + C_6H_5—CH=CH_2 \longrightarrow C_6H_5—\overset{[Fe(CO)_4][PPN]}{\overset{|}{CH}}—CH_3$$

1 **3**

$$\mathbf{3} + \mathbf{1} \longrightarrow \left[C_6H_5—\overset{HFe(CO)_4}{\overset{|}{CH}}—CH_3\right] + [PPN]_2[Fe(CO)_4]$$

$$\left[C_6H_5—\overset{HFe(CO)_4}{\overset{|}{CH}}—CH_3\right] \longrightarrow C_6H_5CH_2CH_3 + “Fe(CO)_4”$$

$$“Fe(CO)_4” + [PPN]_2[Fe(CO)_4] \longrightarrow [PPN]_2[Fe_2(CO)_8]$$

2

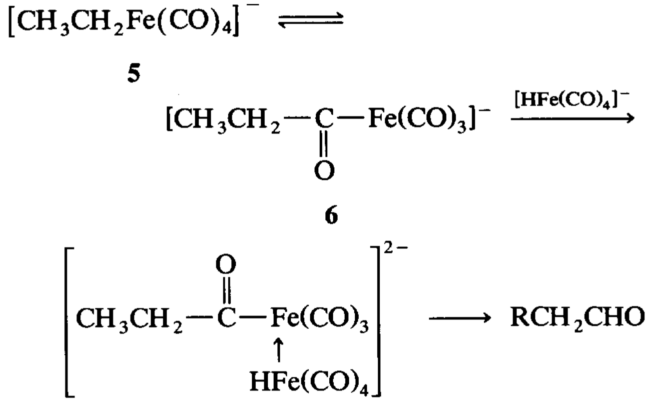
Scheme 1.

The above interpretation appears inconsistent with the results reported by Barborak and Cann [14]. Indeed, these workers demonstrated elegantly that $[Et_4N][HFe(CO)_4]$ (**4**) rapidly reacts with the tetracarbonylethylferrate (**5**) to yield propionaldehyde (eqn. (7)).

$$\underset{\mathbf{4}}{[Et_4N][HFe(CO)_4]} + \underset{\mathbf{5}}{[CH_3CH_2Fe(CO)_4]^-} \xrightarrow[0°C]{THF} \underset{65–70\%}{CH_3CH_2CHO} \quad (7)$$

The organometallic byproduct of this reaction was not identified [14]. The formation of propionaldehyde rather than ethane was interpreted as evidence that $[HFe(CO)_4]^-$ "is reacting with an unsaturated acyliron anion **6**, which is in equilibrium with **5**, but not detectable by IR analysis" (Scheme 2). This interpretation was convincingly supported by complementary experiments [14].

However, two important differences must be kept in mind when comparing Schemes 1 and 2. First, the alkyl ligands of the ferrates **3** and **5** are quite different (1-phenylethyl *vs.* ethyl). Secondly, in Scheme 1, the only gegencation is a poor complexing agent $[PPN]^+$, whereas in Scheme 2, two different cations are involved, $[Et_4N]^+$ (which can be compared to $[PPN]^+$), but also Li^+, introduced during the preparation of **5** [14].



Scheme 2.

Thus the first difference concerns the nature of the alkyl ligand. Acylferrates such as **6** are generated by migration of the alkyl group onto a carbon monoxide ligand. Therefore, their formation is strongly dependent on the electron density at the carbon atom of the migrating alkyl group. This kind of influence has been noted by Collman *et al.* who reported that, for benzyltetracarbonylferrate, migration to the acyl form is very slow, even under carbon monoxide and in THF, which is the preferred solvent [15]. The above considerations explain, at least in part, why the reaction of the tetracarbonyl(1-phenylethyl)ferrate (**3**) (Scheme 1) with $[HFe(CO)_4]^-$ does not lead to the corresponding 2-phenylpropionaldehyde. In contrast, formation of the isomeric tetracarbonyl(2-phenylethyl)ferrate would have led to 3-phenylpropionaldehyde through the bimolecular mechanism depicted by Barborak and Cann. Thus, the absence of any trace of aldehyde in the reaction of styrene with **1** (eqn. (5)) strongly suggests that the addition of $[HFe(CO)_4]^-$ to styrene is 100% regioselective. This hypothesis is consistent with the high regioselectivity found for the hydrocarboxylation of styrene (eqn. (6)) promoted by $[HFe(CO)_4]^-$ in protic media under CO (1 atm) [12].

The second difference, that of cations, must also be taken into account. Indeed, Collman [4] clearly demonstrated that the rate of the insertion which converts alkyltetracarbonylferrates into the corresponding acyl complexes in THF is markedly dependent on the nature of the gegencation, $Li^+ > Na^+ \gg PPN^+$. Thus, the protonation of **3** by **1** (Scheme 1) is the favoured reaction pathway due to the presence of the non-complexing cation $[PPN]^+$. This is also in agreement with the observed cation effect ($Li^+ > Na^+ \approx Ca^{2+} > K^+$) for the $[HFe(CO)_4]^-$ promoted hydrocarboxylation of styrene (eqn. (6)) [12].

In conclusion, the unexpected formation of $[PPN]_2[Fe_2(CO)_8]$ from the reaction of $[PPN][HFe(CO)_4]$ with styrene is due to the reluctance of the intermediate tetracarbonyl(1-phenylethyl)ferrate to equilibrate with an acyl form both because of the electron-withdrawing properties of the phenyl group and because of the non-complexing nature of the $[PPN]^+$.

4. Experimental section

4.1. General

All experiments were carried out under a well-ventilated hood. Manipulations of air-sensitive iron complexes were performed under argon using standard Schlenk tube and vacuum line techniques. Tetrahydrofuran (SDS) was freshly distilled over benzophenone-sodium. Styrene (Janssen) was distilled over calcium hydride before use. $[PPN][HFe(CO)_4]$ was prepared as previously described [3b].

IR spectra were recorded on a Perkin-Elmer 1725 IRFT spectrometer using CaF_2 (0.05 mm) windows. ^1H and ^{13}C NMR spectra were obtained using a Bruker WM 250 spectrometer.

GC analyses were performed on a Hewlett-Packard 5890 chromatograph (FID) equipped with a 3 m Carbowax 20M (10%) column. Peak areas were determined with a Spectra Physics SP 4290 integrator using hexadecane as an internal standard.

4.2. Synthesis of [PPN]$_2$[Fe$_2$(CO)$_8$]

Styrene (5.2 mmol) was added, at room temperature to a light yellow solution of $[PPN][HFe(CO)_4]$ (2.5 mmol) in THF (20 ml) under argon. The reaction mixture was then heated to 60°C and stirred for 24 h (a red precipitate was formed within 1 h). After cooling to room temperature, the red precipitate was filtered under argon, washed with THF (4 × 10 ml), and dried under vacuum to afford $[PPN]_2[Fe_2(CO)_8]$ as a red microcrystalline solid (1.5 g, 85% yield).

IR (nujol mull): ν (CO): 1908br, 1844br, 1831br cm^{-1}; IR (CH_2Cl_2); ν (CO): 1975w, 1939sh, br, 1913m, 1858s, br cm^{-1}; IR(CH_3CN): ν(CO): 1977vw, 1948vw, 1914m, 1862s, br cm^{-1}; ^{13}C NMR (62.896 MHz, CD_2Cl_2): δ (CO) (ppm): 230.7 (CD_2Cl_2 at 53.6).

Acknowledgments

The Centre National de la Recherche Scientifique (France) is gratefully acknowledged for a fellowship to R.S.S. Thanks are due to Dr R. Reed for his help in editing the English of this manuscript.

References

1 J.-J. Brunet, *Chem. Rev.*, *90* (1990) 1041.
2 (a) J.-J. Brunet, F.B. Kindela and D. Neibecker, *Synth. Commun.*, *19* (1989) 1923; (b) J.-J. Brunet and M. Taillefer, *J. Organomet.*

Chem., *384* (1990) 193; (c) J.-J. Brunet and E. Passelaigue, *Organometallics*, *9* (1990) 1711.
3 (a) J.-J. Brunet, G. Commenges, F.B. Kindela and D. Neibecker, *Organometallics*, *11* (1992) 1343; (b) J.-J. Brunet, G. Commenges, F.B. Kindela and D. Neibecker, *Organometallics*, *11* (1992) 3023; (c) J.-J. Brunet, F.B. Kindela and D. Neibecker, *Inorg. Synth.*, *29* (1992) 151 and 156.
4 J.P. Collman, *Acc. Chem. Res.*, *8* (1975) 342.
5 N.K. Bhattacharyya, T.J. Coffy, W. Quintana, T.A. Salupo, J.C. Bricker, T.B. Shay, M. Payne and S.G. Shore, *Organometallics*, *9* (1990) 2368.
6 J.P. Collman, R.L. Finke, P.L. Matlock, R. Wahren, J.I. Komoto, *J. Am. Chem. Soc.*, *100* (1978) 1119.
7 (a) W. Hieber and G. Brendel, *Z. Anorg. Allg. Chem.*, *289* (1957) 324; (b) J.R. Case and M.C. Whiting, *J. Chem. Soc.*, (1960) 4632.
8 C.E. Sumner, J.A. Collier and R. Pettit, *Organometallics*, *1* (1982) 1350.
9 H. Strong, P.J. Krusic and J. San Philippo, *Inorg. Synth.*, *28* (1990) 203.
10 K. Farmery, M. Kilner, R. Greatrex and N.N. Greenwood, *J. Chem. Soc. (A)*, (1969) 2339.
11 (a) H. Masada, M. Mitsuno, S. Suga, Y. Watanabe and Y. Takegami, *Bull. Chem. Soc. Jpn.*, *43* (1970) 3824; (b) J. Palagyi and L. Marko, *J. Organomet. Chem.*, *236* (1982) 343.
12 J.-J. Brunet, D. Neibecker and R.S. Srivastava, *Tetrahedron Lett.*, *34* (1993) 2759.
13 H. Alper, *Tetrahedron Lett.*, (1975) 2257.
14 J.C. Barborak and K. Cann, *Organometallics*, *1* (1982) 1726.
15 J.P. Collman, S.R. Winter and R.G. Komoto, *J. Am. Chem. Soc.*, *95* (1973) 249.