

MONO-SUBSTITUTION OF IRON PENTACARBONYL METAL HYDRIDE. FACILITATION

WALTER O SIEGL

Scientific Research Staff, Ford Motor Company, Dearborn, Michigan 48121 (U S A)

(Received September 25th, 1974)

Summary

Controlling the degree of substitution of iron pentacarbonyl with neutral ligands has usually been difficult. Conditions are reported whereby considerable control may be exercised over the substitution of iron pentacarbonyl, with PPh_3 , the ratio of mono-/disubstitution may be varied over a range of 50. The substituted iron carbonyl complexes were obtained by treating iron pentacarbonyl with lithium aluminum hydride or sodium borohydride in refluxing THF in the presence of a variety of neutral ligands. The method is particularly useful for a simple high yield synthesis for monosubstituted iron carbonyls.

Introduction

Controlling the degree of substitution of iron pentacarbonyl by neutral ligands has usually been difficult. Coordinatively saturated $\text{Fe}(\text{CO})_5$, undergoes substitution only under conditions (thermal or photochemical) which promote dissociation of CO, in general, yields are poor and mixtures of mono- and disubstituted carbonyl complexes are obtained [1-3]. Synthetic routes employing the more expensive polynuclear iron carbonyls also lead to mixtures of $\text{Fe}(\text{CO})_4\text{L}$ and $\text{Fe}(\text{CO})_3\text{L}_2$ [1-4]. The recent publication by Conder and Darensbourg [5] of a high yield photochemical synthesis for mono-substituted derivatives of iron pentacarbonyl prompts us to report a simple, high yield, non-photochemical route which allows considerable control over the ratio of mono- to disubstitution.

It seemed likely that a new synthetic approach might be obtained by the reversible conversion of $\text{Fe}(\text{CO})_5$ to an intermediate capable of generating a vacant coordination site under mild conditions. For example, a vacant coordination site is generated under ambient conditions by the migratory insertion of CO in the alkyl C—Fe bond of alkyl tetracarbonylferrate(0) complexes [6]. Furthermore, if conversion to the active intermediate involved nucleophilic attack on CO it might be possible to take advantage of the predicted difference in reactivity of $\text{Fe}(\text{CO})_5$ and $\text{Fe}(\text{CO})_4\text{L}$ toward nucleophilic attack on coordinated

CO to control the degree of substitution [7]. In this context hydride ion might conceivably serve as an activator for $\text{Fe}(\text{CO})_5$.

Chart and co-workers had previously employed sodium borohydride in refluxing alcohol to activate Group VI metal carbonyls toward substitution by neutral ligands, in this case the products obtained were usually disubstituted [8]. We report here that the reaction of iron pentacarbonyl with lithium aluminum hydride or sodium borohydride in tetrahydrofuran (THF) in the presence of a variety of neutral ligands can be controlled to afford high yields of $\text{Fe}(\text{CO})_4\text{L}$.

Experimental

General information All reactions were run in Schlenk-type glassware under an argon atmosphere unless noted otherwise, no precaution was taken to exclude air or moisture during the work-up and purification of $\text{Fe}(\text{CO})_4\text{L}$. Progress of the reactions was followed by IR spectroscopy using 0.1 mm CaF_2 cells and a Perkin-Elmer model 457 spectrophotometer. THF was distilled from CaH_2 and deoxygenated prior to its use, solvents for chromatography were used as obtained from commercial sources. Iron pentacarbonyl (Strem Chemical) and the liquid phosphites were distilled and stored over molecular sieve 4A. The preparation given below for $\text{Fe}(\text{CO})_4\text{As}(\text{C}_6\text{H}_5)_3$ is representative of that employed for phosphine and arsine complexes listed in Table 1 with the exception of $\text{Fe}(\text{CO})_4\text{P}(\text{CH}_2\text{CH}_2\text{CN})_3$, the preparation given for the triphenyl phosphite complex is representative of that employed with other phosphites.

Progress of the reaction and the ratio $\text{Fe}(\text{CO})_4\text{L}/\text{Fe}(\text{CO})_5$ were monitored by following changes of $\nu(\text{CO})$ in the infrared spectrum. Beer's law plots for $\text{Fe}(\text{CO})_4\text{P}(\text{C}_6\text{H}_5)_3$ and $\text{Fe}(\text{CO})_4[\text{P}(\text{C}_6\text{H}_5)_3]_2$ in CH_2Cl_2 revealed that the extinction coefficients for the E mode of $\text{Fe}(\text{CO})_4\text{L}$ and the E' mode of $\text{Fe}(\text{CO})_5$ were equal $\pm 10\%$. The product ratios reported in this work assume this relationship between extinction coefficients holds for other pairs of mono and disubstituted iron carbonyls [9].

Complexes were identified by comparison of infrared spectra and melting points with literature values and by elemental analyses for new compounds.

TABLE 1

$\text{Fe}(\text{CO})_4\text{L}$ YIELD DATA LiAlH_4 PROMOTED SUBSTITUTION

L	Reaction time ^a	Yield of $\text{Fe}(\text{CO})_4\text{L}$ ^b	Ratio ^c of $\text{Fe}(\text{CO})_4\text{L}/\text{Fe}(\text{CO})_5$
$(\text{C}_6\text{H}_5)_3\text{P}$	50	60	10
$(p\text{-CH}_3\text{C}_6\text{H}_4)_3\text{P}$	17	70	8
$(\text{NCCH}_2\text{CH}_2)_3\text{P}$	22	60	8.4
$(\text{C}_2\text{H}_5\text{O})_3\text{P}$	22	55	8
$(\text{C}_6\text{H}_5\text{O})_3\text{P}$	72	38	5
$(\text{C}_6\text{H}_5)_3\text{As}$	41	68	14
$(\text{C}_6\text{H}_5)_3\text{Sb}$	48	60	22

^a Not optimized. ^b Yield of isolated complex. reaction scale: 4.5 mmol LiAlH_4 , 10 mmol L, and 15 mmol $\text{Fe}(\text{CO})_5$ in 70 ml THF heated in a 75°C oil bath. ^c As determined from the ratio of $\nu(\text{CO})$; see Experimental section.

Preparation of $\text{Fe}(\text{CO})_5\text{As}(\text{C}_6\text{H}_5)_3$ To 4.5 mmol of LiAlH_4 and 10 mmol of triphenylarsine in ca. 60 ml of THF was added 15 mmol of iron pentacarbonyl. The reaction mixture was stirred at 25°C for 1 h, then in a 75°C oil bath until the reaction was complete (usually 12–48 h). The progress of the reaction was monitored by following changes in the carbonyl bands (IR). Upon cooling, the suspension was filtered through a short column (3") of alumina, the column was washed with methylene chloride and the combined eluant was concentrated in vacuo to afford a yellow brown solid, 4.26 g. The solid, in a minimal amount of CH_2Cl_2 , was chromatographed over neutral alumina (ca. 200 g, Brockman activity number 1). The column was eluted first with hexane to remove any unreacted arsine or $\text{Fe}(\text{CO})_5$, then with 4/1 hexane/benzene which removed the desired monosubstituted product.

Preparation of $\text{Fe}(\text{CO})_5\text{P}(\text{CH}_2\text{CH}_2\text{CN})_3$ The reaction was run as described above and the THF solution was filtered through a short (3") column of alumina. The column was eluted with acetone and the combined eluant was concentrated in vacuo to afford a tan-brown solid. Recrystallization from acetone–methanol yielded 2.20 g of off-white crystalline powder. An additional recrystallization from acetone–methanol gave pale-yellow crystals, m.p. $190\text{--}192^\circ\text{C}$ (dec.), $\nu(\text{CN})$ 2254 w, $\nu(\text{CO})$ 2058 s, 1980 s, 1946 vs cm^{-1} . Found: C, 43.38, H, 3.31, N, 12.04, $\text{C}_{13}\text{H}_{11}\text{N}_3\text{O}_5\text{PFe}$ calcd.: C, 43.24, H, 3.35, N, 11.64%.

Preparation of $\text{Fe}(\text{CO})_5\text{P}(\text{OPh})_3$ To 180 mg LiAlH_4 (4.5 mmol) in 60 ml THF was added 10 mmol of $\text{P}(\text{OPh})_3$ and 15 mmol of $\text{Fe}(\text{CO})_5$. The reaction mixture was stirred in a 75°C bath and a slow reaction was observed by infrared analysis. After 44 h of heating, an additional 70 mg of LiAlH_4 was added and heating was continued to a total of 84 h. The reaction product was worked up as indicated for $\text{Fe}(\text{CO})_5\text{AsPh}_3$. The monosubstituted product was obtained in 38% yield as pale yellow needles, m.p. $68\text{--}69^\circ\text{C}$ (lit. $68\text{--}69^\circ\text{C}$).

Preparation of $\text{Fe}(\text{CO})_5(\text{PPh}_3)_3$ To 30 mg LiAlH_4 and 5.0 mmol of PPh_3 in 7 ml THF was added 1.5 mmol $\text{Fe}(\text{CO})_5$. The mixture was stirred in a 75°C bath for 12 h at which time IR analysis indicated that all of the $\text{Fe}(\text{CO})_5$ had reacted. An additional 10 mg of LiAlH_4 was added at 12 and at 36 h. Heating was continued for a total of 50 h, at which time IR analysis indicated that most of the $\text{Fe}(\text{CO})_5\text{L}$ had been converted to $\text{Fe}(\text{CO})_5\text{L}_2$. The reaction mixture was poured into an open beaker and allowed to evaporate. The residue was extracted with THF and H_2O was added in small amounts to the filtered extract to crystallize the product. A total of 713 mg (71% yield) of yellow crystals were collected, m.p. $264\text{--}265^\circ\text{C}$ (lit. 272°C). IR analysis indicated the crystals were pure $\text{Fe}(\text{CO})_5(\text{PPh}_3)_3$.

Treatment of $\text{Fe}(\text{CO})_5$ with LiAlH_4 (A) To 10 mg LiAlH_4 in 7 ml THF was added 1.5 mmol of $\text{Fe}(\text{CO})_5$, the suspension was sampled periodically by IR. At 25°C a weak $\nu(\text{CO})$ appeared at ca. 1910 cm^{-1} which is likely the formyl complex I. On heating to 75°C a new band appeared at 1955 cm^{-1} , but its rate of appearance was much slower than that of the usual substitution reaction (Addition of PPh_3 to this solution resulted in no rapid reactions). (B) To 50 mg LiAlH_4 in 7 ml THF was added 1.5 mmol of $\text{Fe}(\text{CO})_5$. The dark red suspension was sampled immediately under argon and analyzed by IR. One-half to 2/3 of the $\text{Fe}(\text{CO})_5$ had disappeared. New bands appeared at 1968 m, 1932 m, 1910 m, and 1880 w-m cm^{-1} . The band at 1968 increased with time.

This same decomposition of $\text{Fe}(\text{CO})_5$ was observed when the reaction was carried out as described here but with 5.0 mmol of triphenylarsine or trimethyl phosphite present

Isolation of products from treatment of $\text{Fe}(\text{CO})_5$ with LiAlH_4 To 200 mg (5 mmol) of LiAlH_4 in 30 ml of THF under CO was added 2.5 mmol of $\text{Fe}(\text{CO})_5$. The grey suspension darkened in color. After one hour, IR analysis indicated partial conversion to the formyl complex, $\nu(\text{CO})$ 1940, 1912, and 1565, and a small amount of the hydrido complex, $\nu(\text{CO})$ 1880 cm^{-1} . An additional 50 mg of LiAlH_4 was added and 0.5 h later another 100 mg was added. Infrared analysis indicated that most of the $\text{Fe}(\text{CO})_5$ had reacted, in addition to unreacted $\text{Fe}(\text{CO})_5$, there were $\nu(\text{CO})$ bands at 1960 (polynuclear carbonyl), 1940 (formyl), 1912 (formyl and hydrido complexes), 1880 (hydrido), and 1565 (formyl complex). Bis(triphenylphosphine)iminium chloride [10] (1.0 g, 1.75 mmol) was added to the reaction mixture along with 15 ml of methanol. The solvents were evaporated in vacuo. The residue was extracted under argon with CH_2Cl_2 and the extract was filtered. Ether and then hexane was added to the red filtrate in small aliquots.

A crop of dark red crystals, 240 mg, was obtained on standing, in addition to IR bands associated with the bis(triphenylphosphine)iminium cation there were $\nu(\text{CO})$ (KBr) 1936 s(br), 1900 m(br), (DMF) 1925 s, 1895 m-s, and 1870 (sh) cm^{-1} . A survey of anionic polynuclear iron carbonyls reported in the literature revealed that $\text{Fe}_3(\text{CO})_{11}^{2-}$, prepared in solution (DMF) by Edgell and co-workers [11] has a $\nu(\text{CO})$ pattern 1941 s, 1931 m, 1884 w similar to that observed for the dark red crystals.

On standing in the cold, a crop of off-white crystals deposited from the filtrate, 170 mg, IR bands in addition to those associated with the large cation were $\nu(\text{CO})$ (KBr) 2000 w, 1908 m, and 1880 s cm^{-1} , identical to those reported earlier for $(\text{Ph}_3\text{P})_2\text{N}[\text{HFe}(\text{CO})_4]^-$ [6].

We cannot unequivocally establish the presence of the formyl complex I although infrared bands were observed in the appropriate regions (2000, 1935, 1910, and 1565 cm^{-1}) [12]. The formyl complex would be both a likely product from the reaction of $\text{Fe}(\text{CO})_5$ with hydride ion and a likely precursor to the hydrido complex which was also observed. Attempts to isolate the formyl complex were unsuccessful. Infrared analysis of the reaction mixture before and after the work-up procedure suggest that the formyl complex may be converted to the hydrido complex under the conditions of the work-up.

Treatment of $\text{HFe}(\text{CO})_4^-$ with L (A) To 0.21 mmol of $(\text{Ph}_3\text{P})_2\text{N}[\text{HFe}(\text{CO})_4]^-$ and 0.22 mmol of $\text{P}(\text{CH}_2\text{CH}_2\text{CN})_3$ under argon was added 20 ml of THF. The pale yellow solution was stirred and heated in a 75°C oil bath for 2.5 days without any changes in the carbonyl region of the IR spectrum being observed. LiAlH_4 (50 mg) was added and stirring was continued in the bath for an additional 2.5 days but still no conversion to $\text{Fe}(\text{CO})_5\text{L}$ was observed.

(B) To 1.5 mmol of $\text{Fe}(\text{CO})_5$ in 20 ml of THF under a CO atmosphere was added 3 mmol of LiAlH_4 , the mixture was stirred for 11 h at 25°C. IR analysis of the red solution indicated a large amount of unreacted $\text{Fe}(\text{CO})_5$ in addition to $\nu(\text{CO})$ at 1965 (sh), 1932 m, 1910 s, and 1880 m cm^{-1} . One mmol of $\text{P}(\text{CH}_2\text{CH}_2\text{CN})_3$ was added to the reaction mixture and stirring was continued at 25°C. After 2 h most of the $\text{Fe}(\text{CO})_5$ had been converted to $\text{Fe}(\text{CO})_5\text{L}$ but

the other bands were unchanged. Another 50 mg of ligand was added and stirring was continued for 14 h after which time all of the $\text{Fe}(\text{CO})_5$ had been converted to $\text{Fe}(\text{CO})_4\text{L}$ but the other $\nu(\text{CO})$ remained unchanged.

Conversion of $\text{Fe}(\text{CO})_4\text{L}$ to $\text{Fe}(\text{CO})_3\text{L}_2$ To 10 mg LiAlH_4 and 1.0 mmol of PPh_3 in 7 ml THF was added 0.5 mmol of $\text{Fe}(\text{CO})_4\text{PPh}_3$, and the reaction mixture was heated in a 75°C bath under argon. After 48 h an additional 10 mg LiAlH_4 was added and heating was continued for an additional 20 h. The reaction mixture was treated as described above, pure $\text{Fe}(\text{CO})_3\text{L}$ was isolated in 44% yield.

Results and discussion

Synthesis Iron pentacarbonyl does not react with triphenylphosphine in refluxing THF [1], but when a suspension of triphenylphosphine and lithium aluminium hydride or sodium borohydride in THF was treated with excess iron pentacarbonyl and heated, the corresponding monosubstituted iron carbonyl complex was formed in good yield. The reaction appears to be general for a variety of neutral ligands (tertiary phosphines, phosphites, arsines, and stibines), furthermore, the reaction conditions are sufficiently mild to tolerate functional groups such as nitrile in the ligand (Table 1).

Reactions were run with the neutral ligand (L) as the limiting reagent since it is frequently the limiting material economically and excess $\text{Fe}(\text{CO})_5$ is easily removed due to its volatility and ease of autoxidation to insoluble oxides. The THF solution of reaction products was filtered through a short column of alumina to remove insoluble material and then was chromatographed on alumina to give pure $\text{Fe}(\text{CO})_4\text{L}$. No attempt was made to isolate the small yield of $\text{Fe}(\text{CO})_3\text{L}_2$. Yields reported in Table 1 are for isolated products obtained via LiAlH_4 facilitated reactions, similar yields were obtained with NaBH_4 . $\text{Fe}(\text{CO})_4\text{-P}(\text{CH}_2\text{CH}_2\text{CN})_3$ (59%), $\text{Fe}(\text{CO})_4\text{AsPh}_3$ (80%).

We observed an ability to control the degree of substitution which is unique for organometallic synthesis. Factors effecting the ratio of mono- to disubstitution, reactions 1 and 2, will be discussed below.



Effect of concentration and type of metal hydride Metal hydrides were observed to be effective in a reasonably narrow concentration range, a characteristic which led us initially to underestimate the utility of sodium borohydride. The effect of a systematic variation in LiAlH_4 concentration on the substitution of $\text{Fe}(\text{CO})_5$ with PPh_3 , $\text{P}(\text{OCH}_3)_3$, and AsPh_3 is shown in Table 2. The highest ratios of mono- to disubstitution were obtained when the concentration of LiAlH_4 was of the order of 0.125 mmol LiAlH_4 /1.5 mmol $\text{Fe}(\text{CO})_5$, although at this concentration the reaction was quite slow. High ratios of mono-/disubstitution combined with optimum reaction rates (12 h versus 41 h for the conditions cited above) were obtained when 0.25 mmol LiAlH_4 /1.5 mmol $\text{Fe}(\text{CO})_5$ was used. As the relative concentration of LiAlH_4 or NaBH_4 was increased the reaction rate increased but the ratio of mono-/disubstitution decreased.

TABLE 2

EFFECT OF LiAlH_4 AND L CONCENTRATIONS ON THE PRODUCT RATIO^a

LiAlH_4 , (mmol)	L (mmol)	$\text{Fe(CO)}_4\text{L}/\text{Fe(CO)}_3\text{L}_2$ ^b
0.125	1.0 PPh_3	12
0.25	1.0	9
1.25	1.0	1.6
0.25	3.0	3.7
0.50	5.0	1.3
1.25	5.0	0.2
0.25	1.0 AsPh_3	16
0.25	3.0	16
1.25	5.0	1.1
0.50	1.0 $\text{P(OCH}_3)_3$	3.5
0.75	5.0	1.0

^a Run under argon with 1.5 mmol Fe(CO)_5 in 7 ml THF and heated in a 75°C bath. ^b Ratios were read after a constant value was attained or where L was in excess at the end of 24 h. The value reported is an average of at least two runs.

When Fe(CO)_5 and ligand were treated with higher concentrations of LiAlH_4 (e.g., 1.25 mmol LiAlH_4 /1.5 mmol Fe(CO)_5), a very rapid reaction of Fe(CO)_5 with LiAlH_4 was observed (whether or not ligand was present) which resulted in conversion of approximately half of the Fe(CO)_5 to other carbonyl products. (Accordingly, product ratios obtained at higher concentrations of LiAlH_4 were somewhat less accurate than ratios obtained at lower LiAlH_4 concentrations because of some overlap in $\nu(\text{CO})$ of products and side-products.) Yields of isolated complexes from reactions using high LiAlH_4 concentrations were lower than from reactions using lesser amounts of LiAlH_4 , probably due to this initial decomposition of the Fe(CO)_5 .

A comparison of the selectivity of LiAlH_4 and NaBH_4 as substitution promoters for Fe(CO)_5 is reported in Table 3. Sodium borohydride was found, in all cases examined, to lead to more selective formation of monosubstituted complexes. The ratios in Table 3 are consistent with our observation that the conversion of mono- to disubstituted iron carbonyl (eqn. 2) was considerably slower with NaBH_4 than it was with LiAlH_4 . (The rate of metal hydride facilitated monosubstitution (eqn. 1) appeared to be of the same order of mag

TABLE 3

COMPARISON OF LiAlH_4 AND NaBH_4 AS SUBSTITUTION PROMOTERS^a

L	$\text{Fe(CO)}_4\text{L}/\text{Fe(CO)}_3\text{L}_2$ obtained with ^b	
	LiAlH_4	NaBH_4
PPh_3	9	12
AsPh_3	14	20
$\text{P(CH}_2\text{CH}_2\text{CN)}_3$	7	>17
$\text{P(OCH}_3)_3$ ^c	3.5	7

^a Experimental conditions: 10 mg metal hydride, 1.0 mmol L and 1.5 mmol Fe(CO)_5 in 7 ml THF was heated in a 75°C bath under argon. ^b Each value represents average of at least two runs. ^c With phosphites 20 mg of metal hydride was employed.

nitude for NaBH_4 and LiAlH_4 .) Accordingly, NaBH_4 was less effective than LiAlH_4 for promoting the synthesis of disubstituted products

Effect of concentration and type of ligand The effect of neutral ligands on the ratio of mono-/disubstitution is shown in Table 2. Increasing the ratio of $\text{PPh}_3/\text{Fe}(\text{CO})_5$ favored increased disubstitution whereas increasing $\text{AsPh}_3/\text{Fe}(\text{CO})_5$ had little effect, perhaps in response to the greater steric bulk of the AsPh_3 ligand. Higher ratios of mono-/disubstitution were usually favored by the more bulky ligands AsPh_3 and SbPh_3 . Phosphites in general required a larger amount of LiAlH_4 or NaBH_4 for substitution to occur (e.g., 0.5 mmol $\text{LiAlH}_4/1.5$ mmol $\text{Fe}(\text{CO})_5$), substitution by triphenyl phosphite was noticeably slower than substitution with other ligands. Premixing the neutral ligand with LiAlH_4 had a negligible effect on both the substitution rate and the product ratio.

Promoting disubstitution The concentration effects of metal hydride and ligand were additive at least in part as shown in Table 2. Increased concentrations of both metal hydride and ligand favor disubstitution. $\text{Fe}(\text{CO})_5(\text{PPh}_3)_2$ was isolated in good yield (71%) when the larger amount of LiAlH_4 was added over a period of time. It appears likely that the disubstituted product arises via eqn. 2 since $\text{Fe}(\text{CO})_5\text{L}$ could be converted to $\text{Fe}(\text{CO})_3\text{L}_2$ under the same conditions. We have not yet succeeded in applying this sequence satisfactorily to the synthesis of unsymmetrically substituted complexes of the type $\text{Fe}(\text{CO})_3\text{LL}'$. In most cases the crystalline disubstituted iron carbonyl complexes were less soluble than the monosubstituted complexes and, therefore, the former was easily purified by recrystallization.

Observations on the mechanism Although we cannot suggest a mechanism for the substitution, certain observations are reported and discussed as they relate to a possible mechanism. Seemingly, the first possibility to be explored would be that shown in Scheme 1. $\text{Fe}(\text{CO})_5$ is susceptible to nucleophilic attack on CO by strong nucleophiles [13]. The formyl complex I and the hydride complex II are both known and I has been reported to undergo slow (at 25°C) decarbonylation (eqn. 4) to the hydride II [12]. However, several observations as cited below suggest that the hydride and formyl complexes are unlikely intermediates in the substitution reaction.

SCHEME 1



No intermediates were detected by infrared spectroscopy suggesting that the intermediates involved were quite reactive under the usual reaction conditions. In separate experiments the hydride complex II was prepared both as the isolated bis(triphenylphosphine)iminium salt and as the lithium salt in situ and

was treated in each case with $\text{P}(\text{CH}_2\text{CH}_2\text{CN})_3$. There was no conversion to $\text{Fe}(\text{CO})_5\text{L}$.

Iron pentacarbonyl fails to react with L by itself but it does react with LiAlH_4 . At the low concentrations of LiAlH_4 used to promote monosubstitution (e.g. 0.125/0.50 mmol LiAlH_4 /1.5 mmol $\text{Fe}(\text{CO})_5$), there is little reaction between the two reagents in the absence of L. If the LiAlH_4 concentration is increased (to 1.25/1.5 mmol $\text{Fe}(\text{CO})_5$), a rapid reaction takes place (even in the presence of L) in which approximately 1/2 to 2/3 of the $\text{Fe}(\text{CO})_5$ is converted to other carbonyl products. The dark red solution obtained from this reaction appeared to contain three carbonyl products in addition to unreacted $\text{Fe}(\text{CO})_5$, and we tentatively label these products as the formyl complex I, the hydrido complex II, and a polynuclear carbonyl complex (to which we ascribe the red color of the solution). Addition of a neutral ligand to the red solution and heating in a 75°C bath resulted in the conversion of unreacted $\text{Fe}(\text{CO})_5$ to $\text{Fe}(\text{CO})_5\text{L}$ but the other carbonyl products, derived from the action of LiAlH_4 on $\text{Fe}(\text{CO})_5$, remained unchanged. Thus, it appears unlikely that the hydride and formyl complexes are involved in the substitution of $\text{Fe}(\text{CO})_5$, other than as minor byproducts and that Scheme 1 as written represents an unlikely path for the substitution of iron pentacarbonyl.

This work has demonstrated the utility of LiAlH_4 and NaBH_4 for promoting the substitution of $\text{Fe}(\text{CO})_5$ by a variety of neutral ligands under relatively mild conditions. The extent of substitution can be controlled by choosing appropriate concentrations of starting materials. This simple one flask synthesis is particularly useful for the preparation of frequently hard-to-obtain monosubstituted iron carbonyl complexes.

Acknowledgement

The author acknowledges helpful and very stimulating discussion with Dr. Lee Robert Mahoney and technical assistance from Ms. J. Chen.

References

1. F.A. Cotton and R.V. Parrish, *J. Chem. Soc.* (1960) 1440.
2. A.F. Clifford and A.K. Mukherjee, *Inorg. Chem.* 2 (1963) 151; *Inorg. Syn.* 8 (1966) 185. R.L. Bennet, M.I. Bruce and F.G.A. Stone, *J. Organometal. Chem.* 38 (1972) 325.
3. W. Strohmeier and F.J. Muller, *Chem. Ber.* 102 (1969) 3613.
4. G. Bor, *Inorg. Chem. Acta*, 1 (1967) 81.
5. H.L. Conder and M.Y. Darensbourg, *J. Organometal. Chem.* 67 (1974) 93.
6. W.O. Siegl and J.P. Collman, *J. Amer. Chem. Soc.* 95 (1973) 2389.
7. D.J. Darensbourg and M.Y. Darensbourg, *Inorg. Chem.* 9 (1970) 1691.
8. J. Chatt, G.J. Leigh and N. Thankarajan, *J. Organometal. Chem.* 29 (1971) 105.
9. (a) M. Bigorne and D. Benlian, *Bull. Soc. Chim. Fr.* (1967) 4100.
(b) S.F.A. Kettle and I. Paul, *Advan. Organometal. Chem.* 10 (1972) 199.
10. J.K. Ruff and W.J. Schlentz, *Inorg. Syn.*, 15 (1974) 84.
11. W.F. Edgell, M.T. Yang, B.J. Bulkins, R. Bayer and N. Koizumi, *J. Amer. Chem. Soc.* 87 (1965) 3080.
12. J.P. Collman and S.R. Winter, *J. Amer. Chem. Soc.* 95 (1973) 4089.
13. E.O. Fischer and V. Keiner, *J. Organometal. Chem.* 23 (1970) 215.