Organometallics 1988, 7, 2466–2469

A Facile, High-Yield Synthesis of *trans*-$Fe(CO)_3(PR_3)_2$ from $Fe(CO)_5$, $Fe(CO)_4CHO^-$, $HFe(CO)_4^-$, or $HFe(CO)_3PR_3^-$

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Received February 18, 1988

The reaction of $Fe(CO)_5$ with PR_3 and $NaBH_4$ in refluxing *n*-butyl alcohol affords high yields of *trans*-$Fe(CO)_3(PR_3)_2$. It has been shown that $Fe(CO)_4PR_3$, which does not appear in the collected product, is also not a significant intermediate in the reaction. The reaction proceeds by initial formation of H_2 gas and $Fe(CO)_4CHO^-$. The formyl complex decomposes to $HFe(CO)_4^-$ which reacts with PR_3 to give the disubstituted product. The principal intermediate for this substitution is believed to be $HFe(CO)_3PR_3^-$, although polynuclear species may also be important. The substitution of $HFe(CO)_4^-$ by PR_3 is favorable when the counterion is Na^+ but not when it is PPN^+. The overall reaction is very sensitive to choice of solvent; substitution of ethanol for *n*-butyl alcohol leads to greatly reduced yields.

Introduction

Unassisted thermal and photolytic reactions of $Fe(CO)_5$ with PR_3 give rise to mixtures of $Fe(CO)_4PR_3$ and *trans*-$Fe(CO)_3(PR_3)_2$ which are in general difficult to separate.[1] Several useful procedures that maximize the formation of $Fe(CO)_4PR_3$ have been developed, including reactions which are facilitated by AlH_4^- or BH_4^-,[2a] as well as those catalyzed by iron carbonyl anions[2b] or by cobalt salts.[2c] The cobalt-catalyzed reactions are particularly useful because yields are high, starting materials are readily available, reaction times are short, and photolysis is avoided.

Similar success has not been realized for the production of *trans*-$Fe(CO)_3(PR_3)_2$ even though these complexes continue to be widely used.[3] For the thermal preparations, yields typically are low (15–27%) (as for the reactions of PPh_3 with $Fe(CO)_5$ and $Fe_3(CO)_{12}$[1a]), reaction times are long (50 h) (as for $LiAlH_4$ facilitated reactions of $Fe(CO)_5$ and PPh_3[2a]), or reagents are expensive (as for the reaction of PPh_3 with $Fe_3(CO)_{11}^{2-}$, $Fe_2(CO)_8^{2-}$, or $Fe_4(CO)_{13}^{2-}$ [2b,4]). Under some conditions, good yields of disubstituted complexes can be obtained by photolysis. Although the early work of Strohmeier demonstrated that photolytic reactions produce both $Fe(CO)_4PR_3$ and *trans*-$Fe(CO)_3(PR_3)_2$,[1b] Therien and Trogler recently have shown that disubstituted derivatives (R = Me, *n*-Bu, c-C_6H_{11} or Ph) precipitate selectively from solution when formed in cyclohexane.[5] While yields are high, reaction times range from 5 to 16 h, 4–5 equiv of phosphine are required, and photolytic equipment is necessary.

We have found that $Fe(CO)_5$ reacts with PR_3 and $NaBH_4$ in refluxing *n*-butyl alcohol to give *trans*-$Fe(CO)_3(PR_3)_2$ without contamination from $Fe(CO)_4PR_3$. Large excesses of phosphine are unnecessary, reaction times of 2 h are satisfactory, and specialized equipment is not needed. In this paper we present the details of this simple synthesis and supply evidence that the reaction proceeds stepwise through $Fe(CO)_4CHO^-$, $HFe(CO)_4^-$, and $HFe(CO)_3PR_3^-$ intermediates.

Experimental Section

General Procedures. All reactions were carried out under an atmosphere of N_2. Ethanol and *n*-butyl alcohol were obtained from various supply companies and purged with N_2 for 30 min prior to use. THF was distilled from Na and benzophenone under an atmosphere of N_2. Phosphines were purchased from Pressure Chemical Co. The complexes $[PPN][HFe(CO)_4]$, $[Et_4N][HFe(CO)_3PPh_3]$, $K[HFe_3(CO)_{11}]$, and $Fe(CO)_4PPh_3$ were prepared as described previously.[6a,7a,8a,2c] All other chemicals, including $Fe(CO)_5$, were used as received from commercial sources.

Infrared spectra ($CHCl_3$) were recorded on a Nicolet 20 DX-B FT spectrometer. Proton and $^{31}P\{^1H\}$ NMR spectra ($CDCl_3$) were obtained with Varian T-60 and home-built 250-MHz NMR spectrometers, respectively. ^{31}P NMR chemical shifts, relative to 85% phosphoric acid, are reported with positive values downfield from the reference.

Synthesis of *trans*-$Fe(CO)_3(PR)_2$ Complexes. The synthesis of the PPh_3 derivative is detailed below; the same basic procedure was applied for the preparation of the other complexes with a slight modification, as described, for the $P(n\text{-}Bu)_3$ case.

To a stirred mixture of PPh_3 (5.97 g, 22.8 mmol) and $NaBH_4$ (0.289 g, 7.60 mmol) in 150 mL of *n*-butyl alcohol was addded $Fe(CO)_5$ (1.00 mL, 7.60 mmol). Evolution of gas was vigorous and a yellow solution resulted. After gas evolution, the reaction mixture was refluxed for 2 h (longer reaction times do not increase yield), cooled to room temperature, and placed in a freezer (5 °C) for 12 h. During this specific preparation, some yellow precipitate was noted after 15 min of refluxing, and large quantities were observed upon cooling the reaction mixture to room temperature. The precipitate was collected by filtration and washed with several portions of methanol to remove borate salts. The remaining

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0276-7333/88/2307-2466$01.50/0

precipitate was treated with approximately 30 mL of CH_2Cl_2, and undissolved solid was removed by filtration. To the resulting solution approximately 30 mL of CH_3OH was added, which induced immediate precipitation. The mixture was allowed to remain in a freezer for several hours before the product was collected by filtration. Both IR and ^{31}P NMR spectra showed the isolated product to be exclusively *trans*-$Fe(CO)_3(PPh_3)_2$.[5b] Infrared spectra of some crude reaction mixtures showed evidence for small quantities of $Fe(CO)_4PR_3$, but in no case was any monosubstituted derivative observed in the collected product. Yields of the disubstituted complexes, including the effects of varying ligand concentration, are shown in Table II. When identical reactions were carried out in ethanol, yields of approximately 15% were obtained.

The above procedure was modified for the preparation of *trans*-$Fe(CO)_3[P(n\text{-}Bu)_3]_2$, which is soluble in *n*-butyl alcohol. After the reaction, *n*-butyl alcohol was removed under vacuum and the crude reaction mass was crystallized from CH_2Cl_2/CH_3OH.

Reaction of $Fe(CO)_5$ with $NaBH_4$ in *n*-Butyl Alcohol. When $Fe(CO)_5$ is added to $NaBH_4$ in *n*-butyl alcohol in proportions identical with those of the foregoing synthesis, a gas is vigorously evolved. An IR spectrum of this gas shows traces of *n*-butyl alcohol and $Fe(CO)_5$ and an even smaller quantity of CO. The gas cannot be condensed with liquid N_2, and it reacts explosively when it is mixed with O_2 and ignited. The *n*-butyl alcohol solution that remains after gas evolution gives rise to infrared signals in the carbonyl region at 2025, 1935, and 1909 cm^{-1} (lit. for $Fe(CO)_4CHO^-$: 2018, 1930, and 1902 cm^{-1}, THF[9]). A ^1H NMR spectrum of this solution shows a chemical shift at 14.6 ppm (lit. for $Fe(CO)_4CHO^-$: 14.95 ppm, THF[9]).

The solution described above was stirred under N_2 over a period of approximately 2 weeks, with periodic examination of its ^1H NMR spectrum. The signal at 14.6 ppm gradually disappeared and a signal at −9.9 ppm (lit. for $HFe(CO)_4^-$: −8.74 ppm, THF[10]) simultaneously grew into the spectrum, becoming the dominant signal observed after about 5 days. The solution at this point was an orange/red color. Over the remainder of the monitoring period, the color gradually changed to deep red, the NMR signal at −9.9 ppm diminished, and a signal at −14.8 ppm (lit. for $HFe_3(CO)_{11}^-$: −14.9, Me_2SO-d_6[8,10]) appeared.

Synthesis of [PPN][$Fe(CO)_4CHO$]. To a stirred mixture of $NaBH_4$ (0.29 g, 7.6 mmol) in 25 mL of *n*-butyl alcohol at 0 °C was added $Fe(CO)_5$ (1.00 mL, 7.6 mmol) in 20 mL of *n*-butyl alcohol dropwise over 15 min. Gas was evolved, and the reaction mixture was stirred for 1.5 h, followed by addition of [PPN]Cl (4.36 g, 7.6 mmol). Formation of a light pink precipitate was immediate. The precipitate was collected by filtration and washed several times with methanol to remove salts. The light brown product (70%) was identified by its IR spectrum (THF).[9]

Reaction of PPh_3 with [PPN][$Fe(CO)_4CHO$]. A stirred mixture of PPh_3 (1.60 g, 6.11 mmol) and [PPN][$Fe(CO)_4CHO$] (1.50 g, 2.04 mmol) in 100 mL of *n*-butyl alcohol was refluxed for 2 h. Infrared analysis showed the presence of [PPN][$HFe(CO)_4$][6b] but no phosphine-substituted product. When this reaction was carried out in the presence of $NaBH_4$ (2.04 mmol), a 30% yield of disubstituted product was obtained.

Reaction of PPh_3 with [PPN][$HFe(CO)_4$]. A stirred mixture of PPh_3 (1.48 g, 5.65 mmol) and [PPN][$HFe(CO)_4$] (2.00 g, 2.82 mmol) in 100 mL of *n*-butyl alcohol was refluxed for 2 h. No phosphine-substituted product was detected in the infrared spectrum, and 80% of the starting material was recovered.

Reaction of PPh_3 with Na[$HFe(CO)_4$]. A solution (6.5 mL) of Na[$HFe(CO)_4$] was prepared from NaOH and $Fe(CO)_5$ (5.32 mmol) in CH_3OH/H_2O, as descrbed in the literature,[10] and diluted with 100 mL of *n*-butyl alcohol. To this stirred solution was added PPh_3 (16.0 mmol). The reaction mixture was refluxed for 2 h. A copious precipitate resulted upon cooling. The product was collected by filtration, recrystallized from CH_2Cl_2/CH_3OH, and identified by IR as *trans*-$Fe(CO)_3(PPh_3)_2$ (95%).

Reaction of PPh_3 with [Et_4N][$HFe(CO)_3PPh_3$]. A stirred solution of [Et_4N][$HFe(CO)_3PPh_3$] (2.33 mmol) and PPh_3 (2.33 mmol) in 100 mL of *n*-butyl alcohol was refluxed for 2 h. Cooling to room temperature gave a green-black precipitate which was collected by filtration, crystallized from CH_2Cl_2/CH_3OH, and identified by IR as *trans*-$Fe(CO)_3(PPh_3)_2$ (67%).

Table I. ^{31}P NMR and IR Data for *trans*-$Fe(CO)_3(PR_3)_2$

phosphine	chem shift (ppm)	stretching freq (cm^{-1})[a]	ref
PPh_3	82.5	1881 (s), 1886 (s), 1944 (w)	5b
PPh_2H	53.9	1880 (s), 1886 (s), 1978 (w)	20
$PPh_2CH{=}CH_2$	76.5	1880 (s), 1886 (s), 1973 (w)	21
PPh_2Et	77.7	1868 (s), 1882 (s), 1967 (w)	22
PPh_2Me	64.7	1872 (s), 1882 (s), 1966 (w)	2c
$P(Cy)_3$	86.1	1842 (s), 1858 (s), 1947 (w)	5b
$P(n\text{-}Bu)_3$	62.4	1854 (s), 1856 (s), 1955 (w)	5b

[a] Splitting of the E′ mode is not unusual in $CHCl_3$. The weak forbidden A_1' mode was found in all spectra.

Table II. Percentage Yields for *trans*-$Fe(CO)_3(PR_3)_2$

ligand	ratio of $Fe(CO)_5$/ligand	yield, %
PPh_3	1.0:2.0	65
PPh_3	1.0:2.5	75
PPh_3	1.0:3.0	87
PPh_2H	1.0:3.0	66
$PPh_2CH{=}CH_2$	1.0:3.0	72
$PPh_2CH_2CH_3$	1.0:3.0	91
PPh_2Me	1.0:2.0	90
$P(Cy)_3$	1.0:2.0	61
$P(n\text{-}Bu)_3$	1.0:2.0	47

Reaction of $Fe(CO)_4PPh_3$ with PPh_3 and $NaBH_4$ in *n*-Butyl Alcohol. To 100 mL of *n*-butyl alcohol were added $NaBH_4$ (0.289 g, 7.61 mmol), PPh_3 (0.585 g, 2.23 mmol), and $Fe(CO)_4PPh_3$ (0.960 g, 2.23 mmol). This solution was refluxed with stirring for 2 h, cooled to room temperature, and refrigerated for several hours. The yellow precipitate (0.92 g) was collected by filtration and shown by IR to be $Fe(CO)_4PPh_3$[2c] contaminated with traces of *trans*-$Fe(CO)_3(PPh_3)_2$.

Reaction of K[$Fe_3(CO)_{11}$] with PPh_3. A stirred mixture of K[$Fe_3(CO)_{11}$] (prepared from 24 mmol of $Fe(CO)_5$) and PPh_3 (48 mmol) in 100 mL of *n*-butyl alcohol was refluxed for 2 h. A yellow precipitate formed as the solution began to reflux. The product, which was collected after the reaction pot reached room temperature, consisted of a mixture of *trans*-$Fe(CO)_3(PPh_3)_2$ (major component) and $Fe(CO)_4PPh_3$, as shown by IR spectroscopy.

Results and Discussion

The reaction of $Fe(CO)_5$ with PR_3 and $NaBH_4$ in refluxing *n*-butyl alcohol affords *trans*-$Fe(CO)_3(PR_3)_2$, which precipitates from the cooled solution and is uncontaminated by the monosubstituted derivative. Seven complexes with a variety of phosphine ligands have been synthesized by this method and characterized by ^{31}P NMR and IR spectroscopy (Table I). Yields, which range from 47 to 91% for the compounds of this study, are maximized with a reaction time of 2 h and a small excess of phosphine (Table II). Large excesses of $NaBH_4$ lead to reduced yields, presumably due to competing side reactions. The choice of solvent is critical for a successful reaction; when ethanol is substituted for *n*-butyl alcohol, only 15% conversion to the trans product is realized.

Reactions involving $PPh_2CH{=}CH_2$ lead to some reduction of the vinyl group giving *trans*-$Fe(CO)_3(PPh_2CH_2CH_3)(PPh_2CH{=}CH_2)$ and *trans*-$Fe(CO)_3(PPh_2CH_2CH_3)_2$ as minor products. ^{31}P chemical shifts for these two compounds are (76.65 and 76.67) and 76.80 ppm, respectively, and J_{PP} for the mixed ligand complex, which gives rise to an AB spectrum, is 37.9 Hz.

When the reactants for the synthesis are mixed, an immediate vigorous evolution of a gas is observed. This gas has been identified as H_2 by virtue of its infrared silence and failure to condense at 77 K. It also forms when Fe-

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$(CO)_5$ and $NaBH_4$ are allowed to react in *n*-butyl alcohol in the absence of PR_3 at room temperature. No reaction occurs, however, when $NaBH_4$ and *n*-butyl alcohol are mixed at room temperature. Moreover, the reaction between $Fe(CO)_5$ and $NaBH_4$ leads to $Fe(CO)_4CHO^-$, suggesting that the overall reaction is initiated by attack of H^- on bound CO. Although $NaBH_4$ is generally ineffective as a reagent for the production of formyl complexes[11] and the reaction of $Fe(CO)_5$ with $NaBH_4$ in diglyme has been reported to give mixtures of complexes,[12] infrared data show the conversion in *n*-butyl alcohol to be nearly quantitative.

The formyl complex ($Fe(CO)_4CHO^-$) exhibits considerable stability in *n*-butyl alcohol, despite the protic nature of the solvent. Proton NMR shows that slow conversion to $HFe(CO)_4^-$ occurs at room temperature, although this process is rapid in refluxing *n*-butyl alcohol. The decomposition of $Fe(CO)_4CHO^-$ to $HFe(CO)_4^-$ in THF has been well-studied, and recently it has been shown that a free radical pathway is important.[13] It is also possible to isolate the formyl complex in good yield from an *n*-butyl alcohol solution. The reaction of $Fe(CO)_5$ with $NaBH_4$, followed by addition of [PPN]Cl gives [PPN][$Fe(CO)_4CHO$] as an immediate precipitate in 70% yield. Although spectroscopic yields of greater than 90% have been reported for this complex,[14-16] isolation in quantities greater than 50% has not.[16]

The hydride ($HFe(CO)_4^-$), upon forming from the formyl complex at room temperature in *n*-butyl alcohol, slowly decomposes to $HFe_3(CO)_{11}^-$, as shown by proton NMR. In refluxing *n*-butyl alcohol in the presence of PR_3, it yields *trans*-$Fe(CO)_3(PR_3)_2$. This reaction may occur via direct substitution of the hydride to form $HFe(CO)_3PR_3^-$, or it may involve formation of $HFe_3(CO)_{11}^-$, which subsequently undergoes substitution. We have synthesized both $HFe(CO)_4^-$ and $HFe_3(CO)_{11}^-$ independently and investigated their reactions with PPh_3. For $HFe(CO)_4^-$ the collected product is identical with that for the reaction of $Fe(CO)_5$ with PPh_3 and $NaBH_4$: *trans*-$Fe(CO)_3(PPh_3)_2$ with no monosubstituted complex. The trinuclear species also yields the disubstituted derivative but with distinct contamination by $Fe(CO)_4PPh_3$. We therefore conclude that $HFe(CO)_3PPh_3^-$ is more likely to be the principal intermediate, although the polymetallic species probably plays a role as well.

Infrared spectroscopic evidence for reaction intermediates was sought by monitoring the reaction of $Fe(CO)_5$ with PPh_3 and $NaBH_4$. Immediately following evolution of H_2, CO absorption bands for $Fe(CO)_4CHO^-$ at 2025, 1935, and 1909 cm^{-1} are present.[9] As the reaction proceeds, a signal at 2001 cm^{-1}, assigned to $HFe(CO)_4^-$,[6b] gradually appears and grows in intensity. Although $HFe_3(CO)_{11}^-$ also absorbs at 1999 cm^{-1}, absence of other characteristic signals for this compound at 2067 and 1979 cm^{-1} rule it out as the source of the signal at 2001 cm^{-1}.[8a] In addition, the formyl absorption at 1909 cm^{-1} broadens and develops a shoulder at 1895 cm^{-1}, which is also assigned to $HFe(CO)_4^-$. The region in the vicinity of 1900 cm^{-1} is particularly complicated because *trans*-$Fe(CO)_3(PPh_3)_2$ gives its principal CO absorption at 1884 cm^{-1}[5b] and dominates the reaction mixture even in the early stages. A signal at 2050 cm^{-1}, characteristic of $Fe(CO)_4PPh_3$[6b] but never becoming a major absorption, was also observed during the course of the reaction and in the final crude reaction mixture. Minor amounts of this compound may form from direct substitution of $Fe(CO)_5$ or $HFe(CO)_4^-$. Presumably both $HFe(CO)_3PR_3^-$ and $HFe_3(CO)_{11}^-$ would be too unstable under the conditions of the reaction to be observable spectroscopically.

To further test the intermediacy of $HFe(CO)_3PR_3^-$ in the overall reaction, it was prepared independently (with R = Ph) and allowed to react with PPh_3 in refluxing *n*-butyl alcohol. It was found to readily give *trans*-$Fe(CO)_3(PPh_3)_2$. Thus it appears that substituting PR_3 for CO in $HFe(CO)_4^-$ increases the electron density on Fe, thereby enhancing the hydridic nature of the bound hydrogen atom such that it reacts with *n*-butyl alcohol, liberating hydrogen gas and providing a vacant coordination site for the second PPh_3 ligand. In contrast, it appears that $HFe(CO)_4^-$ does not significantly react with *n*-butyl alcohol under the conditions of the reaction and as a consequence a vacant coordination site does not become available which would allow the formation of $Fe(CO)_4PR_3$. Hence the production of the disubstituted complex and the exclusion of the monosubstituted derivative can be accounted for by the relative reactivities of $HFe(CO)_4^-$ and $HFe(CO)_3PR_3^-$ toward refluxing *n*-butyl alcohol.

Whereas $Fe(CO)_5$ is readily converted to the disubstituted trans derivative when subjected to the conditions described herein, $Fe(CO)_4PR_3$ is relatively unreactive under these same conditions (substantial starting material is recovered and only traces of trans product are observed). *It is clear from this result that* $Fe(CO)_4PR_3$ *is not a significant intermediate in the formation of* trans-$Fe(CO)_3(PR_3)_2$. It would appear that either $Fe(CO)_4PR_3$ is not converted to $Fe(CO)_3PR_3CHO^-$ or, if the latter forms, it reduces *n*-butyl alcohol and in so doing regenerates $Fe(CO)_4PR_3$.

A plausible reaction sequence based on the foregoing discussion is

$$\begin{array}{c}
Fe(CO)_5 + BH_4^- \rightarrow Fe(CO)_4CHO^- + BH_3 \\
BH_3 + 3n\text{-}BuOH \rightarrow B(n\text{-}BuO)_3 + 3H_2 \\
Fe(CO)_4CHO^- \rightarrow HFe(CO)_4^- + CO \\
HFe(CO)_4^- + PR_3 \rightarrow HFe(CO)_3PR_3^- + CO \\
HFe(CO)_3PR_3^- + n\text{-}BuOH \rightarrow H_2 + n\text{-}BuO^-\cdots Fe(CO)_3PR_3 \\
n\text{-}BuO^-\cdots Fe(CO)_3PR_3 + PR_3 \rightarrow trans\text{-}Fe(CO)_3(PR_3)_2 + n\text{-}BuO^- \\
B(n\text{-}BuO)_3 + n\text{-}BuO^- \rightarrow B(n\text{-}BuO)_4^- \\
\hline
Fe(CO)_5 + BH_4^- + 4n\text{-}BuOH + 2PR_3 \rightarrow trans\text{-}Fe(CO)_3(PR_3)_2 + 2CO + 4H_2 + B(n\text{-}BuO)_4^-
\end{array}$$

In addition to these reactions, BH_4^- will react with *n*-BuOH at elevated temperatures to give species such as $HB(n\text{-}BuO)_3^-$, $H_2B(n\text{-}BuO)_2^-$, and $H_3B(n\text{-}BuO)^-$ which may also serve as hydride sources.[17]

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As indicated previously, refluxing ethanol provides a much less favorable medium for the reaction. Formyl and hydride complex formation proceed as in *n*-butyl alcohol, but phosphine substitution is unfavorable. The additional energy provided by a higher boiling alcohol such as *n*-butyl alcohol apparently is essential for this step to proceed. Furthermore, substitution depends strongly on the nature of the counterion. We find that $[PPN][HFe(CO)_4]$ reacts with PPh_3 in refluxing *n*-butyl alcohol to give, after 2 h, traces of *trans*-$Fe(CO)_3(PPh_3)_2$ and unreacted starting material. When the same experiment is carried out with $Na[HFe(CO)_4]$, a 95% yield of the trans product is obtained. Moreover, the reaction of PPh_3 with $[PPN][Fe(CO)_4CHO]$ gives only $[PPN][HFe(CO)_4]$ while the reaction with $Na[Fe(CO)_4CHO]$ produces an 87% yield of *trans*-$Fe(CO)_3(PPh_3)_2$ (Table II). This is consistent with Darensbourg's observation that $Na[HFe(CO)_4]$ is much more reactive than $[PPN][HFe(CO)_4]$ toward O_2 in THF.[6b,18] In addition, Ungvary and Wojcicki have shown that $Na[Co(CO)_4]$ undergoes rapid substitution by phosphines while $[PPN][Co(CO)_4]$ is unreactive, further underscoring the importance of the counterion in reactions involving organometallic carbonyl anions.[19]

In the course of elucidating the mechanism for the reaction of PR_3 with $Fe(CO)_5$ and $NaBH_4$, we have also discovered that *trans*-$Fe(CO)_3(PPh_3)_2$ may be prepared in high yield from the reaction of $Fe(CO)_5$, PPh_3, and NaOH. Furthermore, preliminary results suggest that the reaction of $HFe(CO)_3PR_3^-$ with PR'_3 provides a useful route to complexes containing two different phosphines. The generality of both of these reactions is now under investigation.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the National Science Foundation, Grant CHE-85-13021, for support of this research. We are grateful to the University of Illinois for the use of a 250-MHz NMR spectrometer. We thank Robert Newman for some of the initial experimental work.

Registry No. $[PPN][HFe(CO)_4]$, 56791-54-9; $[Et_4N][HFe(CO)_3PPh_3]$, 80612-33-5; $Fe(CO)_4PPh_3$, 35679-07-3; $Fe(CO)_5$, 13463-40-6; *trans*-$Fe(CO)_3(PPh_3)_2$, 21255-52-7; *trans*-$Fe(CO)_3[P(n\text{-}Bu)_3]_2$, 49655-14-3; $NaBH_4$, 16940-66-2; $[PPN][Fe(CO)_4CHO]$, 41900-55-4; $Na[HFe(CO)_4]$, 53558-55-7; $K[Fe_3(CO)_{11}]$, 116466-60-5; *trans*-$Fe(CO)_3(PPh_2H)_2$, 40697-11-8; *trans*-$fe(CO)_3(PPh_2CH{=}CH_2)_2$, 87137-61-9; *trans*-$Fe(CO)_3(PPh_2CH_2CH_3)_2$, 36870-06-1; *trans*-$Fe(CO)_3(PPh_2Me)_2$, 40757-44-6; *trans*-$Fe(CO)_3[P(c\text{-}cy)_3]_2$, 40697-14-1.

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Oxidative Addition Reactions of Compounds of the Type (η^5-C_5Me_5)Os(CO)LR (L = CO, PMe_2Ph; R = Alkyl). The Role of Oxidized Intermediates in Electrophilic Cleavage Reactions of Osmium–Carbon σ-Bonds

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Received February 24, 1988

Compounds of the type Cp*Os(CO)LR (Cp* = η^5-C_5Me_5; L = CO, PMe_2Ph; R = Me, Et, *i*-Pr, CH_2Ph), most of them new, have been prepared and their reactions with the electrophiles CF_3CO_2H, Br_2, and $HgBr_2$ have been investigated. All of the electrophiles oxidatively add to give labile, formally osmium(IV) complexes of the type $[Cp^*Os(CO)(L)(R)(E)]^+X^-$, one of which, $[Cp^*Os(CO)(PMe_2Ph)(Me)(HgBr)]^+$, has been isolated as the PF_6^- salt. In all cases, the osmium(IV) complexes decompose in solution to give the normal products of electrophilic cleavage.

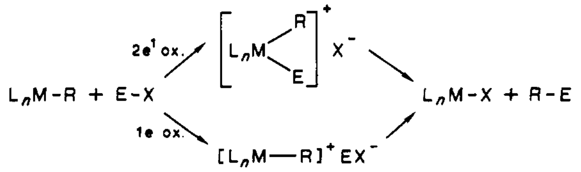
Introduction

Mechanisms of cleavage reactions of transition-metal–carbon bonds by electrophilic reagents have attracted considerable attention in recent years.[1,2] Reactions are generally of the form

$$L_nM\text{–}R + E\text{–}X \rightarrow L_nM\text{–}X + R\text{–}E \qquad (1)$$

M = transition metal; L = neutral, anionic ligands;
R = alkyl; EX = HX, X_2, CuX_2, HgX_2; X = halogen

Scheme I. S_E (Oxidative) Mechanisms



Many of the studies have involved a number of iron alkyl complexes of the type CpFe(CO)LR (L = CO, tertiary phosphine; R = alkyl),[3-9] but similar compounds of ru-

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