(tetrahydrofuran-d_8): δ 2.7 (CH$_3$), 11.2 (CH$_3$), 12.2 (CH$_3$), 17.5 (CH$_3$), 19.4 (CH$_3$), 21.5 (2 C, CH$_3$), 22.1 (CH$_3$), 28.9 (CH$_2$), 30.2 (CH$_2$), 32.0 (CH$_2$), 35.0 (CH$_2$), 78.4 (2 C, C$\equiv$$C$H), 79.9 (2 C, C$\equiv$$C$H), 82.7 (2 C, $C$$\equiv$CH), 83.4 (2 C, $C$$\equiv$CH), 108.6 (C$\equiv$$C$Ar), 119.6 ($C$$\equiv$CAr), 125.3 (Ar CH), 129.6 (Ar CH), 132.1 (Ar CH), 132.5 (Ar CH), 128.0–133.0 (6 C, Ar C), 138.0 (C=CHAr), 157.3 (FeC). λ_{max} (tetrahydrofuran): 232, 295, 435 nm. ν_{max} (KBr disk): 3291, 3984, 2920, 2113, 1681, 1580, 1425, 1205, 1134, 934, 839, 559 cm^{-1}.

Reaction of *cis*-[Fe(η^3-C(C$\equiv$CC$_6$H$_5$)=CHC$_6$H$_5$)(DMPE)$_2$]$^+$[PF$_6$]$^-$ (2c) with Lithium Aluminum Hydride. Lithium aluminum hydride (ca. 2 mg) was added directly to a solution of [Fe(η^3-C(C$\equiv$CPh)=CHPh)(DMPE)$_2$]$^+$[PF$_6$]$^-$ (**3c**; 19 mg, 26 mmol) in tetrahydrofuran-d_8 (0.5 mL). The color of the solution faded, and the solution was filtered and used directly for NMR studies. By ^{1}H and ^{31}P NMR spectroscopy the reaction is quantitative and complete, giving only one product, whose spectroscopic data are consistent with the formulation [Fe—C(=CHPh)CH=CPh(DMPE)$_2$] (**4c**). ^{31}P{^{1}H} NMR (tetrahydrofuran-d_8): δ 57.7 (ddd, $^2J_{PP}$ = 9, 17, 24 Hz, 1 P), 62.3 (ddd, $^2J_{PP}$ = 24, 33 Hz, 1 P), 68.9 (ddd, $^2J_{PP}$ = 151 Hz, 1 P), 73.7 (ddd, 1 P). ^{1}H NMR (tetrahydrofuran-d_8): δ 0.82 (d, $^2J_{PH}$ = 6.4 Hz, 3 H, CH_3), 1.24 (d, $^2J_{PH}$ = 4.9 Hz, 3 H, CH_3), 1.27 (d, $^2J_{PH}$ = 5.2 Hz, 3 H, CH_3), 1.45 (d, $^2J_{PH}$ = 6.5 Hz, 3 H, CH_3), 1.57 (d, $^2J_{PH}$ = 6.2 Hz, 3 H, CH_3), 1.61 (d, $^2J_{PH}$ = 8.0 Hz, 3 H, CH_3), 1.65 (d, $^2J_{PH}$ = 6.7 Hz, 3 H, CH_3), 1.4–2.1 (m, 8 H, CH_2), 1.70 (d, $^2J_{PH}$ = 8.3 Hz, 3 H, CH_3), 6.16 (s, 1 H, C=CHPh), 6.85 (m, 1 H, Ar H), 7.00 (m, 2 H, CH), 7.13 (m, 5 H, Ar H), 7.23 (m, 2 H, Ar H), 7.96 (m, 1 H, C=CH). ^{13}C{^{1}H,^{31}P} NMR (tetrahydrofuran-d_8): δ 17.6 (CH$_3$), 18.3 (CH$_3$), 21.7 (CH$_3$), 22.0 (CH$_3$), 22.1 (CH$_3$), 23.3 (2 C, CH$_3$), 23.4 (CH$_3$), 32.4 (CH$_2$), 32.9 (CH$_2$), 35.9 (CH$_2$), 36.4 (CH$_2$), 123.4 (Ar CH), 124.4 (Ar CH), 126.5 (=CHPh), 127.2 (2 C, Ar CH), 128.6 (2 C, Ar CH), 129.0 (2 C, Ar CH), 129.3 (2 C, Ar CH), 141.9 (=CH), 143.3 (Ar C), 159.3 (Ar C), 166.6 (FeC), 167.5 (FeC).

Reaction of *cis*-[Fe(η^3-C(C$\equiv$CCH$_3$)=CHCH$_3$)(DMPE)$_2$]$^+$[PF$_6$]$^-$ (2a) with Lithium Aluminum Hydride. Lithium aluminum hydride (ca. 2 mg) was added directly to a solution of [Fe(η^3-C(C$\equiv$CCH$_3$)=CHCH$_3$)(DMPE)$_2$]$^+$[PF$_6$]$^-$ (**3a**; 19 mg, 26 mmol) dissolved in tetrahydrofuran-d_8 (0.5 mL). The color of the solution faded, and the solution was filtered and used directly for NMR studies. By ^{1}H and ^{31}P NMR spectroscopy the reaction is quantitative, giving only one product whose spectroscopic data are consistent with the formulation [Fe-C(=CHCH$_3$)CH=CCH$_3$(DMPE)$_2$] (**4a**). ^{31}P{^{1}H} NMR (tetrahydrofuran-d_8): δ 61.5–62.0 (m, 2 P), 72.6 (m, 1 P), 74.9 (m, 1 P). ^{1}H{^{31}P} NMR (tetrahydrofuran-d_8): δ 0.93 (s, 3 H, CH_3), 0.98 (s, 3 H, CH_3), 1.15 (s, 3 H, CH_3), 1.17 (d, 6 H, CH_3), 1.21 (s, 3 H, CH_3), 1.28 (s, 3 H, CH_3), 1.33 (s, 3 H, CH_3), 1.4–2.1 (m, 8 H, CH_2), 1.85 (d, $^3J_{HH}$ = 6.0 Hz, 3 H, C=CHCH_3), 1.91 (s, 3 H, CH_3), 4.82 (q, $^3J_{HH}$ = 6.0 Hz, 1 H, C=CHCH$_3$), 7.79 (s, 1 H, C=CH). ^{13}C{^{1}H,^{31}P} NMR (tetrahydrofuran-d_8): δ 14.9 (CH$_3$), 17.2 (CH$_3$), 18.1 (CH$_3$), 22.6 (CH$_3$), 22.9 (CH$_3$), 23.0 (CH$_3$), 23.5 (CH$_3$), 24.2 (CH$_3$), 24.2 (CH$_2$), 32.0 (CH$_2$), 32.7 (CH$_2$), 32.7 (CH$_3$), 36.5 (CH$_2$), 36.5 (CH$_3$), 115.7 (C=CHCH$_3$), 139.1 (CH=CCH$_3$), 153.2 (FeC), 161.3 (FeC).

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Ligand Substitution Processes on Carbonylmetal Derivatives. 2. Reaction of Tetracarbonylhydridoferrates with Phosphites[1]

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Ligand substitution processes on KHFe(CO)$_4$ (1) have been evidenced by reaction with various phosphites. The nature of the reaction products strongly depends on (i) the nature of the solvent, (ii) the Tolman cone angle of the phosphite, and (iii) the reaction conditions. In *protic* media (H$_2$O–THF), phosphites with small cone angles, such as P(OMe)$_3$, P(OEt)$_3$, and P(OPh)$_3$, react (2 equiv) with 1 at room temperature to give the corresponding complexes H$_2$Fe(CO)$_2$[P(OR)$_3$]$_2$ in >90% yield, whereas a phosphite with a larger cone angle (P[O-*o*-C$_6$H$_4$Ph]$_3$) reacts only at a higher temperature to afford the disubstituted Fe(CO)$_3$[P{O-*o*-C$_6$H$_4$Ph}$_3$]$_2$ derivative in 94% yield. When the reaction with phosphites having small cone angles is conducted with a 3-fold excess of phosphite at 65 °C, the trisubtituted derivatives Fe(CO)$_2$[P(OR)$_3$]$_3$ are formed in 75–96% yield. In *aprotic* medium (THF), 1 reacts with phosphites (2 equiv) at room temperature to yield the monosubstituted anionic hydrides K$^+$[HFe(CO)$_3${P(OR)$_3$}]$^-$, which can be isolated in >90% yield. In refluxing THF the reaction of 1 with P(OMe)$_3$ (3 equiv) demonstrates the first synthesis of the hydridoferrate K$^+$[HFe(CO)$_2${P(OMe)$_3$}$_2$]$^-$. Protonation of K$^+$[HFe(CO)$_3${P(OR)$_3$}]$^-$ with trifluoroacetic acid in THF at −10 °C provides an excellent route for the high-yield synthesis of the monosubstituted dihydrides H$_2$Fe(CO)$_3$[P(OR)$_3$]. In situ reaction of the latter with another phosphane PZ$_3$ (Z = Ph, OPh) leads to the mixed dihydrides H$_2$Fe(CO)$_2$[P(OR)$_3$][PZ$_3$] (R = Me, Et; Z = Ph, OPh), which are reported for the first time. Finally, reaction of H$_2$Fe(CO)$_2$[P(OEt)$_3$]$_2$ with KH under sonication allows the generation of the highly reduced derivative K$_2$[Fe(CO)$_2${P(OEt)$_3$}$_2$], the first disubstituted analogue of the Collman reagent.

Introduction

A large number of Fe(CO)$_{4-n}$L$_n$ (n = 1, 2) complexes have been synthesized directly by ligand substitution on iron pentacarbonyl.[2-4] In contrast, direct ligand substitutions on tetracarbonylhydridoferrates M$^+$[HFe(CO)$_4$]$^-$ have never been reported as a route to the substituted

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Table I. Synthesis of $H_2Fe(CO)_2[P(OR)_3]_2$ Complexes

R	pK_a[a]	θ,[a] deg	reacn time,[b] h	product (yield, %)[c]
Me	2.60	107	1	**2a** (90)
Et	3.35	109	1	**2b** (91)
Ph	−1.20	128	24	**2c** (94)

[a] From refs 11 and 12. [b] At room temperature, minimum time for maximum products. [c] Isolated yields.

anionic hydridoiron carbonyl derivatives $M^+[HFe(CO)_{4-n}L_n]^-$.[5,6]

As part of our interest in developing new synthetic applications of $[HFe(CO)_4]^-$ in organic synthesis[7,8] and coordination chemistry,[9,10] we have recently reported on the reaction of $KHFe(CO)_4$ (**1**) with phosphines.[1] This reaction is a very attractive method for the high-yield synthesis of substituted iron carbonyl derivatives, among which are the dihydrides $H_2Fe(CO)_2(PR_3)_2$ (R_3 = *n*-Bu_3, Me_2Ph) and the hydrido anions $K^+[HFe(CO)_2(PR_3)_2]^-$. One of the main conclusions of that study was that the reaction of a phosphine with **1** is determined mainly by its Tolman cone angle,[11,12] the phosphines exhibiting the smallest cone angle being the most reactive. These results and the lack of literature data in this area led us to examine the reactivity of **1** with some phosphites having small Tolman cone angles. We have recently reported that the reaction of **1** with such phosphites affords (>90% yield) the corresponding $H_2Fe(CO)_2[P(OR)_3]_2$ complexes **2**.[9] We now report full details of the reaction of **1** with phosphites, including a new, very efficient synthesis of trisubstituted $Fe(CO)_2[P(OR)_3]_3$ complexes and of the hydrido anions $M^+[HFe(CO)_3\{P(OR)_3\}]^-$. The latter now allows easy access to the neutral monosubstituted dihydrides $H_2Fe(CO)_3[P(OR)_3]$ and to the new, disymmetrically disubstituted dihydrides $H_2Fe(CO)_2[P(OR)_3][PZ_3]$. The high-yield synthesis of several disubstituted hydridoferrates $K^+[HFe(CO)_2\{P(OR)_3\}_2]^-$ is reported for the first time, and the generation of and spectroscopic data for the highly reduced $K_2Fe(CO)_2[P(OEt)_3]_2$ are described.

Results and Discussion

Synthesis of $H_2Fe(CO)_2[P(OR)_3]_2$ Complexes. Solutions of $KHFe(CO)_4$ (**1**) in protic or aprotic media were prepared from pentacarbonyliron as previously described.[1] The reaction of **1** with $P(OMe)_3$ (2 equiv) in MeOH at room temperature under argon results in the evolution of carbon monoxide (GLC analysis) within 1 h. Evaporation of the solvent, followed by a very simple but careful workup, allows the isolation of $H_2Fe(CO)_2[P(OMe)_3]_2$ (**2a**) in 75% yield. Further studies showed that the reaction of **1** with phosphites is best performed in a H_2O–THF solvent mixture at room temperature and affords (>90% yield) the corresponding $H_2Fe(CO)_2[P(OR)_3]_2$ derivative (eq 1, Table I).[9]

$$\underset{\mathbf{1}}{KHFe(CO)_4} + 2P(OR)_3 \xrightarrow[25\ ^\circ C]{H_2O\text{–}THF} H_2Fe(CO)_2[P(OR)_3]_2 + 2CO \quad (1)$$

$$\begin{gathered}\mathbf{2a},\ R = Me\\ \mathbf{2b},\ R = Et\\ \mathbf{2c},\ R = Ph\end{gathered}$$

Although complexes **2a,c** have been previously synthesized and characterized by Berke et al.,[13] this new reaction is a more rapid and efficient method.[10] As expected from our work on the reaction of **1** with phosphines,[1] the reactivity of a phosphite toward **1** appears to be determined mainly by its steric bulk, as reflected by its Tolman cone angle (Table I). This finding was further confirmed by the fact that, under the conditions of eq 1, $P(O\text{-}o\text{-}C_6H_4Ph)_3$ (cone angle estimated at 152°)[12] failed to react significantly with **1** after 24 h at room temperature. A similar lack of reactivity at room temperature has been observed for triphenylphosphine (cone angle 145°) and tricyclohexylphosphine (cone angle 170°).[1]

In contrast, when the reaction of **1** with $P(O\text{-}o\text{-}C_6H_4Ph)_3$ was performed for 24 h at 70 °C in a H_2O–THF solvent mixture, the corresponding $Fe(CO)_3[P(O\text{-}o\text{-}C_6H_4Ph)_3]_2$ could be isolated in 94% yield. The latter was characterized on the basis of elemental analysis and of spectroscopic data (IR and ^{31}P and ^{13}C NMR; see Experimental Section). In particular, IR and ^{13}C NMR data confirm the expected trans geometry.[14]

Several complexes of the series $Fe(CO)_3[P(OR)_3]_2$ are known, but their synthesis is rather tedious since it always involves purification steps in order to separate the monosubstituted derivative $Fe(CO)_4[P(OR)_3]$, which is formed simultaneously.[4] This observation and the success of the previously reported synthesis of $Fe(CO)_3(PR_3)_2$ by a similar reaction[1] led us to examine the reaction of phosphites with **1** at higher temperatures as a possible selective route to $Fe(CO)_3[P(OR)_3]_2$. The reaction of **1** with $P(OMe)_3$ (2 equiv) for 24 h in refluxing methanol led to only small amounts of **2a**. The main product of this reaction, **3a**, could be separated (56% yield) and identified as $Fe(CO)_2[P(OMe)_3]_3$ by comparison of its spectroscopic properties with those reported in the literature.[15] This result is similar to that obtained for the reaction of **1** with PMe_2Ph (cone angle 122°) in refluxing ethanol leading to the trisubstituted derivative $Fe(CO)_2[PMe_2Ph]_3$.[1] As in the latter case, the formation of **3a** is proposed to occur, in situ, by reaction of the dihydride **2a** with $P(OMe)_3$, as

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Table II. Synthesis of and Spectral Data for $Fe(CO)_2[P(OR)_3]_3$ Complexes

R	solvent	reacn time, h (reacn temp, °C)	yield, %	IR ν_{CO}, cm^{-1}	$^{31}P\{^1H\}$ NMR[f] δ, ppm	$^{13}C\{^1H\}$ NMR[g] δ(CO), ppm	J_{C-P}, Hz (mult)
Me	MeOH[a]	24 (64)	91	1875 (vs),[c] 1935 (s)	193.7	216.1	26 (q)
Et	EtOH[a]	8 (78)	96	1865 (vs),[d] 1925 (s)	188.0	216.5	27 (q)
Ph	H_2O–THF[b]	72 (65)	75	1900 (vs),[e] 1965 (s)	170.7	212.9	28 (q)

[a] 30 mL. [b] 20 mL–10 mL. [c] In MeOH. [d] In EtOH. [e] In THF. [f] Recorded on a Bruker WM 250 spectrometer at 101.26 MHz and 263 K in acetone-d_6. [g] Recorded on a Bruker WM 250 spectrometer at 62.89 MHz and 263 K in acetone-d_6.

Table III. IR and NMR Data for $M^+[HFe(CO)_3\{P(OR)_3\}]^-$ Complexes

			^1H NMR[a]			^{13}C NMR[a]	
M^+	R	IR 1600–2000-cm^{-1} region [solvent]	δ(Fe–H), ppm (mult)	$^2J_{P-H}$, Hz	^{31}P NMR[a] δ, ppm (mult)	δ(CO), ppm	$^2J_{C-X}$, Hz
K^+	Me	1940 (m), 1880 (m), 1850 (s), 1830 (sh) [THF]	−9.2 (d)[b]	10	216.0 (d)[b]	223.6[b]	$J_{C-H} = 14$, $J_{C-P} = 12$
K^+	Et	1945 (m), 1885 (w), 1850 (s), 1830 (sh) [THF]	−9.3 (d)[c]	<3	210.4 (d)[c]	223.4[c]	$J_{C-H} = 15$, $J_{C-P} = 16$
K^+	Ph	1960 (s), 1895 (w), 1865 (s), 1830 (sh) [THF]	−9.7 (d)[b]	47	187.0 (d)[b]	223.8[b]	$J_{C-H} = 11$, $J_{C-P} = 3$
$[PPN]^+$	Me	1940 (m), 1880 (m), 1840 (s) [THF]	−9.1 (d)[b]	12	218.7 (d)[b]	224.3[b]	$J_{C-H} = 13$, $J_{C-P} = 10$
$[PPN]^+$	Et	1935 (w), 1875 (m), 1835 (s) [CH_2Cl_2]	−9.0 (d)[d]	3	213.0 (d)[d]	223.2[d]	$J_{C-H} = 14$, $J_{C-P} = 14$
$[PPN]^+$	Ph	1960 (m), 1890 (m), 1860 (s) [CH_2Cl_2]	−9.7 (d)[d]	50	186.6 (d)[d]	223.3[d]	$J_{C-H} = 11$, $J_{C-P} = 4$

[a] Bruker WM250 spectrometer (298–300 K) at 250, 101.26, and 62.89 MHz for ^1H, ^{31}P, and ^{13}C NMR spectra, respectively. [b] In THF-d_8. [c] In CD_3CN. [d] In acetone-d_6.

strongly suggested by the quantitative reaction of **2a** with excess $P(OMe)_3$ in refluxing methanol (eq 2).

$$\underset{\mathbf{2a}}{H_2Fe(CO)_2[P(OMe)_3]_2} + P(OMe)_3\ (\text{excess}) \xrightarrow{\text{MeOH, reflux}} \underset{\mathbf{3a}\ (98\%)}{Fe(CO)_2[P(OMe)_3]_3} + H_2 \quad (2)$$

Synthesis of $Fe(CO)_2[P(OR)_3]_3$ Complexes. The formation of **3a** directly from **1** is unprecedented. Although **3a** has been known for a long time,[16] the methods of preparation are tedious since they involve either difficult separations or multistep sequences from commercially available materials.[15,16] We thus decided to examine the reaction of **1** with some phosphites as a selective route to the corresponding trisubstituted $Fe(CO)_2[P(OR)_3]_3$ derivatives. In order to prevent alkoxy group exchange on the phosphorus atom, these reactions were performed in methanol and ethanol for $P(OMe)_3$ and $P(OEt)_3$, respectively, and in a H_2O–THF mixture for $P(OPh)_3$. This new reaction (eq 3) proved to be a very efficient route to complexes **3** (Table II).

$$\underset{\mathbf{1}}{KHFe(CO)_4} + 3P(OR)_3 \xrightarrow{\text{ROH }(H_2O)} Fe(CO)_2[P(OR)_3]_3 + H_2 + 2CO \quad (3)$$

3a, R = Me
3b, R = Et
3c, R = Ph

The X-ray structures of **3a**,**b**, reported by Berke et al.[17] and by Chiusoli et al.,[18] respectively, indicate a somewhat distorted trigonal-bipyramidal arrangement with two apical and one equatorial phosphite group. In solution (acetone-d_6), however, **3a** is fluxional, at least down to 183 K, a behavior similar to that observed by Karch et al. for $Fe(CO)_2(PMe_3)_3$.[19]

As for the reaction of **1** with phosphines,[1] the formation of neutral dihydrides (eq 2) from **1** suggested a protonation step. In these cases, the intermediate $K^+[HFe(CO)_3PR_3]^-$ derivatives could not be isolated, even in aprotic medium, because of their high basicity. Since in the case of phosphites the intermediates $K^+[HFe(CO)_3\{P(OR)_3\}]^-$ are conceivably less basic, we examined the reaction of **1** with phosphites first in a protic but poorly acidic solvent and then in an aprotic one.

Table IV. Synthesis of $M^+[HFe(CO)_3\{P(OR)_3\}]^-$ Complexes from $M^+[HFe(CO)_4]^-$

M^+	R	solvent	reacn time, h	product (yield, %)
K^+	Me	*t*-AmOH	1	**4a** (90)
K^+	Me	THF	1	**4a** (91)
$[PPN]^+$	Me	CH_2Cl_2	4	**5a** (94)
K^+	Et	*t*-AmOH	1	**4b** (95)
K^+	Et	THF	1	**4b** (97)
$[PPN]^+$	Et	CH_2Cl_2	4	**5b** (95)
K^+	Ph	THF	2	**4c** (98)
$[PPN]^+$	Ph	CH_2Cl_2	2	**5c** (95)

Synthesis of $M^+[HFe(CO)_3\{P(OR)_3\}]^-$ Complexes. When the reaction of **1** with either $P(OMe)_3$ or $P(OEt)_3$ was carried out at room temperature in *t*-AmOH, the reaction completely stopped after evolution of 1 equiv of carbon monoxide (GLC analysis) and the corresponding $K^+[trans\text{-}HFe(CO)_3\{P(OR)_3\}]^-$ complexes *trans*-**4a** (R = Me) and *trans*-**4b** (R = Et) could be isolated in 95% yield. Metathesis with bis(triphenylphosphine)nitrogen(1+) chloride, $[PPN]^+Cl^-$, in CH_3CN affords the corresponding complexes **5a**,**b** in >90% yield.

Complexes **4a**,**b** and **5a**,**b** were identified as the trans derivatives by comparison of their spectroscopic properties (Table III) with those previously reported for **5a**,**b**.[6] From the elegant work of Darensbourg et al., it is known that these complexes exhibit a special behavior since their ^1H NMR spectra show a dramatic dependence of the J_{P-H} coupling constant on both temperature and solvent polarity.[20]

When the same reaction was attempted with $P(OPh)_3$, a mixture of products was formed which was shown (^{31}P and ^1H NMR) to contain $K^+[cis\text{-}HFe(CO)_3\{P(OPh)_3\}]^-$ (*cis*-**4c**; $^2J_{P-H} = 47$ Hz, THF-d_8) as the major product. The corresponding *trans*-**4c** derivative is presently unknown, although several attempts have been made to generate it.[21]

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(16) (a) Reckziegel, A.; Bigorgne, M. *J. Organomet. Chem.* **1965**, *3*, 341–354. (b) Battaglia, L. P.; Boselli, T.; Chiusoli, G. P.; Nardelli, M.; Pelizzi, C.; Predieri, G. *Gazz. Chim. Ital.* **1985**, *115*, 395–397.

(17) Berke, H.; Huttner, G.; Zsolnai, L. *Chem. Ber.* **1981**, *114*, 3549–3557.

(18) Battaglia, L. P.; Chiusoli, G. P.; Nardelli, M.; Pelizzi, C.; Predieri, G. *Gazz. Chim. Ital.* **1986**, *116*, 207–211.

(19) Karch, H. H.; Klein, H. F.; Schmidbaur, H. *Chem. Ber.* **1977**, *110*, 2200–2212.

(20) Ash, C. E.; Darensbourg, M. Y.; Hall, M. B. *J. Am. Chem. Soc.* **1987**, *109*, 4173–4180.

The possible thermodynamic reason for the instability of *trans*-**4c** has been previously commented on by Darensbourg et al.[21] Thus, the unidentified side products formed in this reaction may result from the possible formation of the unstable *trans*-**4c** derivative.

The reaction of **1** with the above phosphites was also examined in THF at room temperature. Interestingly, this reaction was found to afford the corresponding complexes *trans*-**4a**, *trans*-**4b**, and *cis*-**4c** in nearly quantitative yield (eq 4, Table IV).

$$\underset{\mathbf{1}}{K^+[HFe(CO)_4]^-} + P(OR)_3 \text{ (2 equiv)} \xrightarrow{\text{THF, 25 °C}} \underset{\substack{trans\text{-}\mathbf{4a},\ R = Me \\ trans\text{-}\mathbf{4b},\ R = Et \\ cis\text{-}\mathbf{4c},\ R = Ph}}{K^+[HFe(CO)_3\{P(OR)_3\}]^-} \quad (4)$$

Further experiments indicated that $[PPN]^+[HFe(CO)_4]^-$ (**6**) does not react with $P(OPh)_3$ in THF at room temperature (no evolution of gas and unchanged IR spectrum after 18 h). In contrast, a clean reaction occurs at room temperature in CH_2Cl_2 to give $[PPN]^+[cis\text{-}HFe(CO)_3\{P(OPh)_3\}]^-$ (*cis*-**5c**) in 95% yield. This solvent proved to be convenient for both the formation and isolation of the $[PPN]^+[HFe(CO)_3\{P(OR)_3\}]^-$ complexes **5** (R = Me, Et, Ph) (eq 5, Table IV). The course of the reaction is followed by measurement of the evolution of gas. When the expected amount of gas is evolved (4 h for **5a**,**b**, 2 h for **5c**), the complexes **5** are immediately precipitated by addition of diethyl ether and separated. This procedure avoids the slow decomposition of complexes **5** which was observed to occur in CH_2Cl_2 in the presence of excess phosphite, to generate the corresponding $Fe(CO)_3[P(OR)_3]_2$ complexes (IR analysis).

$$\underset{\mathbf{6}}{[PPN]^+[HFe(CO)_4]^-} + P(OR)_3 \text{ (2 equiv)} \xrightarrow[>94\%]{CH_2Cl_2} \underset{\substack{trans\text{-}\mathbf{5a},\ R = Me \\ trans\text{-}\mathbf{5b},\ R = Et \\ cis\text{-}\mathbf{5c},\ R = Ph}}{[PPN]^+[HFe(CO)_3\{P(OR)_3\}]^-} + CO \quad (5)$$

The only reported synthesis of complexes of this series is that of Ellis et al.[5] and has been developed by Darensbourg et al.[6] It involves the previous preparation and purification (often by column chromatography) of the corresponding $Fe(CO)_4[P(OR)_3]$ derivative, followed by reaction with a methanolic $[Et_4N]^+[OH]^-$ (15–20 equiv) solution maintained under reduced pressure for approximately 20 h.[5,6] The high yields reported in Table IV show that the reaction of **1** or **6** with phosphites is now the most expedient synthesis of complexes **4** or **5**, respectively.

These results give interesting information about the mechanism of formation of the $H_2Fe(CO)_2[P(OR)_3]_2$ complexes **2** by reaction of **1** with the corresponding phosphite at room temperature in protic medium (eq 1). Indeed, although the reaction in *t*-AmOH is conducted in the presence of excess phosphite (2 equiv), the reaction stops after monosubstitution, since neither the $H_2Fe(CO)_2[P(OR)_3]_2$ nor the possible $[HFe(CO)_2\{P(OR)_3\}_2]^-$ complexes could be detected (IR analysis), even after a further 24 h of stirring at room temperature. Thus, it appears that the formation of $H_2Fe(CO)_2[P(OR)_3]_2$ does not proceed by protonation of the disubstituted $[HFe(CO)_2\{P(OR)_3\}_2]^-$ complexes. More probably, the reaction involves the protonation of the monosubstituted anions $[HFe(CO)_3\{P(OR)_3\}]^-$ to generate the dihydrides $H_2Fe(CO)_3[P(OR)_3]$,[17,22] which, by a further CO substitution, afford the disubstituted dihydrides $H_2Fe(CO)_2[P(OR)_3]_2$. An observation that supports the above hypothesis is the following: addition of methanol at room temperature to a THF (or *t*-AmOH) solution of $K^+[HFe(CO)_3\{P(OMe)_3\}]^-$ in the presence of an excess of $P(OMe)_3$ rapidly and quantitatively yields $H_2Fe(CO)_2[P(OMe)_3]_2$ with evolution of 1 equiv of carbon monoxide (GLC analysis). The $[HFe(CO)_3\{P(OR)_3\}]^-$ complexes are conceivably more basic than $[HFe(CO)_4]^-$ because of the weaker π-accepting properties of phosphites as compared to those of carbon monoxide. It has been previously reported that when phosphite complexes are associated with the $[PPN]^+$ cation, as in **5**, they do not react with methanol or water.[21] However, we observed that, when associated with K^+, as in **4**, they do react with water to give the corresponding $H_2Fe(CO)_3[P(OR)_3]$ derivatives. The latter, in turn, have been found to react very rapidly with phosphites to give the corresponding disubstituted dihydrides **2** within a few seconds.

Another interesting observation is that the reaction of **1** with only 1 equiv of $P(OMe)_3$ in a H_2O–THF solvent mixture under the conditions of eq 1 stops after consumption of nearly 50% of the $KHFe(CO)_4$ (IR analysis) with simultaneous formation of $H_2Fe(CO)_2[P(OMe)_3]_2$ as the sole reaction product. Thus, displacement of CO by phosphite on $H_2Fe(CO)_3[P(OMe)_3]$ appears to be faster than on $K^+[HFe(CO)_4]^-$, in agreement with the lower back-bonding on the carbonyl ligands of the neutral dihydride (see IR data, Table VI).

On the basis of the above arguments the formation of complexes **2** is proposed to occur according to eqs 6–8.

$$[HFe(CO)_4]^- + P(OR)_3 \rightarrow [HFe(CO)_3\{P(OR)_3\}]^- + CO \quad (6)$$

$$[HFe(CO)_3\{P(OR)_3\}]^- + H^+ \rightleftarrows H_2Fe(CO)_3[P(OR)_3] \quad (7)$$

$$H_2Fe(CO)_3[P(OR)_3] + P(OR)_3 \xrightarrow{\text{fast}} H_2Fe(CO)_2[P(OR)_3]_2 + CO \quad (8)$$

The high-yield synthesis of $[HFe(CO)_3\{P(OR)_3\}]^-$ complexes by reaction of $P(OR)_3$ with either **1** (in *t*-AmOH or THF) or **6** (in CH_2Cl_2) clearly establishes that a direct ligand substitution occurs on $[HFe(CO)_4]^-$. As in the case of ^{13}CO exchange on $[HFe(CO)_4]^-$,[23] ion-pairing phenomena are involved in THF since, in this solvent, **1** reacts with phosphites, whereas **6** does not (vide supra).

Synthesis of $[HFe(CO)_2\{P(OR)_3\}_2]^-$ Complexes. We were also interested in examining whether a second CO substitution could occur on complexes **4** under more forcing conditions. Reacting $P(OMe)_3$ (3 equiv) with **1** (free from $KHCO_3$) for 24 h in refluxing THF promotes the evolution of 2 equiv of carbon monoxide (GLC analysis) with formation of $K^+[HFe(CO)_2\{P(OMe)_3\}_2]^-$, which was isolated for the first time (eq 9).

$$\underset{\mathbf{1}}{KHFe(CO)_4} + P(OMe)_3 \text{ (3 equiv)} \xrightarrow[\text{24 h}]{\text{THF, reflux}} \underset{\mathbf{7a}\ (95\%)}{K^+[HFe(CO)_2\{P(OMe)_3\}_2]^-} + 2CO \quad (9)$$

The spectral data obtained for **7a** are given in Table V. The main features of the NMR spectra are as follows: the

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[21] Ash, C. E.; Kim, C. M.; Darensbourg, M. Y.; Rheingold, A. L. *Inorg. Chem.* **1987**, *26*, 1357–1361.

[22] Arndt, L. W.; Ash, C. E.; Darensbourg, M. Y.; Hsiao, Y. M.; Kim, C. M.; Reibenspies, J.; Youngdahl, K. A. *J. Organomet. Chem.* **1990**, *394*, 733–741.

[23] Darensbourg, M. Y.; Darensbourg, D. J.; Barros, H. L. C. *Inorg. Chem.* **1978**, *17*, 297–300.

Table V. Spectral Characteristics of $M^+[HFe(CO)_2\{P(OR)_3\}_2]^-$ Complexes

			^{1}H NMR[a]			^{13}C NMR[a]		
M^+	R	IR (THF) 1600–2000-cm^{-1} region	δ(Fe–H), ppm (mult)	$^2J_{H-P}$, Hz	$^{31}P\{^1H\}$ NMR[a] δ, ppm	δ(CO), ppm (mult)	$^2J_{C-P}$,[b] Hz	$^2J_{C-H}$,[c] Hz
K^+	Me	1870 (s, br) 1900 (sh), 1800 (s, br)	−10.6 (t)	52	210.7	226.7 (td)	9	7
K^+	Ph	1920 (s, br), 1830 (s, br)	−10.7 (t)	49	180.7	224.8 (d)	~0	8
$[PPN]^+$	Ph	1925 (s), 1890 (w), 1850 (s)	−10.8 (t)	59	178.9	224.4 (d)	~0	9

[a] Recorded on a Bruker WM250 spectrometer at 303–313 K in THF-d_8; at 250, 101.26, and 62.89 MHz for ^{1}H, ^{31}P, and ^{13}C, respectively. [b] From the $^{13}C\{^1H\}$ spectrum. [c] From the $^{13}C\{^{31}P\}$ spectrum.

Table VI. Spectral Data for $H_2Fe(CO)_3[P(OR)_3]$ Complexes

			^{1}H NMR[a]			
R	yield, %	IR ν_{CO}, cm^{-1} (THF)	δ(Fe–H), ppm (mult)	$^2J_{H-P}$, Hz	$^{31}P\{^1H\}$ NMR[a] δ, ppm	$^{13}C\{^1H, ^{31}P\}$ NMR[a] δ(CO), ppm
Me	98	2065 (m), 2000 (s)	−10.2 (d)	62	180	209.1
Et	98	2065 (m), 2000 (s)	−10.1 (d)	62	173.5	209.4
Ph	95	2075 (m), 2015 (s)	−10.2 (d)	60	175	207.5

[a] Bruker WM250 spectrometer at 263 K in THF-d_8, at 250, 101.26, and 62.89 MHz for ^{1}H, ^{31}P, and ^{13}C, respectively.

hydride ligand (δ −10.6 ppm) is coupled with two equivalent phosphorus atoms with a coupling constant ($^2J_{H-P}$ = 52 Hz) characteristic of cis H–P arrangements. The carbonyl ligands are coupled both with the hydride ($^2J_{C-H}$ = 7 Hz) and with two equivalent phosphorus atoms ($^2J_{C-P}$ = 9 Hz). These spectroscopic data are in agreement either with trigonal-bipyramidal or with distorted-square-pyramidal geometry. The ^{1}H NMR hydride resonance, a triplet, was shown to be invariant with temperature in the range 253–307 K (THF-d_8). This behavior contrasts with that observed for the monosubstituted $[trans\text{-}HFe(CO)_3\{P(OMe)_3\}]^-$ derivative.[20]

When the same experiment was performed with $P(OEt)_3$, a more complex reaction was observed, leading to the precipitation of a white solid. On reaction with 1 equiv of MeOH the separated solid gave $K^+[HFe(CO)_3\{P(OEt)_3\}]^-$ (IR and NMR analysis) and is thus believed to be $K_2[Fe(CO)_3\{P(OEt)_3\}]$. When this reaction was monitored by IR and ^{31}P NMR spectroscopy, it appeared that the reaction first generates $K^+[HFe(CO)_3\{P(OEt)_3\}]^-$. Then, $H_2Fe(CO)_2[P(OEt)_3]_2$ and $Fe(CO)_2[P(OEt)_3]_3$ are formed while $K_2[Fe(CO)_3\{P(OEt)_3\}]$ precipitates. The overall reaction can be rationalized by eqs 10–13.

$$[HFe(CO)_4]^- + P(OEt)_3 \rightarrow [HFe(CO)_3\{P(OEt)_3\}]^- + CO \quad (10)$$

$$[HFe(CO)_3\{P(OEt)_3\}]^- + P(OEt)_3 \rightarrow [HFe(CO)_2\{P(OEt)_3\}_2]^- + CO \quad (11)$$

$$[HFe(CO)_2\{P(OEt)_3\}_2]^- + [HFe(CO)_3\{P(OEt)_3\}]^- \rightarrow H_2Fe(CO)_2[P(OEt)_3]_2 + [Fe(CO)_3[P(OEt)_3]]^{2-}\downarrow \quad (12)$$

$$H_2Fe(CO)_2[P(OEt)_3]_2 + P(OEt)_3 \rightarrow Fe(CO)_2[P(OEt)_3]_3 + H_2 \quad (13)$$

This overall process must be related to that observed for the reaction of phosphines with $KHFe(CO)_4$ in refluxing THF.[1] In the latter case, the monosubstituted derivative $K^+[HFe(CO)_3\{PR_3\}]^-$ is basic enough to react in situ with $KHFe(CO)_4$, thus generating $K_2Fe(CO)_4$, which precipitates, and the corresponding $H_2Fe(CO)_3(PR_3)$, which further evolves to yield $Fe(CO)_2(PR_3)_3$ and/or $Fe(CO)_3(PR_3)_2$. These results clearly show that the nature of the phosphane has a strong influence on the reactivity (basicity) of the $K^+[HFe(CO)_3(\text{phosphane})]^-$ derivatives.

Finally, in the case of $P(OPh)_3$, a still more complex reaction occurred, leading to a mixture of products which was not further investigated. The corresponding **7c**, however, can be cleanly obtained by deprotonation of the dihydride **2c** with excess KH in THF (eq 14). Metathesis with $[PPN]^+Cl^-$ quantitatively affords $[PPN]^+[HFe(CO)_2\{P(OPh)_3\}_2]^-$ (Table V).

$$\underset{\mathbf{2c}}{H_2Fe(CO)_2[P(OPh)_3]_2} \xrightarrow[\text{THF}]{\text{KH (excess)}} \underset{\mathbf{7c}}{K[HFe(CO)_2\{P(OPh)_3\}_2]} + H_2 \quad (14)$$

Deprotonation of **2b** by a similar process is less satisfactory. Indeed, the reaction is more difficult and must be conducted at higher temperature so that it leads to **7b** contaminated by significant amounts of the dianionic $K_2[Fe(CO)_2\{P(OEt)_3\}_2]$ derivative **8b** (vide infra).

Synthesis of $H_2Fe(CO)_3[P(OR)_3]$ Complexes. As shown above, the reaction of **1** with phosphites is the best synthetic method for the preparation of the $M^+[HFe(CO)_3\{P(OR)_3\}]^-$ derivatives. Protonation of the latter with CF_3COOH in THF is now proved to be a good route to the corresponding dihydrides (eq 15). Full IR and NMR data are reported in Table VI.

$$\underset{R\,=\,Me,\,Et,\,Ph}{K[HFe(CO)_3\{P(OR)_3\}]^-} \xrightarrow[\text{THF, -10 °C}]{CF_3COOH} \underset{>95\%}{H_2Fe(CO)_3[P(OR)_3]} \quad (15)$$

The first reported dihydride of this series (R = Ph) has been synthesized by Berke et al. (43% yield) by reaction of $H_2Fe(CO)_4$ with triphenyl phosphite.[17] Its spectroscopic data have been interpreted on the basis of a "$Fe(CO)_3[P(OPh)_3]$" tetrahedron, capped by the two hydride ligands. Other examples have been obtained more recently by reaction of $[PPN]^+[HFe(CO)_3\{P(OR)_3\}]^-$ with Ph_3PAuCl, a reaction that results in a quantitative partitioning into $H_2Fe(CO)_3[P(OR)_3]$ and $(Ph_3PAu)_2Fe(CO)_3[P(OR)_3]$.[22] Thus, the two-step synthesis reported here appears as the most efficient method for the preparation of $H_2Fe(CO)_3[P(OR)_3]$.

Synthesis of $H_2Fe(CO)_2[P(OR)_3][PZ_3]$ Complexes. As expected from our mechanistic hypothesis (eqs 6–8), protonation of the anionic monohydrides $K^+[HFe(CO)_3\{P(OR)_3\}]^-$ followed by addition of another phosphane PZ_3 (Z = OPh, Ph) allows the in situ generation of the new $H_2Fe(CO)_2[P(OR)_3][PZ_3]$ dihydrides. In all cases the mixed dihydride is contaminated by the corresponding $H_2Fe(CO)_2[P(OR)_3]_2$ and $H_2Fe(CO)_2(PZ_3)_2$ or $Fe(CO)_3(PZ_3)_2$ complexes, which are easily identified (^{31}P NMR). In three cases, however, the mixed dihydride was found to be predominant and could be isolated (>50%) in a pure form (eq 16). The main spectroscopic data for these new complexes are given in Table VII.

$$\mathrm{K[HFe(CO)_3\{P(OR)_3\}]} \xrightarrow[\text{(2) PZ}_3\text{, 25 °C}]{\text{(1) CF}_3\text{COOH, THF, -10 °C}}$$
$$\mathrm{R = Me,\ Z = OPh}$$
$$\mathrm{R = Et,\ Z = OPh}$$
$$\mathrm{R = Me,\ Z = Ph}$$
$$\mathrm{H_2Fe(CO)_2[P(OR)_3][PZ_3] + CO} \quad (16)$$

The IR spectrum of each complex exhibits two ν_{CO} absorption bands of equal intensity, indicating the presence of two carbonyl ligands cis to each other. The two different phosphorus ligands are clearly attributed on the basis of the ^{31}P NMR spectra, since the trialkyl phosphite signal is easily recognized by its multiplicity ($^3J_{P-H}$). In the cases where Z = OPh, the signal for the hydride ligands appears as a triplet in the ^1H NMR spectrum. This feature is attributable to the fact that in each of the $H_2Fe(CO)_2[P(OR)_3]_2$ complexes, the $^2J_{H-P}$ coupling constants exhibit very similar values (60–62 Hz).[9]

The special case of $H_2Fe(CO)_2[P(OMe)_3][PPh_3]$ has been quite thoroughly studied. In the ^{13}C NMR spectrum the carbons of the carbonyl ligands give rise to a doublet of doublets at 213 ppm. The $^{13}C\{^1H, ^{31}P$ broad-band decoupling$\}$ spectrum indicates that the two carbonyl ligands are equivalent. Selective phosphorus decoupling experiments allow the measurement of the coupling constants $^2J_{C-P^1} = 18$ Hz and $^2J_{C-P^2} = 12$ Hz ($P^1 = P(OMe)_3$, $P^2 = PPh_3$). Lastly, a $^1H\{^{31}P$ broad-band decoupling$\}$ NMR experiment revealed that the two hydride ligands are equivalent, and selective decoupling experiments enable one to measure the $^2J_{H-P}$ constants given in Table VII.

On the basis of the above spectral data these complexes are proposed to have a *cis*-dihydrido-*trans*-bis(phosphane)dicarbonyliron geometry (Figure 1) similar to that of the $H_2Fe(CO)_2(PR_3)_2$ and $H_2Fe(CO)_2[P(OR)_3]_2$ complexes previously reported.[1,9,13]

Generation of $K_2Fe(CO)_2[P(OR)_3]_2$ Complexes. Ellis et al. have recently succeeded in isolating some monosubstituted dianionic derivatives $[Fe(CO)_3(PR_3)]^{2-}$ by deprotonation of the corresponding $K^+[HFe(CO)_3(PR_3)]^-$ with K-Selectride.[5b] These are the first reported (phosphine)carbonylmetalate dianions. They also succeeded in preparing the corresponding $Fe(CO)_3\{P(OR)_3\}]^{2-}$ by ligand exchange. To the best of our knowledge, there is no reported example of a bis(phosphane)carbonylmetalate dianion.

The now simple synthesis of the dihydrides **2** (eq 1) led us to try to generate the disubstituted dianionic derivatives $K_2Fe(CO)_2[P(OR)_3]_2$. This task was attempted by reacting the dihydrides **2b,c** with excess KH in THF under sonication. In both cases the expected evolution of gas was observed, but the resulting dark red complexes are very poorly soluble and, above all, exceedingly air-sensitive. Nevertheless, by reacting the dihydride **2b** in the presence of an excess of KH in THF-d_8 under sonication (eq 17), we succeeded in recording the IR and NMR spectra of $K_2[Fe(CO)_2\{P(OEt)_3\}_2]$ (**8b**).

$$\underset{\mathbf{2b}}{\mathrm{H_2Fe(CO)_2[P(OEt)_3]_2}} \xrightarrow[\text{sonication}]{\text{KH, THF, 40°C}} \underset{\mathbf{8b}}{\mathrm{K_2[Fe(CO)_2\{P(OEt)_3\}_2]}} + 2H_2 \quad (17)$$

The highly reduced nature of this complex is indicated by its very low ν_{CO} values (1730 and 1650 cm^{-1}). These frequencies, however, are higher than those (1682, 1619 cm^{-1}) reported for the monosubstituted dianion $[Fe(CO)_3(PMe_3)]^{2-}$.[5] The presence of two strong ν_{CO} bands is in agreement with the expected tetrahedral geometry. The NMR data are also characterized by downfield chemical shifts (Bruker WM 250, THF-d_8, $\delta(^{31}P\{^1H\})$ 208 ppm, $\delta(^{13}C)$ 237.8 ppm).

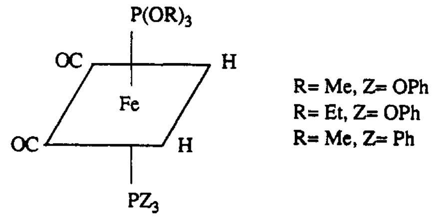
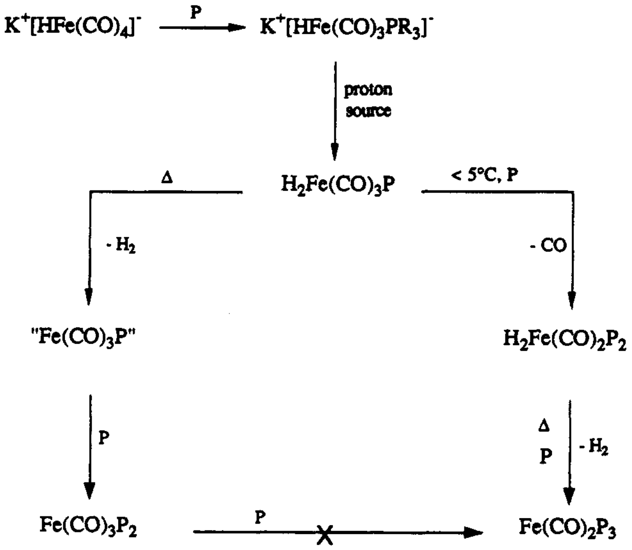


Figure 1. Idealized geometry for $H_2Fe(CO)_2[P(OR)_3][PZ_3]$.

Scheme I[a]



[a] P = phosphine or phosphite.

A comparison of the ^{13}C NMR data for four complexes prepared in this work is given in Table VIII. As may be seen, the higher the back-bonding on the carbonyl ligands (IR), the higher the chemical shift δ(CO) and the lower the J_{C-P} coupling constant.

Conclusion

The results of this study on the reactivity of $KHFe(CO)_4$ with phosphites confirm and complete our results on its reactivity with phosphines.[1] The following general conclusions can be proposed. Phosphanes (P) react with $KHFe(CO)_4$ to yield complexes containing one, two, or three phosphane ligands. The reactivity of the phosphane is determined mainly by its cone angle, the smallest phosphanes being the most reactive. However, even large phosphanes react in refluxing ethanol. The primary products are the anionic hydrides $K^+[HFe(CO)_3P]^-$. These complexes are not prone to a second CO substitution unless the reaction is conducted in refluxing THF with a phosphite exhibiting a small cone angle. In protic medium, the $K^+[HFe(CO)_3P]^-$ derivatives are protonated to generate the dihydrides $H_2Fe(CO)_3P$, which, depending on the reaction temperature, either (i) decompose by loss of H_2 to generate the coordinatively unsaturated "$Fe(CO)_3P$" species which react further with an excess of ligand to give the disubstituted $Fe(CO)_3P_2$ derivatives or (ii) react with an excess of ligand to give the corresponding dihydrides $H_2Fe(CO)_2P_2$ by a new CO substitution. In all cases the dihydride $H_2Fe(CO)_2P_2$ may react with an excess of P to yield the corresponding trisubstituted $Fe(CO)_2P_3$ derivative. The general reaction mechanism proposed for the reaction of **1** with phosphanes is outlined in Scheme I.

Finally, it must be emphasized that $KHFe(CO)_4$ is a versatile reagent which allows the selective, high-yield synthesis of a large variety of iron carbonyl complexes, among which are the anionic $K^+[HFe(CO)_{4-n}P_n]^-$ (n = 1,

Table VII. Spectral Data for $H_2Fe(CO)_2[P(OR)_3][PZ_3]$ Complexes

R	Z	IR ν_{CO}, cm^{-1}	$^{31}P\{^1H\}$ NMR δ, ppm	^1H NMR δ, ppm (mult)	 $^2J_{H-P}$, Hz
Me	OPh	2020 (s), 1975 (s)[a]	185 $[P(OMe)_3]$, 183 $[P(OPh)_3]$[c,d]	−11.0 (t)[c]	61
Et	OPh	2030 (s), 1985 (s)[a]	181 $[P(OPh)_3]$, 180 $[P(OEt)_3]$[c,d]	−11.1 (t)[c]	60
Me	Ph	2000 (s), 1960 (s)[b]	191 $[P(OMe)_3]$, 80 $[PPh_3]$[e,f]	−10.2 (dd)[e]	66, 49

[a] Hexane solution. [b] THF solution. [c] Bruker AC 80 spectrometer, acetone-d_6, 310 K, at 32.43 and 80 MHz for ^{31}P and ^1H, respectively. [d] J_{P-P} not observed. [e] Bruker WM 250 spectrometer, CD_2Cl_2 solution, 263 K, at 101.26 and 250 MHz for ^{31}P and ^1H, respectively. [f] J_{P-P} = 158 Hz.

Table VIII. Comparison of IR and ^{13}C NMR Data for Phosphite-Substituted Carbonylferrates (K^+ Salts)

complex (anionic part)	IR[a] 1600–2000-cm^{-1} region	^{13}C NMR[b] δ(CO), ppm	 $^2J_{C-P}$, Hz
$[HFe(CO)_3\{P(OMe)_3\}]^-$	1940 (m), 1880 (w), 1850 (s), 1830 (sh)	223.6	12
$[HFe(CO)_3\{P(OEt)_3\}]^-$	1940 (m), 1880 (w), 1850 (s), 1830 (sh)	223.4	16
$[HFe(CO)_2\{P(OMe)_3\}_2]^-$	1900 (m), 1870 (m), 1800 (s)	226.7	9
$[Fe(CO)_2[P(OEt)_3]_2]^{2-}$	1730 (s), 1650 (sh)	237.8	<1

[a] THF solution. [b] Bruker WM 250 spectrometer, THF-d_8, at 62.89 MHz.

2). The latter are currently being investigated to determine how the substitution by phosphane(s) modifies the reactivity of $[HFe(CO)_4]^-$.

Experimental Section

A. Methods and Materials. All sample manipulations were carried out under argon using standard Schlenk tube and reduced pressure techniques. Absolute ethanol and methanol (Prolabo, Normapur) were used without further purification but degassed by purging with argon for 0.5 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. Trimethyl phosphite, triethyl phosphite, and triphenyl phosphite (Aldrich) were purified by distillation before use. The tris(*o*-biphenylyl) phosphite was kindly supplied by Prof. P. W. Jolly. Argon U (L'Air Liquide) was used after passage through 3-Å molecular sieves. KH was obtained as a dispersion in mineral oil (Aldrich).

B. Instrumentation. Infrared spectra were recorded on a Perkin-Elmer 597 or a Perkin-Elmer 1725X FT-IR spectrometer using CaF_2 (0.05-mm) windows. ^1H, ^{31}P, and ^{13}C NMR spectra were recorded on either a Bruker WP 80-MHz or WM 250-MHz spectrometer, as noted in the footnotes of the tables. 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. These solutions were prepared according to the procedure described in ref 1.

2. Preparation of $KHFe(CO)_4$ Solutions in H_2O–THF. A 250-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 reduced-pressure–argon cycles. Water (50 mL) is added, followed by THF (30 mL), and when the dissolution of KOH is complete, the solution is degassed by purging with argon for 0.5 h. $Fe(CO)_5$ (1.5 mL, 11 mmol) is injected into the resulting solution through the septum cap, and stirring is continued for 0.5 h. The IR spectrum of the pale pink reaction medium indicates complete reaction of $Fe(CO)_5$ (no absorption bands near 2015 and 2035 cm^{-1}) and exhibits the characteristic absorption bands of solutions of $KFeH(CO)_4$ in H_2O–THF solvent mixtures at 2000 (w), 1911 (sh), and 1882 (s) cm^{-1}.

3. Preparation of $KHFe(CO)_4$ Solutions in THF. These solutions were prepared according to the procedure described in ref 1. Unless otherwise specified, these solutions were used without separating the insoluble $KHCO_3$. Alternatively, $KHCO_3$ may be separated by filtration under argon.

4. Preparation of [PPN][$HFe(CO)_4$]. A solution of [PPN]Cl (6.5 g, 11 mmol) in MeOH (20 mL) is added under argon to a solution of $KHFe(CO)_4$ (11 mmol) prepared in MeOH–H_2O (15 mL–10 mL) as described for the H_2O–THF mixture. A white voluminous solid rapidly precipitates. Degassed MeOH (40 mL) is added, and the mixture is further stirred for 0.5 h at room temperature and then filtered through sintered glass, the residue is washed with degassed, distilled water (6 × 50 mL), and the resulting white solid is dried under reduced pressure for 24 h; yield 7.7 g (98%).

5. Synthesis of $H_2Fe(CO)_2[P(OR)_3]_2$ Complexes (Table I). The synthesis of the $H_2Fe(CO)_2[P(OR)_3]_2$ complexes **2a–c** according to eq 1 and their full spectroscopic data have been reported previously.[9,10]

6. Synthesis of $Fe(CO)_3[P(O\text{-}o\text{-}C_6H_4Ph)_3]_2$. A solution of $KHFe(CO)_4$ (11 mmol) in H_2O–THF (50 mL–30 mL) is prepared as described above. Tris(*o*-biphenylyl) phosphite (11.8 g, 22 mmol) is added into the Schlenk flask under argon and the reaction medium heated at reflux for 24 h, during which time gas evolution is observed. The reaction medium is cooled to room temperature, and the organic solvent is evaporated under reduced pressure. Water is drawn off, and the resulting white solid is washed with water (3 × 30 mL) and then dissolved in THF (60 mL). Addition of pentane (120 mL) precipitates a white solid, which is separated by filtration, washed with pentane (3 × 30 mL), and dried under reduced pressure to constant weight; yield 12.4 g (94%). Anal. Calcd for $C_{75}H_{54}FeO_9P_2$: C, 74.02; H, 4.47. Found: C, 74.17; H, 4.65. IR (acetone): 1965 (s) and 1995 (m) cm^{-1}. ^{31}P NMR (Bruker WM 250, CD_2Cl_2): δ 177.8 ppm. $^{13}C\{^1H\}$ NMR (Bruker WM 250, CD_2Cl_2): δ(CO) 209.5 (t, $^2J_{C-P}$ = 42 Hz); other signals at 120.2, 124.6, 127.2, 127.9, 128.4, 129.7, 131.3, 133.8, 137.6, and 148.5 ppm.

7. Synthesis of $Fe(CO)_2[P(OR)_3]_3$ Complexes (Table II). Synthesis of 3a. A 30-mL methanolic solution of $KHFe(CO)_4$ (11 mmol) is prepared in a Schlenk flask fitted with a reflux condenser connected to an oil bubbler. Trimethyl phosphite (4.10 g, 33 mmol) is added through a septum cap, and vigorous stirring is maintained for 48 h at reflux. After the mixture is cooled to room temperature, the solvent is removed under reduced pressure to give a white slurry. This mixture is treated with *n*-pentane (60 mL), and the resulting white-green suspension is filtered to remove $KHCO_3$. The latter is washed with *n*-pentane (3 × 20 mL), and the combined filtrates are concentrated under reduced pressure to a 30-mL volume. Cooling at −78 °C for 6 h precipitates white crystals, which are collected, washed with cooled (−78 °C) *n*-pentane (2 × 20 mL), and dried at room temperature under reduced pressure to constant weight to give $Fe(CO)_2[P(OMe)_3]_3$ as an off-white solid (mp 46–47 °C); yield 4.9 g (91%). Anal. Calcd for $C_{11}H_{27}FeO_{11}P_3$: C, 27.29; H, 5.62. Found: C, 27.56; H, 5.82.

Synthesis of 3b. A 30-mL ethanolic solution of $KFeH(CO)_4$ (11 mmol) is prepared as described above. Triethyl phosphite (5.48 g, 33 mmol) is then added through a septum cap, and the reaction mixture is refluxed for 8 h. The same workup as that described for **3a** affords $Fe(CO)_2[P(OEt)_3]_3$ as an off-white solid (mp 51–52 °C); yield 6.5 g (96%). Anal. Calcd for $C_{20}H_{45}FeO_{11}P_3$: C, 39.36; H, 7.43. Found: C, 40.31; H, 7.63.

Synthesis of 3c. A 30-mL H_2O–THF (20 mL–10 mL) solution of $KFeH(CO)_4$ (11 mmol) is prepared and heated to reflux.

Triphenyl phosphite (10.3 g, 33 mmol) is added dropwise through the septum cap. Stirring is maintained for 72 h at reflux. After the mixture is cooled to room temperature, the upper yellow phase is transferred via a syringe into another Schlenk flask and the water phase extracted with THF until the latter is no longer colored (3 × 40 mL). The combined THF phases are evaporated under reduced pressure to give a yellow oily residue, which is dissolved in dichloromethane (40 mL). This solution is filtered under argon and concentrated to a 5-mL volume. Addition of *n*-pentane (100 mL) precipitates a white solid. The liquid phase is drawn off and the solid dried under reduced pressure to a constant weight (6 g). The liquid phase is concentrated to half of its volume and cooled at −20 °C for 12 h. Additional white solid precipitates, which is dried under reduced pressure to constant weight (2.6 g). $Fe(CO)_2[P(OPh)_3]_3$ is a white solid (mp 85–86 °C); yield 8.6 g (75%). Anal. Calcd for $C_{56}H_{45}FeO_{11}P_3$: C, 64.51; H, 4.35. Found: C, 64.22; H, 4.47.

8. Reaction of 2a with an Excess of Trimethyl Phosphite (Eq 2). The dihydride **2a** (2.174 g, 6 mmol), dissolved in methanol (30 mL) is added under argon to a solution of trimethyl phosphite (4.10 g, 33 mmol) in refluxing methanol (30 mL) and the mixture stirred for 24 h at reflux. At the end of the reaction, the solvent and excess trimethyl phosphite are evaporated under reduced pressure. The resulting material is dissolved in pentane (60 mL) and the solution cooled to −78 °C for 6 h to give white crystals, which are separated, washed with cold pentane (−78 °C, 2 × 20 mL), and dried to constant weight to give **3a**; yield 2.861 g (99%).

9. Synthesis of $K[HFe(CO)_3\{P(OR)_3\}]$ Complexes 4a and 4b in *t*-AmOH (Table IV). A solution of $KHFe(CO)_4$ (11 mmol) in methanol is prepared as described above. The solvent is evaporated under reduced pressure, *t*-AmOH (40 mL) is added, and the resulting mixture is stirred for 0.25 h. Trimethyl or triethyl phosphite (2.73 or 3.66 g, 22 mmol) is then added dropwise with a syringe through the septum cap, and the Schlenk flask is connected to a gas buret. Stirring is continued until the expected amount of gas has evolved (270 mL, ca. 1 h). The solvent is then evaporated under reduced pressure at 40 °C. The residue is washed with pentane (3 × 30 mL) to remove the excess phosphite and any trace of the corresponding dihydride $H_2Fe(CO)_2[P(OR)_3]_2$. Anhydrous THF (40 mL) is added, and the solution is filtered over Celite on sintered glass under argon to remove $KHCO_3$. The filtrate is then concentrated to 10 mL. Addition of pentane (30 mL) precipitates the product, which is separated and dried under reduced pressure to constant weight; yield >95% for both **4a** (3.2 g) and **4b** (3.6 g).

10. Synthesis of $K[HFe(CO)_3\{P(OR)_3\}]$ Complexes 4a–c in THF (Table IV). A solution of $KHFe(CO)_4$ (11 mmol) in THF (40 mL) is prepared as described above. The phosphite (23 mmol) is then added ($P(OMe)_3$, 2.9 g; $P(OEt)_3$, 3.7 g; $P(OPh)_3$, 6.9 g) at 25–28 °C, and the Schlenk flask is immediately connected to a gas buret. Vigorous stirring is maintained over 1 h for $P(OMe)_3$ and $P(OEt)_3$ and over 2 h for $P(OPh)_3$, during which time a gas is evolved (ca. 270 mL). When the expected amount of gas has evolved, the reaction mixture is filtered under argon through sintered glass, and the filtrate is evaporated under reduced pressure. The remaining material (white solid for $P(OMe)_3$ and $P(OEt)_3$, yellow oil for $P(OPh)_3$) is washed with pentane (3 × 30 mL) and dried under reduced pressure to constant weight. In each case the yield is >90% (**4a**, 3.29 g; **4b**, 3.72 g; **4c**, 5.31 g). In the special case of $P(OPh)_3$, possible traces of $H_2Fe(CO)_2[P(OPh)_3]_2$ may be further eliminated by washing with hexane (3 × 30 mL).

11. Synthesis of $[PPN][HFe(CO)_3\{P(OR)_3\}]$ Complexes 5a–c (Table IV). The phosphite (11 mmol) is added through a septum cap to a solution of $[PPN][HFe(CO)_4]$ (3.6 g, 5 mmol) in degassed CH_2Cl_2 (10 mL), and the Schlenk flask is connected to a gas buret. Stirring is continued until the evolution of gas ceases (ca. 2 h for $P(OPh)_3$, 4 h for $P(OMe)_3$ and $P(OEt)_3$). The reaction product is immediately precipitated by addition of anhydrous diethyl ether (30 mL) (the reaction products slowly decompose in CH_2Cl_2), filtered, washed with diethyl ether (3 × 30 mL), and dried under reduced pressure to constant weight. The yield is >90% in each case (**5a**, 3.8 g; **5b**, 4.0 g; **5c**, 4.7 g).

12. Synthesis of $M^+[HFe(CO)_2\{P(OR)_3\}_2]^-$ Complexes (Table V). Synthesis of 7a. A solution of $KHFe(CO)_4$ (11 mmol) in THF (60 mL) is prepared (free of $KHCO_3$) as described above. Trimethyl phosphite (4.10 g, 33 mmol) is added under argon through a septum cap, and the reaction medium is heated to reflux. After 24 h a 520-mL evolution of gas is obtained (analyzed by GLC as pure carbon monoxide). The reaction medium is cooled to room temperature and concentrated to 10 mL. Addition of pentane (30 mL, distilled over KH) precipitates a white solid, which is washed with pentane (3 × 30 mL) to give **7a**; yield 4.2 g (95%).

Synthesis of 7c. Potassium hydride is placed in a Schlenk flask under argon, washed with anhydrous THF (3 × 10 mL), and dried under reduced pressure to constant weight (0.22 g, 5.6 mmol). A solution of **2c** (2.06 g, 2.75 mmol) in THF (10 mL) is then added under argon through a septum cap, and the flask is connected to an oil bubbler. After 5 min at room temperature without stirring, the evolution of gas ceases. The red solution is drawn off, the solvent evaporated under reduced pressure, and the resulting brown material dissolved in THF-d_8 (2.5 mL) for IR and NMR analyses (Table V).

13. Synthesis of $H_2Fe(CO)_3[P(OR)_3]$ Complexes (Table VI). The anionic hydrides **4a–c** (11 mmol) are each dissolved in THF (40 mL) in a Schlenk flask, which is then placed in a thermostated bath at −10 °C. A solution of CF_3COOH (1.254 g, 11 mmol) in cooled THF (−10 °C, 10 mL) is added dropwise and stirring continued for 0.25 h. The solvent is then evaporated under reduced pressure while the Schlenk tube is maintained in the cooled bath, and the resulting dihydride is extracted with cooled pentane (3 × 30 mL). Evaporation of the solvent under reduced pressure to constant weight affords a green oil in 98% yield for R = Me (2.9 g) and Et (3.27 g) and a purple oil in 95% yield for R = Ph (4.63 g).

14. Synthesis of $H_2Fe(CO)_2[P(OR)_3][PZ_3]$ Complexes (Table VII). The synthesis of $H_2Fe(CO)_2[P(OR)_3][PZ_3]$ complexes is exemplified in the case where R = Me and Z = Ph. The anionic complex $K[HFe(CO)_3\{P(OMe)_3\}]$ (3.3 g, 10.8 mmol) is dissolved in THF (40 mL) and the Schlenk flask placed in a thermostated bath at −10 °C. A solution of CF_3CO_2H (1.254 g, 11 mmol) in cold THF (−10 °C, 10 mL) is added dropwise, and stirring is continued for 0.25 h. A solution of triphenylphosphine (2.0 g, 11.06 mmol) in THF (10 mL) is then added and the Schlenk flask connected to a gas buret. After 24 h of stirring at 0 °C, the expected amount of gas has evolved (270 mL). The reaction mixture is filtered to remove CF_3CO_2K, which is washed with THF (3 × 30 mL), and the filtrates are concentrated to 10 mL. Addition of hexane (30 mL) precipitates a yellow solid. Crystallization from CH_2Cl_2–MeOH (20 mL–20 mL) affords $H_2Fe(CO)_2[P(OMe)_3][PPh_3]$; yield 4.0 g (73%). Anal. Calcd for $C_{23}H_{26}FeO_5P_2$: C, 55.19; H, 5.24. Found: C, 55.57; H, 5.23.

15. Generation of $K_2[Fe(CO)_2\{P(OEt)_3\}_2]$. Potassium hydride is placed in a Schlenk flask, washed with anhydrous THF (3 × 10 mL), and dried under reduced pressure to constant weight (0.71 g, 17.7 mmol). A solution of **2b** (2.3 g, 5.16 mmol) in THF-d_8 (3 mL) is then added under argon through a septum cap. The flask is connected to an oil bubbler and sonicated (ca. 40 °C) in a common ultrasonic cleaner until no more evolution of gas is observed (1 h). The dark red solution is then analyzed immediately by IR and NMR spectroscopy.

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