

MONO-SUBSTITUTION OF IRON PENTACARBONYL CATALYZED BY POLYNUCLEAR IRON CARBONYL ANIONS

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Summary

The specific formation of $LFe(CO)_4$ ($L = PPh_3, P(OPh)_3, P(OMe)_3$) can be achieved by the reaction of $Fe(CO)_5$ with L in the presence of a catalytic amount of iron carbonyl anion. A convenient synthetic procedure was developed in which the iron carbonyl anion catalyst is generated in situ. It is shown that the mechanism does not proceed by the simple cleavage of the $Fe_2(CO)_8^{2-}$ or $Fe_3(CO)_{11}^{2-}$ anions, because triphenylphosphine reacts with these anions in the absence of $Fe(CO)_5$ to produce $(PPh_3)_2Fe(CO)_3$.

Introduction

Iron pentacarbonyl is inert toward substitution with Group VA ligands except under conditions, either thermal or photochemical, which promote CO dissociation. Under these conditions yields are generally poor and a mixture of $LFe(CO)_4$ and $L_2Fe(CO)_3$ is formed [1,2]. Mono- and di-substituted iron carbonyls also are produced by ligand cleavage of Fe—Fe bonds in polynuclear species such as $Fe_3(CO)_{12}$ and $(\mu_2-H)Fe_2(CO)_8^-$ [1,3]. These synthetic routes suffer from the disadvantages of producing difficult to separate mixtures of $LFe(CO)_4$ and $L_2Fe(CO)_3$, giving low yields, or requiring long reaction times.

We have found that polynuclear iron carbonyl anions activate $Fe(CO)_5$ toward substitution. This reaction was developed into a specific, convenient and fairly high yield method for preparing $LFe(CO)_4$ from $Fe(CO)_5$, and some possible mechanisms for the reaction were explored.

Experimental

General information

Air and water were rigorously excluded by performing all reactions in Schlenk-ware under an atmosphere of purified nitrogen. All product work-ups were carried out in the air, but, since $(PhO)_3PFe(CO)_4$ decomposes slowly in air,

solutions of this product were stored and handled under nitrogen whenever possible.

Triphenylphosphine (Aldrich, 99%) was used as received; $(\text{PhO})_3\text{P}$ (Matheson, Coleman and Bell), $(\text{MeO})_3\text{P}$ (Eastman Organic Chemicals), and $\text{Fe}(\text{CO})_5$ (Strem, 99.5%) were degassed and dried over 4A molecular sieves before use. Pentane was distilled from sodium; THF was distilled under nitrogen from a deep blue solution of sodium benzophenone ketyl, and CH_3CN was distilled under nitrogen from P_2O_5 . Salts of the polynuclear anions, $[\text{Ph}_4\text{As}]_2[\text{Fe}_2(\text{CO})_8]$ and $[\text{PPN}]_2[\text{Fe}_3(\text{CO})_{11}]$ (PPN = bis(triphenylphosphine)iminium), were prepared by a variation of the general procedure given by Farmery et al. [4], and $[\text{PPN}]_2[\text{Fe}_4(\text{CO})_{13}]$ by variations of the general procedures given by Hieber and Werner [5] and Farmery et al. [4].

Progress of reactions was monitored by observing changes in the $\nu(\text{CO})$ region of the infrared spectra of reaction mixtures. All spectra were taken with a Perkin-Elmer 283 spectrophotometer using matched, 0.1 mm pathlength, sealed, NaCl solution cells. Phosphine- and phosphite-substituted products were identified by comparing their $\nu(\text{CO})$ bands and melting points (taken in open capillary tubes) with literature values as well as by elemental analysis.

One-step synthesis of $\text{Ph}_3\text{PFe}(\text{CO})_4$

In a typical preparation, 20 ml of a blue solution of sodium benzophenone ketyl in THF (prepared by adding sodium wire (approximately 0.2 g) to a 0.1 M solution of benzophenone in 100 ml dry, oxygen-free THF) was added to a mixture of 2.6 g of Ph_3P (10 mmol) and 3.5 ml of $\text{Fe}(\text{CO})_5$ (27 mmol). The blue color of the THF solution was discharged immediately on contact with $\text{Fe}(\text{CO})_5$, and $\text{Na}_2\text{Fe}_2(\text{CO})_8 \cdot X\text{THF}$ precipitated as a yellow solid. The reaction mixture was stirred and refluxed under nitrogen for 3 h. The solution quickly developed the deep red-brown color characteristic of polynuclear anions. After refluxing, volatiles were removed under reduced pressure. The remaining solid was stirred with 100 ml boiling heptane in a container open to the air until the solution color changed from red-brown to yellow. The hot solution was filtered and chilled to induce precipitation of yellow crystals, which were rinsed with pentane and dried in vacuo. The yield of $\text{Ph}_3\text{PFe}(\text{CO})_4$ was 2.96 g (69%), m.p. 198–201°C (dec.) (lit.: 201–203°C (dec.)); $\nu(\text{CO})(\text{THF})$: 2050s, 1973m, 1940vs cm^{-1} ; C and H analyses were satisfactory.

One-step synthesis of $\text{LFe}(\text{CO})_4$ ($\text{L} = (\text{MeO})_3\text{P}$, $(\text{PhO})_3\text{P}$)

The procedure was the same as that used for $\text{Ph}_3\text{PFe}(\text{CO})_4$ except that the liquid ligand (19 mmol of $(\text{MeO})_3\text{P}$ or 10 mmol of $(\text{PhO})_3\text{P}$) was added to the refluxing $\text{Fe}(\text{CO})_5$ anion solution. After refluxing, the volatiles were removed under reduced pressure, and the oily residue was purified on an F-20 alumina column (0.5 × 6 in.) using 100 to 200 ml of pentane as eluent. The product is eluted in the leading yellow band.

In the $(\text{MeO})_3\text{P}$ synthesis the product was isolated by stripping the pentane from the eluent. A total of 3.88 g (70% yield) of yellow powder was obtained, m.p.: 42–44°C (lit.: 43–43.5°C); $\nu(\text{CO})$ (pentane): 2063m, 1992m, 1963s, 1950s cm^{-1} ; C and H analyses were satisfactory.

In the $(\text{PhO})_3\text{P}$ synthesis the product was isolated by reducing the eluent

volume to about 40 ml and cooling the solution to -78°C . A total of 1.2 g (25% yield) of pale yellow powder was obtained, m.p. $66\text{--}69^{\circ}\text{C}$ (lit.: $68\text{--}69^{\circ}\text{C}$); $\nu(\text{CO})$ (pentane): $2070\text{m}, 1996\text{m}, 1961\text{s cm}^{-1}$; C and H analyses were satisfactory.

Reaction of $\text{Fe}(\text{CO})_5$ with Ph_3P in the presence of $[\text{Fe}_2(\text{CO})_8]^{2-}$, $[\text{Fe}_3(\text{CO})_{11}]^{2-}$ or $[\text{Fe}_4(\text{CO})_{13}]^{2-}$

A solution of 0.58 g of Ph_3P (2.2 mmol) and an excess of $\text{Fe}(\text{CO})_5$ (0.5 ml, 4 mmol) in 25 ml of CH_3CN was added to 0.1 g of $[\text{PPN}]_2[\text{Fe}_3(\text{CO})_{11}]$ (0.1 mmol), and the reaction mixture was stirred for 18 h under nitrogen at room temperature. The yellow precipitate was collected by filtration, washed with methanol and pentane and dried in air. The 0.48 g (51% yield) of product was identified as $\text{Ph}_3\text{PFe}(\text{CO})_4$ by melting point and IR analysis. Similar results were obtained when 0.1 g of $[\text{Ph}_4\text{As}]_2[\text{Fe}_2(\text{CO})_8]$ (0.1 mmol) was used in place of $[\text{PPN}]_2[\text{Fe}_3(\text{CO})_{11}]$.

A solution of 0.52 g of Ph_3P (2.0 mmol), 0.2 g of $[\text{PPN}]_2[\text{Fe}_4(\text{CO})_{13}]$ (0.1 mmol), and an excess of $\text{Fe}(\text{CO})_5$ (0.5 ml, 4 mmol) in 25 ml of CH_3CN reacted very slowly at room temperature but produced 0.45 g (52% yield) of $\text{Ph}_3\text{PFe}(\text{CO})_4$ after 3.5 h of refluxing. The product was isolated by crystallization from boiling heptane.

Reaction of Ph_3P with $[\text{Fe}_2(\text{CO})_8]^{2-}$, $[\text{Fe}_3(\text{CO})_{11}]^{2-}$, and $[\text{Fe}_4(\text{CO})_{13}]^{2-}$

A solution of 0.52 g of Ph_3P (2.0 mmol) in 25 ml of CH_3CN was added to 1.5 g of $[\text{PPN}]_2[\text{Fe}_3(\text{CO})_{11}]$ (0.98 mmol). The reaction mixture was stirred for 40 h under nitrogen at room temperature. The yellow precipitate, which was collected by filtration, washed with CH_3CN and pentane, and dried in air, was identified as $(\text{Ph}_3\text{P})_2\text{Fe}(\text{CO})_3$ by melting point and IR analysis. The yield of $(\text{Ph}_3\text{P})_2\text{Fe}(\text{CO})_3$ was 0.48 g (74% based on 1 $\text{L}_2\text{Fe}(\text{CO})_3$ per $[\text{Fe}_3(\text{CO})_{11}]^{2-}$); m.p. $265\text{--}266^{\circ}\text{C}$ (dec.) (lit.: 272°C (dec.)); $\nu(\text{CO})(\text{THF})$: 1887 cm^{-1} . A similar reaction between Ph_3P and $[\text{Ph}_4\text{As}]_2[\text{Fe}_2(\text{CO})_8]$ produced a 97% yield (based on 1 $\text{L}_2\text{Fe}(\text{CO})_3$ per $[\text{Fe}_2(\text{CO})_8]^{2-}$) of $(\text{Ph}_3\text{P})_2\text{Fe}(\text{CO})_3$ after 5 days of reaction.

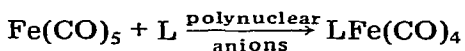
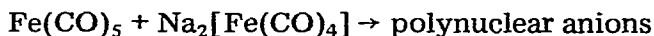
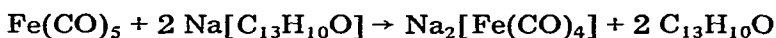
A mixture of 0.52 g of Ph_3P (2.0 mmol) and 1.7 g of $[\text{PPN}]_2[\text{Fe}_4(\text{CO})_{13}]$ (1.0 mmol) in 25 ml CH_3CN showed no sign of reaction after 1 day at room temperature but produced 0.59 g $(\text{Ph}_3\text{P})_2\text{Fe}(\text{CO})_3$ (89% yield based on 1 $\text{L}_2\text{Fe}(\text{CO})_3$ per $[\text{Fe}_4(\text{CO})_{13}]^{2-}$) after 4 h of refluxing.

Control reactions

Two sets of control reactions were performed. In one set, an excess of $\text{Fe}(\text{CO})_5$ was stirred with Ph_3P (in the absence of anions) in THF and in CH_3CN . No reaction occurred except in refluxing CH_3CN , where $\text{Ph}_3\text{PFe}(\text{CO})_4$ and $(\text{Ph}_3\text{P})_2\text{Fe}(\text{CO})_3$ were each produced in a yield of less than 5%. In the second set, an excess of $\text{Fe}(\text{CO})_5$ was stirred with $(\text{Ph}_3\text{P})_2\text{Fe}(\text{CO})_3$ in THF and CH_3CN in the presence of polynuclear anions. No conversion of $(\text{Ph}_3\text{P})_2\text{Fe}(\text{CO})_3$ to $\text{Ph}_3\text{PFe}(\text{CO})_4$ was observed in any of these reactions. All reaction mixtures were characterized by solution IR, which can detect yields of $\text{Ph}_3\text{PFe}(\text{CO})_4$ and $(\text{Ph}_3\text{P})_2\text{Fe}(\text{CO})_3$ as low as about 2%.

Discussion

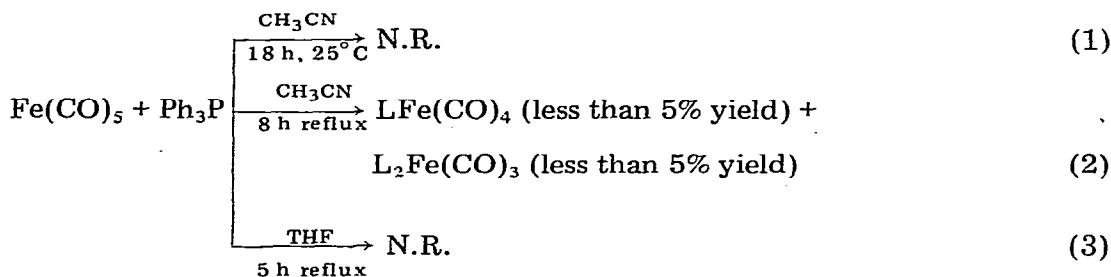
Recently several ligand cleavage reactions of polynuclear iron carbonyl anions were observed in our laboratory. These observations, along with the knowledge that the reaction of $\text{Fe}(\text{CO})_5$ with iron carbonyl anions leads to cluster anions, prompted us to try metal carbonyl anions as catalysts for ligand substitution on $\text{Fe}(\text{CO})_5$. The initial studies clearly demonstrated that the introduction of catalytic amounts of $\text{Fe}(\text{CO})_4^{2-}$, $\text{Fe}_2(\text{CO})_8^{2-}$, or $\text{Fe}_3(\text{CO})_{11}^{2-}$ activate $\text{Fe}(\text{CO})_5$ toward substitution by triphenylphosphine. The product of this reaction was found to be almost exclusively the monosubstituted compound, $\text{Ph}_3\text{PFe}(\text{CO})_4$, and therefore, convenient synthetic procedures were developed (see Experimental) which are based on the generation of the anionic catalyst in situ by reducing a small fraction of the reactant, $\text{Fe}(\text{CO})_5$, with sodium benzophenone ketyl:



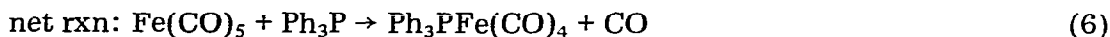
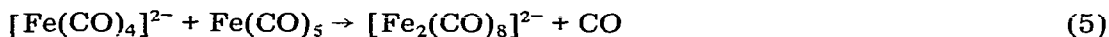
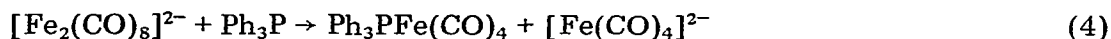
There are two other general approaches to the production of $\text{LFe}(\text{CO})_4$: the thermal or photochemical activation of $\text{Fe}(\text{CO})_5$ and ligand cleavage of $\text{Fe}-\text{Fe}$ bonds in polynuclear iron carbonyl species. The thermal methods generally produce a low-yield mixture of $\text{LFe}(\text{CO})_4$ and $\text{L}_2\text{Fe}(\text{CO})_3$ [1,2]. Strohmeier and Müller achieved substitution by irradiating $\text{Fe}(\text{CO})_5$ and ligand in a hydrocarbon solvent for an extended period of time [6]. The yields varied greatly for different ligands, and often a difficult to separate mixture of $\text{LFe}(\text{CO})_4$ and $\text{L}_2\text{Fe}(\text{CO})_3$ was produced. Ligand cleavage reactions have been carried out on both neutral and anionic hydrido complexes. Clifford and Mukherjee obtained a mixture of $\text{LFe}(\text{CO})_4$ and $\text{L}_2\text{Fe}(\text{CO})_3$ (each in a yield of about 20%) when $\text{Fe}_3(\text{CO})_{12}$ was refluxed in THF with Ph_3P , Ph_3As or Ph_3Sb [1]. Collman et al. have shown that the anionic hydride-bridged compound $(\mu_2\text{-H})\text{Fe}_2(\text{CO})_8^-$ is readily cleaved by Ph_3P in THF at 25°C to produce $\text{Ph}_3\text{PFe}(\text{CO})_4$ (22% yield), $(\text{Ph}_3\text{P})_2\text{Fe}(\text{CO})_3$ (39% yield), $\text{Fe}(\text{CO})_5$ and $[\text{HFe}(\text{CO})_4]^-$ [3]. Work done by Darensbourg et al. on the cleavage of $(\mu_2\text{-H})\text{M}_2(\text{CO})_{10}^-$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) by Group VA donor ligands suggests that substitution reactions of $\text{Fe}(\text{CO})_5$ catalyzed by LiAlH_4 or NaBH_4 may actually involve μ -hydrido polynuclear anions as intermediates [7]. In such a reaction Siegl produced $\text{Ph}_3\text{PFe}(\text{CO})_4$ in 60% yield while reducing the ratio of $\text{LFe}(\text{CO})_4$ to $\text{L}_2\text{Fe}(\text{CO})_3$ to 10 to 1 by adjusting the concentration of LiAlH_4 in a refluxing THF solution of $\text{Fe}(\text{CO})_5$ and Ph_3P [8]. Perhaps the most versatile synthesis of $\text{LFe}(\text{CO})_4$ was published by Condor and Darensbourg [9]. In their procedure, $\text{Fe}_2(\text{CO})_9$, which is generated photochemically from $\text{Fe}(\text{CO})_5$, is cleaved by L at elevated temperatures to give a mixture of products. The $\text{L}_2\text{Fe}(\text{CO})_3$ is then converted to $\text{LFe}(\text{CO})_4$ by reaction with $\text{Fe}(\text{CO})_5$ in the presence of heat and UV light, but this conversion is not always complete. Yields of $\text{LFe}(\text{CO})_4$ and $\text{L}_2\text{Fe}(\text{CO})_3$ were reported for a variety of ligands including Ph_3P (85%, 0%), $(\text{MeO})_3\text{P}$ (49%, 33%), and $(\text{PhO})_3\text{P}$ (17%, 14%). The synthetic procedure reported in this paper compares favorably with the Condor and Darensbourg method in product specificity, ease of

preparation and ease of product work-up. Although the yield of $(\text{PhO})_3\text{PFe}(\text{CO})_4$ is only fair (25%), the product is virtually uncontaminated by $[(\text{PhO})_3\text{P}]_2\text{Fe}(\text{CO})_3$.

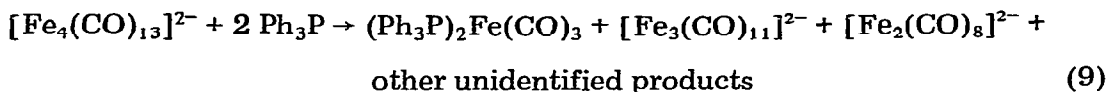
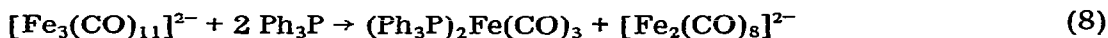
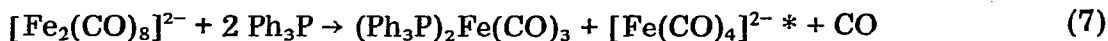
The exact mechanism by which this substitution reaction occurs is not known, but it is clear that the reducing agent (sodium benzophenone ketyl) generates some species which acts as a catalyst in the activation of $\text{Fe}(\text{CO})_5$. Reactions using $[\text{Ph}_4\text{As}]_2[\text{Fe}_2(\text{CO})_8]$, $[\text{PPN}]_2[\text{Fe}_3(\text{CO})_{11}]$ and $[\text{PPN}]_2[\text{Fe}_4(\text{CO})_{13}]$ in place of the reducing agent give the same result (CH_3CN was used as the reaction solvent since these salts are insoluble in THF). This indicates that these anions, rather than some other species generated by the reducing agent, are responsible for activating $\text{Fe}(\text{CO})_5$. Infrared analysis of the reaction mixture after reduction clearly shows the presence of $[\text{Fe}_2(\text{CO})_8]^{2-}$ ($\nu(\text{CO})$: 1922s, 1873s, 1827m cm^{-1}) which is probably converted to either $[\text{Fe}_3(\text{CO})_{11}]^{2-}$ or $[\text{Fe}_4(\text{CO})_{13}]^{2-}$ after refluxing (the similarity of the spectra of these two anions makes it difficult to distinguish between them in dilute solution; $[\text{Fe}_3(\text{CO})_{11}]^{2-}$ $\nu(\text{CO})$ in CH_3CN : 1943vs, 1913m, 1670vw(br) cm^{-1} ; $[\text{Fe}_4(\text{CO})_{13}]^{2-}$ $\nu(\text{CO})$ in CH_3CN : 2018w, 1943vs, 1680vw(br) cm^{-1}). These anions must function catalytically since they are not consumed during the course of the substitution reaction. Control reactions verify that $\text{Fe}(\text{CO})_5$ will not react with Ph_3P to a significant extent under the conditions of the catalyzed reaction when the polynuclear anions are not present.



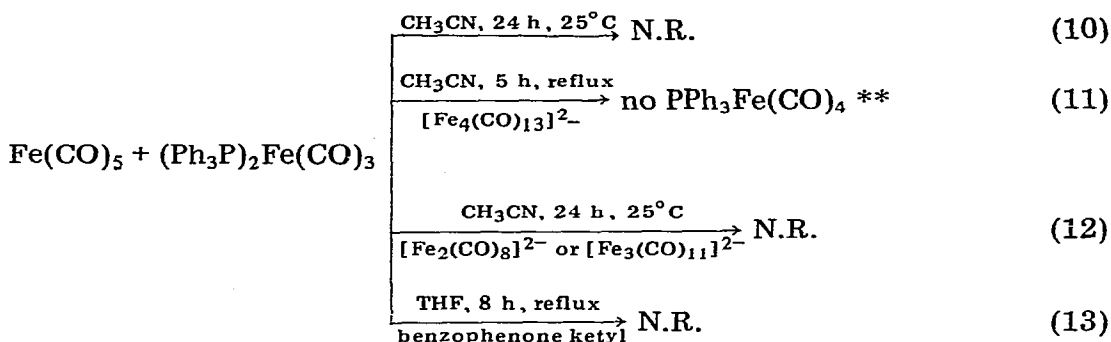
Since Group VA ligands are known to cleave Fe—Fe bonds in neutral and anionic polynuclear species, it would be reasonable to suggest that the catalytic action of the anions is due to a simple anion-cleavage, anion-regeneration cycle. Analogous cycles involving the coordinatively unsaturated intermediate $[\text{Fe}_2(\text{CO})_7]^{2-}$ and $[\text{Fe}_3(\text{CO})_9]^{2-}$ can be written for $[\text{Fe}_3(\text{CO})_{11}]^{2-}$ and $[\text{Fe}_4(\text{CO})_{13}]^{2-}$.



Reaction 5 has been reported in the literature [3,10], and the analogous cluster-building reactions for $[\text{Fe}_2(\text{CO})_7]^{2-}$ and $[\text{Fe}_3(\text{CO})_9]^{2-}$ with $\text{Fe}(\text{CO})_5$ can be envisioned. However, we have found that reaction 4 and the analogous reactions do not proceed as written. Ph_3P reacts with the polynuclear anions to produce the disubstituted and not the monosubstituted product. Thus, it is clear that



$\text{LFe}(\text{CO})_4$ does not arise from simple ligand cleavage of these polynuclear anions. The possibility of ligand interaction with some unstable structural isomers of these anions cannot, however, be ruled out. Control reactions demonstrate that $\text{Ph}_3\text{PFe}(\text{CO})_4$ from the anion catalyzed reaction does not arise from a reaction between $\text{Fe}(\text{CO})_5$ and $(\text{Ph}_3\text{P})_2\text{Fe}(\text{CO})_3$.



It would be difficult to suggest a mechanism for the anion-catalyzed substitution reactions on the basis of the experimental evidence available at this time. There are, however, several types of mechanisms which should be considered.

It is possible that $\text{Fe}(\text{CO})_5$ activation may involve the generation of labile, coordinatively unsaturated iron carbonyl radicals or radical anions. Brown demonstrated that radical chain mechanisms involving labile 17-electron species are responsible for substitution reactions of several mononuclear species [11,12]. No attempt was made in our study to detect the presence of radical species, but ESR signals have been observed for solutions of several iron carbonyl anions [3,13]. It does not seem likely that adventitious or photochemically generated radicals play a role in our $\text{Fe}(\text{CO})_5$ substitution reactions since the results of these reactions are quite reproducible and are the same whether the reaction is carried out in the presence or absence of light.

Siegl [8], Darendbourg [7], and Collman [3] all implicate hydrido carbonyl anions as the reactive species in their substitution reactions. Although it is possible that hydrido species may be present in low concentrations, differences between our results and those of Siegl and Collman make it unlikely that hydrides play a major role in our substitution reactions. (In our catalyzed reactions a weak band is observed at about 1885 cm^{-1} which may be due to

* Although $[\text{Fe}(\text{CO})_4]^{2-}$ is the expected product of the cleavage reaction, its presence was not detected in the reaction mixture. There was, however, an infrared band at 1835 cm^{-1} , which could not be assigned, and a band at 1880, which may be due to $[\text{HFe}(\text{CO})_4]^-$.

** Complete decomposition of $\text{Fe}(\text{CO})_5$ occurred, but 70% of the $(\text{PPh}_3)_2\text{Fe}(\text{CO})_3$ was recovered from the reaction.

$[\text{HFe}(\text{CO})_4]^-$ or to $(\text{Ph}_3\text{P})_2\text{Fe}(\text{CO})_3$, but there is no IR evidence for $[\text{HFe}_2(\text{CO})_8]^-$ or $[\text{HFe}_3(\text{CO})_{11}]^-$.) Under reaction conditions comparable to ours (15 mmol $\text{Fe}(\text{CO})_5$ and 10 mmol Ph_3P in 60 ml THF), Siegl found that 50 h of refluxing with 4–5 mmol LiAlH_4 were required to produce a 60% yield of $\text{Ph}_3\text{PFe}(\text{CO})_4$. In our reaction the anion to $\text{Fe}(\text{CO})_5$ ratio is less than 1 to 10, but 3 h of refluxing were sufficient to produce a 69% yield of $\text{Ph}_3\text{PFe}(\text{CO})_4$. The Ph_3P cleavage of $(\mu_2\text{-H})\text{Fe}_2(\text{CO})_8^-$ reported by Collman produced $\text{L}_2\text{Fe}(\text{CO})_3$ and $\text{LFe}(\text{CO})_4$ in a ratio of nearly 2 to 1, whereas our reaction produced only $\text{LFe}(\text{CO})_4$ (no more than a trace of $\text{L}_2\text{Fe}(\text{CO})_4$ was ever detected by IR in these reactions).

Other instances of anion-assisted substitution have been reported in the literature. Hui and Shaw found that hydroxide ion promotes the substitution of phosphine and arsine ligands for CO in $\text{M}(\text{CO})_6$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) [14]. They propose that the anion attacks a CO ligand to form the substitution labile species $[\text{M}(\text{CO})_5\text{COOH}]^-$, which can lose OH^- after substitution occurs.

The exact nature of the polynuclear anion activation of $\text{Fe}(\text{CO})_5$ toward ligand substitution is not known, although it seems likely that an unstable polynuclear intermediate or transition state is involved. Nonetheless, the reaction provides a specific, quick and convenient synthesis of $\text{LFe}(\text{CO})_4$ ($\text{L} = \text{Ph}_3\text{P}, (\text{PhO})_3\text{P},$ and $(\text{MeO})_3\text{P}$) and may well be useful for substitutions on $\text{Fe}(\text{CO})_5$ with a wide variety of ligands.

Acknowledgments

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