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Ligand Substitution Processes on Carbonylmetal Derivatives. 1. Reaction of Tetracarbonylhydridoferrates with Phosphines

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Ligand substitution processes on $KHFe(CO)_4$ (1) have been demonstrated for the first time by reaction with various phosphines (2 equiv). The reaction times and the nature of the reaction products strongly depend on (i) the nature of the solvent, (ii) the cone angle of the phosphine, and (iii) the reaction conditions. In protic media (e.g. EtOH), phosphines with small cone angles ($P(n\text{-}Bu)_3$, PMe_2Ph) react with 1 below room temperature to give the newly characterized $H_2Fe(CO)_2(PR_3)_2$ in good yield, whereas phosphines with larger cone angles react only at higher temperature and afford the disubstituted $Fe(CO)_3(PR_3)_2$ derivatives in quantitative yield. In aprotic medium (THF), phosphines ($P(n\text{-}Bu)_3$, PPh_3) react only slowly with 1 at room temperature but do so at reflux temperature to yield $K_2Fe(CO)_4$ (50%) and bis- or tris(phosphine)carbonyliron derivatives. The reaction mechanism involves the formation of a monosubstituted $K^+[HFe(CO)_3(PR_3)]^-$ derivative with a rate strongly dependent on the Tolman cone angle of the phosphine. *In THF*, this basic hydrido carbonyl anion reacts with 1 to yield $K_2Fe(CO)_4$ and $H_2Fe(CO)_3(PR_3)$. The latter further reacts to give bis- or tris(phosphine)carbonyliron derivatives. *In ethanol*, the monosubstituted $K^+[HFe(CO)_3(PR_3)]^-$ derivative is protonated to give the neutral dihydride $H_2Fe(CO)_3(PR_3)$, which, depending on the reaction conditions, is converted either to $H_2Fe(CO)_2(PR_3)_2$ by CO substitution (at low temperature) or to $Fe(CO)_3(PR_3)_2$ by H_2 elimination (at higher temperature). For phosphines exhibiting small cone angles, the disubstituted dihydride may react further with an excess of phosphine to yield the trisubstituted $Fe(CO)_2(PR_3)_3$ derivative in good yield.

Introduction

Ligand substitution processes in transition-metal complexes have attracted much attention, both for the study of mechanisms of these reactions and for the synthesis of a variety of new heteroleptic complexes.[1] In this respect, metal carbonyls have been particularly studied.[2] In the series of neutral carbonyliron derivatives, a large number of $Fe(CO)_{4-n}L_n$ ($n = 1, 2$) complexes have been synthesized *directly* by ligand substitution on pentacarbonyliron.[3] In contrast, in the series of anionic hydridocarbonyliron derivatives $[HFe(CO)_{4-n}L_n]^-$, only monosubstituted $[HFe(CO)_3L]^-$ (L = phosphite or phosphine) complexes have been synthesized.[4,5] To the best of our knowledge, no $[HFe(CO)_2L_2]^-$ complexes have ever been reported.[6]

The synthesis of the anionic $[HFe(CO)_3L]^-$ complexes, first reported by Ellis et al.,[4] involves the preparation of the corresponding $Fe(CO)_4L$ complex,[3] followed by reaction with $[Et_4N]^+OH^-$.[4,5]

Curiously, no attempts have been reported for the preparation of the above complexes directly from $[HFe(CO)_4]^-$, although the latter has been known for a long time and is very easy to generate.[7] The lack of effort in this area is perhaps due to previous reports indicating that $NaHFe(CO)_4$ does not react with PPh_3 in THF at room temperature[8] and that $[PPN]^+[HFe(CO)_4]^-$ ($[PPN]^+$ = bis(triphenylphosphine)nitrogen(1+)) does not react with $P(CH_2CH_2CN)_3$, even in refluxing THF.[3g]

Over the last few years, we have been interested in developing new synthetic applications of $[HFe(CO)_4]^-$ in protic (alcoholic or aqueous) solvents.[9–20] During studies aimed at developing the use of $KHFe(CO)_4$ for the functionalization of carbon–carbon double bonds,[11,12] we incidentally observed that PPh_3 does react with $KHFe(CO)_4$ in hot ethanol. A brief examination of this reaction led us to report that it selectively produces $Fe(CO)_3(PPh_3)_2$ in a high yield.[18] We now report full details of the reaction of phosphines with $[HFe(CO)_4]^-$, including improved syntheses of some known complexes, some high-yield preparations of new complexes, and mechanistic infor-

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Table I. Synthesis of $Fe(CO)_3(PR_3)_2$ Complexes

PR_3			reacn time,[b]	product
R	pK_a[a]	θ,[a] deg	h	(yield, %)[c]
n-Bu	8.43	132	1	**2a** (98)
Ph	2.73	145	24	**2b** (98)
Cy	9.70	170	144	**2c** (90)

[a] From ref 22. [b] Minimum time for maximum products. [c] Isolated yields.

mation about these reactions.

Results and Discussion

Reactions in Protic Medium. The most straightforward method of preparing $KHFe(CO)_4$ (**1**) involves the reaction of pentacarbonyliron with 2 equiv of potassium hydroxide in a protic medium (see eq 1).[7]

$$\mathrm{Fe(CO)_5 + 2KOH \xrightarrow{\text{protic solvent}} \underset{\mathbf{1}}{KHFe(CO)_4} + KHCO_3} \qquad (1)$$

Throughout this work, the reactions of phosphines with **1** in protic solvents were conducted by adding the phosphine directly to the above solution, i.e. in the presence of $KHCO_3$ formed during the preparation of **1** and of a small amount of water introduced with potassium hydroxide. In contrast, for reactions conducted in aprotic solvents, potassium bicarbonate and all traces of protic solvents were eliminated (see Experimental Section).

We have reported previously that the reaction of PPh_3 (2 equiv) with **1** in ethanol at 70 °C over a 24-h period selectively affords *trans*-$Fe(CO)_3(PPh_3)_2$ (**2b**) in 82% yield.[18] A quantitative yield was obtained when the reaction was performed in refluxing ethanol. Similar results can be obtained by reacting PPh_3 with either $Na^+[HFe(CO)_4]^-$ or $[Bu_4N]^+[HFe(CO)_4]^-$, although in the latter case, the reaction time was a little longer. Interestingly, we have shown that the monosubstituted derivative $Fe(CO)_4PPh_3$, prepared independently,[3e] does not react with PPh_3 under the reaction conditions and thus is not an intermediate in the formation of the disubstituted derivative $Fe(CO)_3(PPh_3)_2$.

This promising reaction (eq 2) was extended to phosphines exhibiting varied stereoelectronic properties.[21,22] Some representative results are given in Table I.

$$\mathrm{\underset{\mathbf{1}}{KHFe(CO)_4} + 2PR_3 \xrightarrow[\text{reflux}]{\text{EtOH}} \underset{\mathbf{2}}{Fe(CO)_3(PR_3)_2}} \qquad (2)$$

2a, R = *n*-Bu; **2b**, R = Ph; **2c**, R = Cy

In each case, the crude reaction medium was analyzed (IR and ^{31}P NMR spectroscopy) and shown to contain trace amounts of side products (identified as $Fe(CO)_4(PR_3)$ for R = Ph and Cy and $Fe(CO)_2(PR_3)_3$ for R = *n*-Bu; vide infra) which were easily eliminated.[20] Complexes **2** were identified[20] by their elemental analyses and by comparison of their spectroscopic properties (IR, ^1H, $^{31}P\{^1H\}$) with those reported in the literature.[3] The trans geometry previously assigned on the basis of IR data was further confirmed by $^{13}C\{^1H\}$ and $^{13}C\{^{31}P\}$ NMR spectroscopy, which showed a triplet and a singlet, respectively, for the carbon atoms of the carbonyl ligands.

For these reactions conducted in refluxing ethanol, no information could be obtained on possible intermediates by recording the IR spectra at regular intervals since only the characteristic absorption bands of **1** and **2** could be observed. As expected, in each case evolution of a gas was observed, which was shown to be a 1/1 mixture of carbon monoxide and hydrogen (GLC analysis). In the case of PPh_3, however, the volume of evolved gas was smaller than that observed (ca. 2 equiv) with the other two phosphines. This particular point has not been investigated but raises the possibility of CO + H_2 condensation products.

Examination of the reaction times vs pK_a and Tolman cone angle values of the substituting phosphine (Table I) clearly suggests that the ease with which a phosphine reacts with **1** is related to its steric bulk rather than to its intrinsic basicity.[21,22]

As a matter of fact, PPh_3 and PCy_3 do not react with **1** in ethanol at room temperature over a 24-h period. In contrast, $P(n\text{-Bu})_3$ (2 equiv) does react with **1** at room temperature with evolution of nearly 2 equiv of gas. Unexpectedly, however, this gas was identified (GLC analysis) as carbon monoxide contaminated with only small amounts of hydrogen. The crude reaction medium was shown (IR and ^{31}P NMR spectra) to contain small amounts of **2a** in addition to the compound **3a**, whose ^{31}P NMR spectrum exhibited a triplet near 64 ppm (J_{P-H} = 56.5 Hz). This new compound appeared to be unstable under these conditions, since it decomposed slowly during the NMR experiment (at 37 °C). Yet, when the reaction was conducted for 24 h near 5 °C in methanol, a ^{31}P NMR spectrum of the crude reaction medium showed that **3a** was the only substitution product formed, which was isolated in 81% yield (eq 3).

$$\mathrm{\underset{\mathbf{1}}{KHFe(CO)_4} + 2P(\mathit{n}\text{-Bu})_3 \xrightarrow[-2CO]{\text{MeOH, <5 °C}} \underset{\mathbf{3a}\ (81\%)}{H_2Fe(CO)_2[P(\mathit{n}\text{-Bu})_3]_2}} \qquad (3)$$

The dihydride **3a** is stable below 5 °C and may be kept for weeks under argon in the refrigerator. At room temperature, however, it slowly decomposes to give $Fe(CO)_2[P(n\text{-Bu})_3]_3$ (identified on the basis of IR and ^{31}P NMR spectra; vide infra, Table III) and unidentified iron complexes. The spectroscopic characteristics of **3a** are given in Table II.

The IR spectrum of **3a** in pentane exhibits two strong absorption bands of nearly equal intensity with a frequency difference of 40 cm^{-1}, thus implying a *cis*-$Fe(CO)_2$ arrangement.[23]

The main features of the NMR data obtained for **3a** (Bruker WM 250, 263K) are as follows.

(i) The $^1H\{^{31}P\}$ (hydride region), $^{31}P\{^1H\}$, and $^{13}C\{^1H,^{31}P\}$ (carbonyl region) spectra all give sharp singlet signals at −10.46, +63.6, and +217 ppm, respectively. Therefore, the hydridic hydrogens are magnetically equivalent, as are the phosphorus atoms and the two carbon atoms of the carbonyl ligands.

(ii) The ^1H (hydride region) and ^{31}P NMR spectra exhibit well-resolved 1:2:1 triplets with a coupling constant $^2J_{H-P}$ of 56.5 Hz, in agreement with a cis H–P arrangement of two equivalent hydridic hydrogens with two equivalent phosphorus atoms.[24] Variable-temperature ^1H NMR experiments between 193 and 263 K show that **3a** is neither fluxional nor a molecular hydrogen complex (T^1 > 150 ms at 193 K).[25,26]

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Table II. Spectroscopic Characteristics of $H_2Fe(CO)_2(PR_3)_2$ Complexes

		NMR:[b] δ, ppm; J, Hz		
compd	IR[a] ν_{CO}, cm^{-1}	^1H (250 MHz)	^{31}P (101.26 MHz)	^{13}C (62.89 MHz)
3a (R_3 = n-Bu_3)	1972 (s)	δ_{Fe-H} −10.46 (t)	δ 63.6 (t)	δ_{CO} 217.0 (t)
	1932 (s)	$^2J_{H-P}$ = 56.5	$^2J_{P-H}$ = 56.5	$^2J_{C-P}$ = 13.0
3d (R_3 = Me_2Ph)	1982 (s)	δ_{Fe-H} −9.6 (t)	δ 45.5 (t)	δ_{CO} 215.5 (t)
	1940 (s)	$^2J_{H-P}$ = 59.5	$^2J_{P-H}$ = 59.5	$^2J_{C-P}$ = 14.5

[a] Perkin-Elmer 597 spectrophotometer (pentane solution). [b] Bruker WM 250 spectrometer, CD_3COCD_3, 263 K.

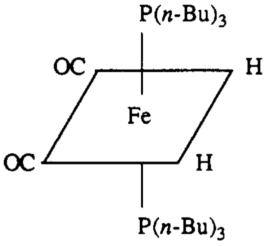

Figure 1. Idealized geometry for $H_2Fe(CO)_2[P(n\text{-}Bu)_3]_2$.

(iii) In the ^{13}C NMR spectrum, the signals of the carbon atoms of the carbonyl ligands appear as a well-resolved triplet ($^2J_{C-P}$ = 13 Hz). The $^{13}C\{^1H\}$ spectrum shows no difference, thus indicating a very small $^2J_{C-H}$ coupling constant. These data indicate that the two phosphorus atoms are magnetically equivalent with respect to *each* carbon monoxide ligand, thus implying that the two phosphine ligands occupy the axial positions.

(iv) Finally, the $^{13}C\{^1H\}$ NMR spectrum exhibits four other signals, two singlets (δ 13.55 and 25.90 ppm), one five-line figure (δ 32.10 ppm), and one three-line figure (δ 24.45 ppm). According to Pregosin and Kunz,[27] each of the last two figures originates from an AXX′ spin system, one (δ 32.10 ppm) with $^1J_{A-X}$ = 28 Hz, $^3J_{A-X'}$ < 0.5 Hz, and $^2J_{X-X'}$ = 80 Hz and the other (δ 24.45 ppm) with $^3J_{AX}$ = 12 Hz. Comparison of the $^2J_{X-X'}$ value found for **3a** with that reported (18 Hz) for $H_2Fe(CO)_2$(dppe), which exhibits cis-phosphorus atoms,[28] confirms the trans arrangement of the phosphine ligands in **3a**.[27]

On the basis of the above data, the *cis*-dihydrido *trans*-bis(phosphine) dicarbonyliron configuration (Figure 1) is proposed.

To the best of our knowledge, the latter dihydride is only the second *characterized* example of the series $H_2Fe(CO)_2(phosphine)_2$. Indeed, although the synthesis of the disubstituted complex $H_2Fe(CO)_2(PPh_3)_2$ has been claimed, no yield was given and the only available spectroscopic characteristic was the IR spectrum.[29] In fact, the only well-characterized complex of this series, $H_2Fe(CO)_2$(dppe), has been reported very recently by Schubert et al., but obviously it exhibits a cis geometry of the phosphorus atoms.[28]

Thus, it appeared that $P(n\text{-}Bu)_3$ does react with **1** in ethanol to afford either the corresponding $Fe(CO)_3[P(n\text{-}Bu)_3]_2$ or the $H_2Fe(CO)_2[P(n\text{-}Bu)_3]_2$ derivative depending on the reaction conditions. The same reactions were performed with another phosphine exhibiting a small cone angle, PMe_2Ph (cone angle 122°).[22] As expected, the reaction of PMe_2Ph (2 equiv) with **1** in ethanol (or methanol) near 5 °C yields $H_2Fe(CO)_2(PMe_2Ph)_2$ (**3d**), which was isolated in 60% yield. The dihydride **3d** unambiguously exhibits the same trans geometry as **3a** (Table II).

Table III. Spectroscopic Characteristics of $Fe(CO)_2(PR_3)_3$ Complexes

		NMR:[b] δ, ppm; J, Hz	
compd	IR[a] ν_{CO}, cm^{-1}	$^{31}P\{^1H\}$ (101.26 MHz)	$^{13}C\{^1H\}$ (62.89 MHz)
4a (R_3 = n-Bu_3)	1875 (s)	49.4	δ_{CO} 222.9 (q)[c]
	1830 (s)		$^2J_{C-P}$ = 23
	1820 (vs)		
4d (R_3 = Me_2Ph)	1880 (s)	41.1	δ_{CO} 220.3 (q)[d]
	1825 (s)		$^2J_{C-P}$ = 22

[a] Perkinz-Elmer 597 spectrophotometer, n-hexane solution. [b] Bruker WM 250 spectrometer, CD_3COCD_3, 263 K. [c] Other signals at 13.7, 24.6, 26.0, and 31.0 ppm. [d] Other signals at 21.1, 128.0, 128.7, 130.3, and 142.5 ppm.

However, when the reaction of PMe_2Ph (2 equiv) with **1** was conducted in refluxing ethanol, the reaction unexpectedly stopped before complete consumption of **1** (IR analysis). Besides small amounts of the expected $Fe(CO)_3(PMe_2Ph)_2$, the crude reaction medium was shown to contain a new substitution derivative exhibiting two strong IR absorption bands (1825 and 1870 cm^{-1}) and a singlet (δ 41.1 ppm) in the ^{31}P NMR spectrum. This compound was isolated and identified as $Fe(CO)_2(PMe_2Ph)_3$ (**4d**) on the basis of IR and NMR data (Table III).

Only very few $Fe(CO)_2(phosphine)_3$ complexes have been reported, supported, in most cases, only by the IR spectrum.[30] Since the syntheses of such complexes are cumbersome,[30] a one-pot synthesis from **1** would be of interest. For this purpose, **1** was treated with 3 equiv of PMe_2Ph for 3 h in refluxing ethanol (eq 4) to give **4d** (93% isolated yield).

$$\underset{\mathbf{1}}{KHFe(CO)_4} + 3PMe_2Ph \xrightarrow[3\ h]{EtOH,\ reflux} \underset{\mathbf{4d}}{Fe(CO)_2(PMe_2Ph)_3} \quad (4)$$

The above results raised the question as to why the reaction of $P(n\text{-}Bu)_3$ (which exhibits, at room temperature, a reactivity toward **1** similar to that of PMe_2Ph) does not lead to the corresponding $Fe(CO)_2[P(n\text{-}Bu)_3]_3$ derivative **4a** in refluxing ethanol. In fact, traces of **4a** had been detected (vide supra) in the reaction of $P(n\text{-}Bu)_3$ (2 equiv) with **1**. This observation led us to react **1** with 3 equiv of $P(n\text{-}Bu)_3$ in refluxing ethanol. Although this reaction leads, as expected, to **4a** (eq 5), **2a** always was present as

$$\underset{\mathbf{1}}{KHFe(CO)_4} + 3P(n\text{-}Bu)_3 \xrightarrow[reflux]{EtOH} \underset{\mathbf{4a}}{Fe(CO)_2[P(n\text{-}Bu)_3]_3} + \underset{\mathbf{2a}}{Fe(CO)_3[P(n\text{-}Bu)_3]_2} \quad (5)$$

well (Ratio **4a**/**2a** = 2/1, via ^{31}P NMR). Control experi-

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ments showed that **2a** does not react with $P(n\text{-}Bu)_3$ in refluxing ethanol, which suggests that **2a** is not an intermediate in the formation of **4a**.

In contrast, the reaction of **3a** with $P(n\text{-}Bu)_3$ in refluxing ethanol was shown to lead selectively to **4a**. A similar reaction could be performed with **3d** (eq 6), thus allowing us to rationalize the in situ formation of complexes 4.

$$\underset{\mathbf{3a,d}}{H_2Fe(CO)_2(PR_3)_2} + 3PR_3 \xrightarrow[-H_2]{\text{EtOH, reflux}} \underset{\mathbf{4a,d}}{Fe(CO)_2(PR_3)_3} \tag{6}$$

Further control experiments allowed us to show *qualitatively* that **4a** reacts with 1 in refluxing ethanol to lead to **2a** by some redistribution process. This observation was taken into account in order to perform the one-pot, selective synthesis of **4a**. The reaction of 1 with $P(n\text{-}Bu)_3$ (3 equiv) in ethanol was conducted near room temperature until complete consumption of 1 (24 h) was observed; then, the reaction medium was heated to reflux for 2 h. Under these conditions, **4a** was formed very selectively and could be isolated in 85% yield.

The formation of the neutral complexes $H_2Fe(CO)_2(PR_3)_2$ (**3a,d**) from the hydridoferrate 1 (eq 3) suggests that a protonation step occurs during the reaction. An interesting question is at which level this protonation does occur, i.e. $[HFe(CO)_4]^-$, $[HFe(CO)_3PR_3]^-$ or $[HFe(CO)_2(PR_3)_2]^-$. The first possibility is to consider the intervention of $H_2Fe(CO)_4$, the conjugate acid of 1 ($pK_a = 4.0$ at 20 °C).[7] In fact, there is some ambiguity in the literature data about the reaction of $H_2Fe(CO)_4$ with PPh_3. Farmery and Kilner first reported that the reaction of $H_2Fe(CO)_4$ with 1 equiv of PPh_3 in toluene at 0 °C yields $Fe(CO)_4PPh_3$ *by loss of hydrogen*, which was shown to be the only gaseous product.[31] Unfortunately, no yields were reported. When the reaction was conducted with 2 equiv of PPh_3, the disubstituted $Fe(CO)_3(PPh_3)_2$ derivative was obtained as the only product.[31] Later, Pearson et al. reported that $H_2Fe(CO)_4$ reacts with PPh_3 (either in acetone at −70 °C or in methanol at room temperature) to generate $H_2Fe(CO)_3PPh_3$ *by CO substitution*.[32] Decomposition of the latter in the presence of PPh_3 gives $Fe(CO)_3(PPh_3)_2$.[32] Unfortunately, no quantitative data are available.

As mentioned previously, Collman et al. reported that $NaHFe(CO)_4$ does not react with PPh_3 in THF *at room temperature* after 3 h (^1H NMR observation).[8] When acetic acid was added to the above solution, the ^1H NMR singlet due to $NaHFe(CO)_4$ decreased and a doublet (δ −9.39 ppm, $J_{H-P} = 43$ Hz) grew in, which disappeared within 15 min. Hydrogen was identified above a similar reaction mixture, but no indication was given about the possible evolution of carbon monoxide.[8] The observed doublet was attributed to $NaHFe(CO)_3PPh_3$, which was unknown in 1978. The monosubstituted hydrido anionic complexes $[M]^+[HFe(CO)_3PPh_3]^-$ have been synthesized more recently,[4,5] and shown to exhibit a trans configuration with a small J_{H-P} coupling constant (e.g. for $M^+ = [Et_4N]^+$, $J_{H-P} = 11.98$ Hz, δ −9.12 ppm, THF-d_8, room temperature).[5b] In our opinion, the doublet observed by Collman et al. must be attributed to $H_2Fe(CO)_3(PPh_3)$ having the phosphine cis to both hydrogens and the hydrogens cis to each other, as in $H_2Fe(CO)_3[P(OPh)_3]$ (δ −10.4 ppm, $J_{H-P} = 60$ Hz).[33] Indeed, in the series of iron carbonyl hydrides, large J_{H-P} coupling constants are known to result from a cis configuration.[34] On the basis of the above considerations, the results from the Collman group may be interpreted in terms of the formation of $H_2Fe(CO)_4$, which reacts with PPh_3, as observed by Pearson et al.,[32] to give the unstable $H_2Fe(CO)_3(PPh_3)$, which then changes (either by decomposition or by further reaction with PPh_3) with hydrogen gas evolution.

However, the possible intervention of $H_2Fe(CO)_4$ in the reaction of 1 with phosphines in ethanol is not favored on the basis of the following considerations: (i) reactions 2 and 3 are conducted in the presence of 1 equiv of $KHCO_3$ (a coproduct in the preparation of 1, vide supra); (ii) heating an ethanolic solution of 1 at reflux for 24 h results in the formation of only very small amounts of the red $[HFe_3(CO)_{11}]^-$ (IR analysis), in agreement with the observation by Keiter et al. that $Na^+[HFe(CO)_4]^-$ does not significantly react with refluxing 1-butanol (at 127 °C).[3j]

The second possibility is to consider that the reaction begins with a ligand substitution on 1 and that the protonation step occurs on $[HFe(CO)_3PR_3]^-$. A related possibility has been proposed by Keiter et al. for the selective production of *trans*-$Fe(CO)_3(PPh_3)_2$ by reaction of $Fe(CO)_5$ with PPh_3 (3 equiv) in the presence of $NaBH_4$ (1 equiv) in refluxing 1-butanol (eq 7–11).[3j]

$$Fe(CO)_5 + BH_4^- \rightarrow Fe(CO)_4CHO^- + BH_3 \tag{7}$$

$$Fe(CO)_4CHO^- \rightarrow HFe(CO)_4^- + CO \tag{8}$$

$$HFe(CO)_4^- + PR_3 \rightarrow HFe(CO)_3PR_3^- + CO \tag{9}$$

$$HFe(CO)_3PR_3^- + n\text{-}BuOH \rightarrow H_2 + n\text{-}BuO^-\text{---}Fe(CO)_3PR_3 \tag{10}$$

$$n\text{-}BuO^-\text{---}Fe(CO)_3PR_3 + PR_3 \rightarrow Fe(CO)_3(PR_3)_2 \tag{11}$$

Although these authors have no direct evidence for the intermediate formation of $[HFe(CO)_3PPh_3]^-$ *during the reaction*, they clearly showed that $[Et_4N]^+[HFe(CO)_3PPh_3]^-$, prepared independently, rapidly reacts with 1 equiv of PPh_3 in refluxing 1-butanol to yield selectively $Fe(CO)_3(PPh_3)_2$ (67% isolated yield). This result allowed them to propose that $[HFe(CO)_3PPh_3]^-$ was more likely to be the principal intermediate. In contrast to $[HFe(CO)_4]^-$, which does not significantly react with 1-butanol under the reaction conditions, $[HFe(CO)_3PPh_3]^-$ is believed to react with 1-butanol, liberating dihydrogen and thus providing a coordination site for the second PPh_3 ligand.[3j]

The questionable step in the mechanism proposed by Keiter et al. is the direct ligand substitution on 1 to generate the monosubstituted hydrido anion $[HFe(CO)_3PR_3]^-$. The substitution of a carbonyl ligand on carbonylmetalates is well established in the case of $[Co(CO)_4]^-$. Indeed, substitution of a carbonyl ligand in $NaCo(CO)_4$ by ^{13}CO, phosphines, and phosphites have been observed in THF.[35]

$$Na^+[Co(CO)_4]^- + PR_3 \xrightarrow{\text{THF, reflux}} Na^+[Co(CO)_3PR_3]^- + CO \tag{12}$$

$$R = OPh,\ O\text{-}n\text{-}Bu,\ Ph,\ n\text{-}Bu$$

Although no quantitative data are available, the authors reported that the most facile substitution occurred with $P(OPh)_3$. This observation is in agreement with our own results since, among the phosphorus compounds tested by these authors, $P(OPh)_3$ is the one which exhibits the smallest cone angle.

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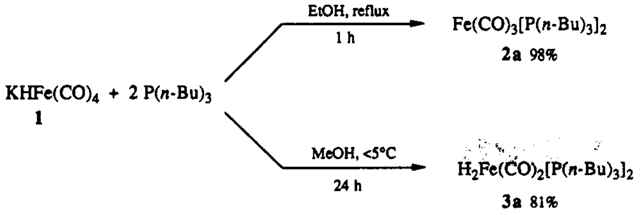
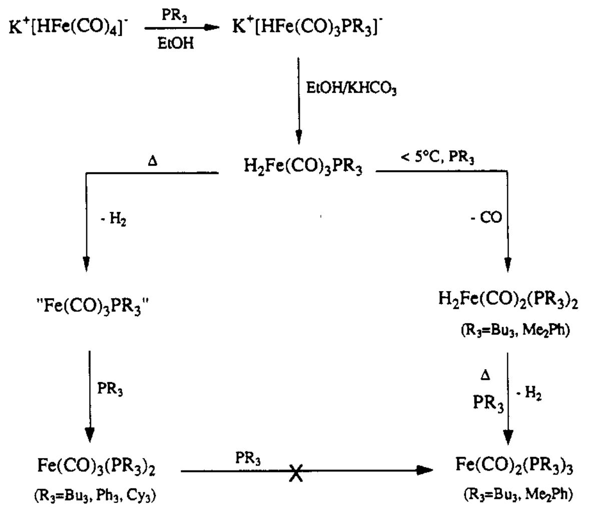
Scheme I



Scheme II



However, to the best of our knowledge, the only reported direct ligand substitution on 1 concerns a reaction of $Na^+[HFe(CO)_4]^-$ with ^{13}CO.[36] No proven example of a direct substitution of a carbonyl ligand of 1 by a *weaker π-acceptor ligand* has been reported.[5,37] This led us to try to prove the intermediate formation of some $[HFe(CO)_3PR_3]^-$ complex during the reaction of 1 with a phosphine. For that purpose, we examined the reaction of PPh_3 (2 equiv) with $[Bu_4N]^+[HFe(CO)_4]^-$ in ethanol at a moderate temperature. This choice was directed by two considerations: (i) among the known $[Et_4N]^+[HFe(CO)_3PR_3]^-$ complexes,[5] the PPh_3 derivative is the least sensitive to methanol and (ii) it is our experience that the nature of the cation plays an important part in the reactivity of the related $M^+[HFe(CO)_3[P(OR)_3]]^-$ complexes toward methanol or ethanol, the potassium derivative being more easily protonated than the $[PPN]^+$ or $[Bu_4N]^+$ derivatives.[38] This reaction was performed at 40 °C and stopped after 72 h. After evaporation of the solvent under reduced pressure, the reaction mixture was dissolved in THF. IR analysis showed the presence of two compounds, namely $Fe(CO)_3(PPh_3)_2$ (ν_{CO} 1887 cm^{-1}) and the expected $[Bu_4N]^+[HFe(CO)_3PPh_3]^-$ (ν_{CO} = 1926 (m), 1832 (s), and 1820 (sh) cm^{-1}), identified by comparison with the IR spectra of the $[Et_4N]^+$ derivative.[5] This result clearly establishes the intermediate formation of $[Bu_4N]^+[HFe(CO)_3PPh_3]^-$ and suggests that it evolves by protonation to generate the conjugate acid $H_2Fe(CO)_3PPh_3$. The stability of the dihydrides $H_2Fe(CO)_3PR_3$ (vide supra) appears to be the factor that determines whether the reaction gives the corresponding $Fe(CO)_3(PR_3)_2$ or $H_2Fe(CO)_2(PR_3)_2$ derivatives. Indeed, the direction of these reactions is determined by the reaction conditions, as evidenced in the case of $P(n\text{-}Bu)_3$ (Scheme I).

The reaction of 1 with phosphines exhibiting large cone angles (PPh_3, 145°; PCy_3, 170°) must be conducted in refluxing ethanol, since it was shown to be extremely slow at room temperature (vide supra). This, in turn, promotes the decomposition of the intermediate $H_2Fe(CO)_3PR_3$ by loss of H_2 and affords the corresponding $Fe(CO)_3(PR_3)_2$ complexes by reaction of a coordinatively unsaturated "$Fe(CO)_3PR_3$" species (possibly stabilized by a solvent molecule or by an alkoxide, as suggested by Keiter et al.)[3j] with excess PR_3. To the best of our knowledge, until recently, only the PPh_3 derivative of the series $H_2Fe(CO)_3$(phosphine) has been reported, with reference to its thermal instability.[6,32] Decomposition of this complex in methanol in the presence of PPh_3 has been reported to give *trans*-$Fe(CO)_3(PPh_3)_2$.[32] Similarly, protonation of $[Et_4N]^+[HFe(CO)_3(PPh_3)]^-$ in the presence of 5 equiv of PPh_3 has been demonstrated to give a practically quantitative yield of *trans*-$Fe(CO)_3(PPh_3)_2$.[6] More recently, the PPh_3 and the PMe_3 derivatives of this series have been obtained in a quite different way, but no further information about their stability or reactivity has been given.[39] It must also be noted that, at least for $P(n\text{-}Bu)_3$ (vide supra), part of the disubstituted derivative **2a** formed could come from a reaction of 1 with **4a**. However, this particular pathway is not believed to play an important role, since it appeared to be slower than the formation of **2a** by reaction of 1 with $P(n\text{-}Bu)_3$ in refluxing ethanol.

In contrast, the reaction of 1 with phosphines exhibiting small Tolman cone angles can be conducted at room temperature or below. Under these conditions, the intermediate $H_2Fe(CO)_3PR_3$ derivatives do not decompose but react with the second equivalent of PR_3 by CO substitution to yield the disubstituted $H_2Fe(CO)_2(PR_3)_2$ complexes. With such phosphines, a further reaction is possible, leading to the trisubstituted derivatives $Fe(CO)_2(PR_3)_3$. With $P(n\text{-}Bu)_3$, this reaction is observed in refluxing ethanol only when more than 2 equiv of phosphine is used. On the other hand, in the case of PMe_2Ph, the formation of the trisubstituted derivative **4d** is observed even in the presence of only 2 equiv of phosphine. This difference may be rationalized by considering either that, in refluxing ethanol, the monosubstituted dihydride $H_2Fe(CO)_3(PMe_2Ph)$ is more stable than the corresponding $H_2Fe(CO)_3[P(n\text{-}Bu)_3]$ or that a second ligand substitution on $H_2Fe(CO)_3(PMe_2Ph)$ is easier than on $H_2Fe(CO)_3[P(n\text{-}Bu)_3]$ because of the smaller cone angle of PMe_2Ph (122°), as compared to that of $P(n\text{-}Bu)_3$ (132°).[21,22]

Finally, the third possibility, i.e. the formation of the disubstituted $K^+[HFe(CO)_2(PR_3)_2]^-$ derivatives, is not a likely one since their monosubstituted hydrido anionic precursors are rapidly protonated.

The general reaction mechanism thus proposed for the reaction of 1 with phosphines in protic media is described in Scheme II.

Reactions in Aprotic Medium. The above results led us to reinvestigate the reaction of phosphines with 1 in THF. As previously noted, $Na^+[HFe(CO)_4]^-$ has been reported not to react with PPh_3 in THF over a 3-h period at room temperature,[8] whereas we found that 1 does react with phosphines in protic solvents. The reaction of 1 (free of potassium bicarbonate) with PPh_3 (2 equiv) for 24 h at room temperature in THF yields only traces of $Fe(CO)_3(PPh_3)_2$, in agreement with the result reported by Collman et al.[8] However, when the same reaction is conducted for

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24 h in refluxing THF, gas evolution is observed and a white solid precipitates. The gas was shown to be a mixture of hydrogen and carbon monoxide in nearly 1/1 ratio (GLC analysis). Further reaction of the separated solid with $(C_6H_5)_3SnCl$ resulted in the formation of $K^+[(C_6H_5)_3SnFe(CO)_4]^-$, which, on metathesis with $[Et_4N]Br$, yielded the known $[Et_4N]^+[(C_6H_5)_3SnFe(CO)_4]^-$ (95%), thus allowing us to conclude that the white solid is $K_2Fe(CO)_4$ (48% yield, based on 1).[6,40] Further evidence was obtained by showing that the reaction of this compound with 1-iodohexane in THF in the presence of triphenylphosphine, followed by classical workup,[41] yields heptanal in high yield (GLC analysis). Finally, the supernatant THF solution was shown to contain **2b**, isolated in 45% yield (based on 1). The overall reaction is represented by eq 13.

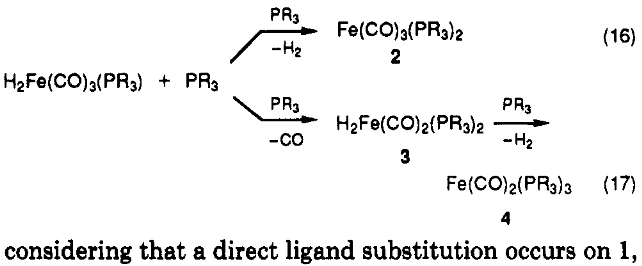
$$\underset{\mathbf{1}}{2KHFe(CO)_4} + 2PPh_3 \xrightarrow[48\ h]{THF,\ reflux} K_2Fe(CO)_4 + \underset{\mathbf{2b}}{Fe(CO)_3(PPh_3)_2} + CO + H_2 \quad (13)$$

When the same reaction was conducted with $P(n\text{-}Bu)_3$, a more rapid reaction occurred and $K_2Fe(CO)_4$ was isolated in nearly 50% yield (based on 1). During the course of the reaction, the intermediate formation of **3a** was observed (^{31}P NMR and IR). At the end of the reaction, the supernatant THF solution was shown to contain $Fe(CO)_3[P(n\text{-}Bu)_3]_2$ (**2a**) and $Fe(CO)_2[P(n\text{-}Bu)_3]_3$ (**4a**), identified on the basis of their spectroscopic properties (vide supra). In this case, the gas evolution was more thoroughly studied. At the beginning of the reaction, the evolved gas is mainly carbon monoxide, whereas at the end of the reaction it is a 1/1 mixture of carbon monoxide and hydrogen. When the same reaction was conducted at room temperature, a very slow reaction occurred. It was stopped after 72 h (i.e., before completion), to give $K_2Fe(CO)_4$ in 15% yield. In this case also, the reaction medium was shown to contain **2a**, **4a**, and, transiently, **3a**.

The above experiments clearly show that phosphines do react with 1 in THF and confirm that the Tolman cone angle of the phosphine plays an important role in such reactions. These results can be rationalized (eq 14–17) by

$$\underset{\mathbf{1}}{KHFe(CO)_4} + PR_3 \xrightarrow{THF,\ reflux} K^+[HFe(CO)_3(PR_3)]^- + CO \quad (14)$$

$$K^+[HFe(CO)_3(PR_3)]^- + KHFe(CO)_4 \longrightarrow K_2Fe(CO)_4\downarrow + H_2Fe(CO)_3(PR_3) \quad (15)$$



$$H_2Fe(CO)_3(PR_3) + PR_3 \xrightarrow[-H_2]{PR_3} \underset{\mathbf{2}}{Fe(CO)_3(PR_3)_2} \quad (16)$$

$$H_2Fe(CO)_3(PR_3) + PR_3 \xrightarrow[-CO]{PR_3} \underset{\mathbf{3}}{H_2Fe(CO)_2(PR_3)_2} \xrightarrow[-H_2]{PR_3} \underset{\mathbf{4}}{Fe(CO)_2(PR_3)_3} \quad (17)$$

considering that a direct ligand substitution occurs on 1, leading to the monosubstituted derivative $K^+[HFe(CO)_3(PR_3)]^-$. This complex, which is conceivably more basic than $K^+[HFe(CO)_4]^-$,[5] then deprotonates 1 to produce $K_2Fe(CO)_4$, which precipitates, and the monosubstituted dihydride $H_2Fe(CO)_3PR_3$, which, depending on the exact nature of R, evolves to yield either $Fe(CO)_3(PR_3)_2$ by itself or in a mixture with $Fe(CO)_2(PR_3)_3$ (via $H_2Fe(CO)_2(PR_3)_2$, vide supra).

Thus, although there was no evidence of the postulated intermediates $K^+[HFe(CO)_3(PR_3)]^-$, because of their reactivity toward 1 in THF, the isolation of $K_2Fe(CO)_4$ strongly suggests their formation. A result that further supports this hypothesis is that the related $K^+[HFe(CO)_3\{P(OR)_3\}]^-$ could be isolated from similar reactions of 1 with phosphites in THF.[38] In the latter case, the better π-acceptor properties of the phosphites (as compared to those of phosphines) decrease the basicity of the monosubstituted hydrido anionic complexes, thus preventing their further reaction with 1 and allowing them to be isolated in very high yields.[38]

Generation of $K^+[HFe(CO)_2(PR_3)_2]^-$ Complexes. As mentioned in the Introduction, no $[HFe(CO)_2(PR_3)_2]^-$ derivative has ever been reported. The easy preparation of the dihydrides **3** reported in this work encouraged us to treat them with a base in order to generate the corresponding hydrido dicarbonyl anion. The reaction of **3a** or **3d** with an excess of KH in THF-d_8 at room temperature allows the in situ generation of the corresponding dark red hydridodicarbonylbis(phosphine)iron complexes **5** for the first time (eq 18).

$$\underset{\mathbf{3}}{H_2Fe(CO)_2(PR_3)_2} \xrightarrow[25\ °C]{KH,\ THF\text{-}d_8} K^+[HFe(CO)_2(PR_3)_2]^- \quad \begin{matrix}\mathbf{5a},\ R_3 = n\text{-}Bu_3\\ \mathbf{5d},\ R_3 = Me_2Ph\end{matrix} \quad (18)$$

The spectroscopic characteristics of complexes **5** are given in Table IV.

The main features of the NMR data of complexes **5** are as follows.

(i) The $^{31}P\{^1H\}$ spectra show a sharp singlet in each case, indicating that the two phosphorus atoms are equivalent. The J_{P-H} coupling constants are 41 and 31 Hz for **5a** and **5d**, respectively, suggesting a cis H–P arrangement of the two equivalent phosphorus atoms with respect to the hydridic hydrogen.[5]

(ii) The $^{13}C\{^1H,^{31}P\}$ spectra also exhibit sharp singlets for the carbonyl ligands, at 232.9 and 229.7 ppm for **5a** and **5d**, respectively, thus indicating that the two carbonyl ligands are equivalent.

Examination of the IR spectra suggests that **5d** exhibits a trigonal-bipyramidal geometry, with the hydridic ligand and the carbonyl ligands occupying equatorial positions. Curiously, the geometry of **5a** is best described as a distorted square pyramid with the hydridic ligand in an apical position and the carbonyl ligands trans to each other. Attempts to grow X-ray-quality crystals have been unsuccessful.

Reactivity of $KHFe(CO)_4$. The experimental results described in this paper establish for the first time that phosphine for carbon monoxide substitutions occur with both anionic and neutral hydridocarbonyliron complexes, namely $[HFe(CO)_4]^-$ and $H_2Fe(CO)_3PR_3$. Although kinetic data which would allow us to discuss the reaction mechanism(s) by which these substitutions occur are lacking, we feel that some interesting observations on the reactivity of $KHFe(CO)_4$ have been made which deserve further comment. Darensbourg et al. clearly established (IR experiments) that, for $NaHFe(CO)_4$ in THF, a site-selective ion-pairing interaction occurs between the sodium cation and an equatorial carbonyl ligand. Such an interaction is not observed when sodium is replaced by a more bulky cation such as $[PPN]^+$. This interaction is believed to make the carbonyl ligands of $NaHFe(CO)_4$ more labile. This explains why $NaHFe(CO)_4$ readily exchanges carbonyl ligands with gaseous ^{13}CO whereas $[PPN]^+[HFe(CO)_4]^-$ does not.[36]

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Table IV. Spectroscopic Characteristics of Complexes $KHFe(CO)_2(PR_3)_2$

		NMR:[b] δ, ppm; *J*, Hz			
compd	IR[a] ν_{CO}, cm^{-1}	^1H	$^{31}P\{^1H\}$	$^{13}C\{^1H\}$	$^{13}C\{^{31}P\}$
5a (R_3 = *n*-Bu_3)	1735 (sh) 1740 (s) 1777 (m)	δ_{FeH} −10.5 (t) $^2J_{H-P} = 41$	δ 61.0 (s)	δ_{CO} 232.9 (t) $^2J_{C-P} = 7$	δ_{CO} 232.9 (d) $^2J_{C-H} = 12$
5d ($R_3 = Me_2Ph$)	1751 (s) 1800 (vw) 1817 (s)	δ_{FeH} −10.1 (t) $^2J_{H-P} = 31$	δ 41.8 (s)	δ_{CO} = 229.7 (s) $^2J_{C-P} \approx 0$	δ_{CO} 229.7 (d) $^2J_{C-H} = 16$

[a] Perkin-Elmer 1725 FTIR spectrophotometer, THF solution. [b] Bruker WM 250 spectrometer, THF-d_8, 309 K for **5a**, 305 K for **5d**, at 250, 101.26, and 62.89 MHz for ^1H, ^{31}P and ^{13}C NMR spectra, respectively.

The IR spectrum of $K^+[HFe(CO)_4]^-$ has been recorded in THF, and a similar interaction has been observed (absorption band at 1856 cm^{-1}, as compared to 1854 cm^{-1} for $NaHFe(CO)_4$). In this solvent, phosphines do react with $K^+[HFe(CO)_4]^-$, the bulkiest one, PPh_3 ($\theta = 145°$), reacting more slowly than $P(n\text{-}Bu)_3$ ($\theta = 132°$) (vide supra).

When the IR spectrum of $K^+[HFe(CO)_4]^-$ is recorded in methanol or ethanol, no interaction between K^+ and a carbonyl ligand is observed. Further experiments conducted by adding increasing amounts of methanol (or ethanol) to a THF solution of $K^+[HFe(CO)_4]^-$ showed that the absorption band attributed to the carbonyl ligand interacting with K^+ (1856 cm^{-1}) gradually disappears. On the basis of the above observations, it could be expected that $K^+[HFe(CO)_4]^-$ would react with a phosphine more slowly in ethanol than in THF. However, the reverse is observed, since the reaction of $K^+[HFe(CO)_4]^-$ with $P(n\text{-}Bu)_3$ in ethanol at room temperature is complete within 24 h whereas, in THF, it is far from complete after 72 h (vide supra). This observation can be related to another piece of evidence found when the IR spectra of $K^+[HFe(CO)_4]^-$ in THF and in ethanol are compared. Indeed, besides the absence of the absorption band attributed to the carbonyl ligand interacting with K^+ (1856 cm^{-1}), the frequencies of all the other absorption bands in THF are shifted to higher values in ethanol (1999 to 2008, 1911 to 1921, and 1878 to 1893 cm^{-1}). This shift to higher frequencies reflects a decrease of the back-bonding from the metal to the carbonyl ligands, thus explaining that the latter are more labile in ethanol.

Comparison of the ^1H NMR spectra of **1** in THF-d_8 and in CD_3OD also reveals some different aspects. In THF-d_8, the hydride resonance of **1** appears at −8.75 ppm (as compared to −8.68 ppm for $NaHFe(CO)_4$ and −8.70 ppm for $[PPN]^+[HFe(CO)_4]^-$).[5b] In CD_3OD, although a slow H–D exchange is observed, the hydride resonance of **1** clearly appears at −9.05 ppm. This difference confirms that the hydridic character of **1** is more pronounced in methanol than in THF, in agreement with a more important back-bonding to the carbonyl ligands in the latter solvent (IR data, vide supra). The possible role of protic solvents in the polarization of the $[H\text{–}Fe]^-$ bond is not clearly understood at the present time.

Conclusion

This work emphasizes the versatility of $KHFe(CO)_4$, a very easily available starting material, for the expedient, high-yield synthesis of a variety of phosphine-substituted iron carbonyl complexes, either neutral, such as $Fe(CO)_3(PR_3)_2$, $Fe(CO)_2(PR_3)_3$, and $H_2Fe(CO)_2(PR_3)_2$, or anionic, such as $KHFe(CO)_2(PR_3)_2$, most of which are reported here for the first time. Our study also provides an original, very easy access to $K_2Fe(CO)_4$.

The formation of these substituted iron carbonyl derivatives initially occurs via substitution of one carbonyl ligand of $KHFe(CO)_4$ by the phosphine. The rate of this ligand substitution and the nature of the final product are determined mainly by the cone angle of the phosphine, by the nature (protic or aprotic) of the solvent, and by the reaction temperature.

Work aimed at confirming these conclusions by studying the reactivity of $KHFe(CO)_4$ with various phosphites is in progress.

Experimental Section

A. Methods and Materials. All sample manipulations were carried out under argon using standard Schlenk tube and vacuum techniques. Absolute ethanol and methanol (Prolabo, Normapur) were used without further purification but degassed by bubbling argon for 0.25 h. Tetrahydrofuran (SDS) was distilled over Na/benzophenone and transferred under argon. Iron pentacarbonyl (Aldrich) and potassium hydroxide (Prolabo, 86%) were used without further purification. Phosphines were purified before use, either by recrystallization (PPh_3, PCy_3) or by distillation ($P(n\text{-}Bu)_3$, PMe_2Ph) under argon. Argon U (L'Air Liquide) was used after passage on 3-Å molecular sieves. KH is obtained as a dispersion in mineral oil (Aldrich).

B. Instrumentation. Infrared spectra were recorded on a Perkin-Elmer 597 or a Perkin-Elmer 1725X IRFT spectrometer using CaF_2 (0.05-mm) windows. ^1H, ^{31}P, and ^{13}C NMR spectra were recorded on either a Bruker WP 80 or WM 250 spectrometer (80 and 250 MHz, respectively), as noted in the footnotes of Tables II–IV. Gas chromatographic analyses were performed on an Intersmat IGC 16 chromatograph (catharometer) fitted with a 2 m × $^1/_8$ in. column containing 5-Å molecular sieves (40–60 mesh) with helium as carrier gas.

C. Preparations and Reactions. 1. Preparation of $KHFe(CO)_4$ Solutions in Ethanol or Methanol. A 100-mL Schlenk flask containing a Teflon-coated magnetic stirring bar is charged with KOH (content 86%, the remaining being water; 1.47 g, 22 mmol), closed with a septum cap, and submitted to three vacuum–argon cycles. Absolute ethanol or methanol (60 mL), previously degassed by bubbling argon for 0.5 h, is syringed into the Schlenk flask through the septum cap and the mixture stirred until dissolution (ca. 0.5 h). $Fe(CO)_5$ (1.5 mL, 11 mmol) is syringed into the resulting solution through the septum cap, and stirring is continued for 0.5 h, during which time precipitation of $KHCO_3$ is observed. The IR spectrum of the pale pink solution indicates complete reaction of $Fe(CO)_5$ and exhibits the characteristic absorption bands of an ethanolic solution of $K[HFe(CO)_4]$ at 2008 (vw), 1921 (sh), and 1893 (s) cm^{-1}.

2. Preparation of $KHFe(CO)_4$ Solutions in THF. A solution of $KHFe(CO)_4$ (11 mmol) in methanol is prepared as described above. The solvent is then evaporated under vacuum to yield a white solid. In order to get rid of any traces of methanol or water, anhydrous THF (2 × 10 mL) is added and then evaporated again under vacuum up to a constant weight.

Freshly distilled anhydrous THF (40 mL) is then added to the above solid to give a pink-red solution and a white solid ($KHCO_3$), which is separated by filtration under argon. The IR spectrum of the resulting THF solution exhibits absorptions at 1999, 1911, 1888, 1878, and 1856 (sh) cm^{-1}, as expected.[36] It is noteworthy that no absorption band due to water or methanol is observed.

3. Synthesis of $Fe(CO)_3(PR_3)_2$ Complexes (Table I). The synthesis of $Fe(CO)_3(PR_3)_2$ complexes **2a–c** according to reaction 2 and their full spectroscopic data have been reported previously.[20]

4. Synthesis of $H_2Fe(CO)_2(PR_3)_2$ Complexes (3a,d). A solution of $KHFe(CO)_4$ (11 mmol) in methanol (30 mL) is cooled to 5 °C in a thermostated ethanol bath. Tri-*n*-butylphosphine

(4.45 g, 22 mmol) or dimethylphenylphosphine (3.04 g, 22 mmol) is then added at 5 °C and the Schlenk tube is immediately connected to a gas buret. Vigorous stirring is continued for 24 h at this temperature, during which time a slow gas evolution (ca. 450 mL) occurs. The solvent is then evaporated under reduced pressure at 5 °C, and the resulting material is extracted with cold hexane (60 mL). After filtration and further washing with cold hexane (3 × 20 mL), the hexane solution is concentrated to 5 mL and $CoCl_2{\cdot}6H_2O$ (2.5 g) is added. After the mixture is stirred for 0.5 h below 5 °C, cold hexane (30 mL) is added and the resulting blue-green solution is filtered through a 6 × 3.5 cm (45 g) neutral alumina column. The filtrate is evaporated under reduced pressure to give **3a** (4.6 g, 81%) and **3d** (2.7 g, 64%) as pale yellow oils (their spectroscopic characteristics are given in Table II). These compounds must be kept cold (<5 °C) throughout the workup because, at higher temperatures, they slowly decompose with hydrogen evolution (see text).

5. Synthesis of $Fe(CO)_2(PMe_2Ph)_3$. A solution of $KHFe(CO)_4$ (5.5 mmol) in ethanol (30 mL) is heated under argon to reflux in a Schlenk flask equipped with a reflux condenser connected to an oil bubbler. Dimethylphenylphosphine (2.28 g, 16.5 mmol) then is added through the condenser and the reaction medium heated for 3 h, during which time gas evolution is observed. After the mixture is cooled to room temperature, the solvent is evaporated under vacuum. The resulting oily material is then extracted with hexane (60 mL) and filtered under argon to remove potassium bicarbonate. The resulting hexane solution is evaporated to dryness to give a yellow oil. Further purification by crystallization from CH_2Cl_2/MeOH (1/2) at −20 °C leads to an analytically pure product which is a yellow oil at room temperature (2.7 g, 93%). Anal. Calcd for $C_{26}H_{33}FeO_2P_3$: C, 59.33; H, 6.32. Found, C, 59.38; H, 6.61.

6. Synthesis of $Fe(CO)_2[P(n\text{-}Bu)_3]_3$. Tri-*n*-butylphosphine (6.68 g, 33 mmol) is added to a solution of $KHFe(CO)_4$ (11 mmol) in ethanol (30 mL), and the reaction medium is stirred for 24 h at 20 °C and then for a further 2 h at reflux temperature. At the end of the reaction, the solvent is removed under vacuum to give an oily yellow residue. Hexane (60 mL) is then added, and the reaction medium is filtered. The hexane solution is then concentrated to 5 mL and chromatographed on a $CoCl_2{\cdot}6H_2O$/neutral alumina/silica gel column (three layers: 2.5 g/10 g/10 g) with pentane (ca. 200 mL) as eluent. The solvent is then removed under vacuum to leave **4a** as a pale yellow oil (6.62 g, 84%). Anal. Calcd for $C_{38}H_{81}FeO_2P_3$: C, 63.49; H, 11.36. Found: C, 63.31; H, 11.40.

7. Reaction of $KHFe(CO)_4$ with $P(n\text{-}Bu)_3$ or PPh_3 in THF. Tri-*n*-butylphosphine (4.45 g, 22 mmol) or triphenylphosphine (5.8 g, 22 mmol) is added to a solution of $KHFe(CO)_4$ (11 mmol) in refluxing THF (60 mL) and the reflux condenser immediately connected to a gas buret. The reaction medium is stirred vigorously for 18 h ($P(n\text{-}Bu)_3$) or 48 h (PPh_3), during which time a white solid precipitates. The reaction medium is cooled to room temperature. The THF solution is syringed off, and the residual solid is washed several times with anhydrous THF. The resulting white solid is dried under vacuum to constant weight to yield $K_2Fe(CO)_4$ (1.28 g, 96% of the theoretical yield).

To the above solid (1.14 g, 4.65 mmol) is added a solution of Ph_3SnCl (3.584 g) in THF (30 mL), and the resulting mixture is stirred for 1 h at room temperature. After filtration and evaporation of the solvent, the resulting solid is treated with CH_2Cl_2 (40 mL) and the mixture filtered. The resulting insoluble material, $K^+[Ph_3SnFe(CO)_4]^-$ (2.4 g, 4.3 mmol, 92%), exhibits the following IR absorption bands (THF): 1995 (s), 1905 (s), 1885 (vs), and 1850 (m) cm^{-1}. Metathesis with Et_4NBr (0.921 g, 4.39 mmol) in acetonitrile, followed by the usual workup and recrystallization from THF/Et_2O (1/1), affords $[Et_4N]^+[Ph_3SnFe(CO)_4]^-$ in 80% yield (mp 145 °C dec). The IR spectrum (THF) exhibits absorption bands at 1990 (s), 1905 (s), and 1880 (vs) cm^{-1}, in agreement with literature data.[40]

8. Generation of $KHFe(CO)_2(PR_3)_2$ Complexes. The dihydride **3a** or **3d**, dissolved in THF-d_8 (2.5 mL), is added under argon to a 4-fold excess of KH (previously washed with anhydrous THF and dried up to constant weight) in a Schlenk flask connected to an oil bubbler. The reaction medium is sonicated (ca. 40 °C) in a common ultrasonic cleaner until no more gas evolution is observed (ca. 4 h for **3a** and 1 h for **3d**). NMR spectra (Table IV) have been obtained in 10-mm NMR tubes in the presence of a slight excess of KH.

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Registry No. 1, 17857-24-8; **3a**, 138606-23-2; **3d**, 138606-24-3; **4a**, 138606-26-5; **4d**, 138606-25-4; **5a**, 138606-27-6; **5d**, 138606-28-7; $K_2Fe(CO)_4$, 16182-63-1; $[Et_4N]^+[Ph_3SnFe(CO)_4]^-$, 55703-22-5; Ph_3SnCl, 639-58-7.