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REACTIONS OF MONONUCLEAR TRANSITION METAL CARBONYL COMPLEXES WITH HYDRIDE DONORS. THE REDUCTION OF COORDINATED CARBON MONOXIDE AND A CONVENIENT SYNTHESIS OF FORMYLTETRACARBONYLFERRATE(0) SALTS

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Summary

The reactions of $Fe(CO)_5$, $Fe(CO)_4P(C_6H_5)_3$, $M(CO)_6$ (M = W, Mo, Cr), and $(CH_3C_5H_4)Mn(CO)_3$ with KH and several boron and aluminium hydrides were investigated. Iron pentacarbonyl was converted quantitatively to $K^+Fe(CO)_4(CHO)^-$ by hydride transfer from $KBH(OCH_3)_3$ allowing isolation of $[P(C_6H_5)_3]_2N^+ Fe(CO)_4(CHO)^-$ in 50% yield. Lower yields were obtained with $LiBH(C_2H_5)_3$, and other hydride sources gave little or no formyl product. The stability of $Fe(CO)_4(CHO)^-$ in THF was found to depend on the cation, decreasing in the order $[P(C_6H_5)_3]_2N^+ > K^+ > Na^+ > Li^+$. No formyl complexes were isolated and no spectroscopic evidence for formyl formation was observed in the reactions of the other transition metal carbonyls with several hydride sources. $Fe(CO)_4P(C_6H_5)_3$ gave $K_2Fe(CO)_4$ when treated with $KHB(OCH_3)_3$. When treated with $LiBH(C_2H_5)_3$, $W(CO)_6$ gave a mixture of $HW_2(CO)_{10}^-$ and $(OC)_5W(COC_2H_5)^-$; the latter was methylated to give the carbene complex $(OC)_5WC(OCH_3)C_2H_5$.

Introduction

A key step in certain schemes proposed for the methanization of coal involves the reduction of oxides of carbon, in particular carbon monoxide, with hydrogen using transition metal catalysts [1]. Transition metal formyl complexes have been postulated as key intermediates in several of these schemes. The economic potential of coal methanization has generated interest in the reduction of coordinated carbon monoxide in transition metal complexes and in the preparation and reactions of transition metal formyl complexes [2].

Formyl complexes have also been of interest as possible intermediates in sub-

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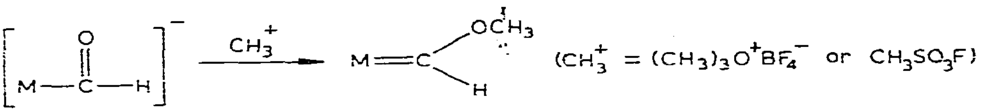
stitution and exchange reactions of transition metal carbonyl hydrides. The migration of hydride to CO to form an unsaturated formyl intermediate has been suggested as an explanation for the lability of certain transition metal carbonyl hydrides [3] although recent evidence suggests other explanations for this lability [4].

We have had an interest in anionic transition metal formyl complexes since these complexes could presumably be *O*-alkylated to produce secondary * alkoxycarbene complexes, eq. 1. There is currently no general route to secondary



$(\mathrm{CH_3^+} = (\mathrm{CH_3})_3\mathrm{O^+BF_4^-}$ or $\mathrm{CH_3SO_3F})$ (1)

carbene complexes available and no secondary alkoxycarbene complexes have been reported. Secondary alkoxycarbene complexes would be of interest on theoretical grounds and would also be convenient for mechanistic studies since the secondary carbene proton is found at very low field in the NMR [6]. Such complexes also would be of interest as potential reagents for use in organic synthesis [7].

Thus far only one transition metal formyl complex, formyltetracarbonyferrate(0), has been reported [8] **. This compound was prepared by the formylation of disodium tetracarbonylferrate(II—) with formic acetic anhydride and was isolated as the bis(triphenylphosphine)iminium salt [9]. We report here a more convenient method of preparing formyltetracarbonylferrate salts and attempts to prepare other anionic formyl complexes via the reaction of neutral transition metal carbonyls with a variety of hydride donors **.

Results and discussion

Reactions of Fe(CO)$_5$ with hydride sources

The reactions of iron pentacarbonyl with various hydride agents are summarized in Table 1. The simplest hydride source shown in Table 1, KH, did not react with iron pentacarbonyl (25° C, THF). In the presence of a crown ether (dicyclohexyl-18-crown-6) reaction occurred but no formyl product was observed.

Boron and aluminum hydrides reacted with iron pentacarbonyl to give formyltetracarbonylferrate(0) (I) in varying yields, eq. 2 and Table 1. The most ef-

$$\mathrm{Fe(CO)_5} + \mathrm{HAY_3^-} \rightarrow \underset{\text{(I)}}{\mathrm{(OC)_4Fe(CHO)^-}} + \mathrm{AY_3} \qquad (2)$$

(A = B or Al; Y = alkoxy or alkyl group)

fective of these reagents was HB(OCH$_3$)$_3^-$ which was generated in situ as the potassium salt from potassium hydride and trimethylborate [10]. NMR analysis of

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* Carbene complexes with one hydrogen attached to the carbene carbon have been termed secondary carbene complexes [5].

** Subsequent to the submission of this manuscript, a report by Casey and Newman [14] appeared describing the isolation of (OC)$_4$Fe(CHO)$^-$ and (OC)$_3$P(OC$_6$H$_5$)$_3$Fe(CHO)$^-$ and the observation by NMR of (OC)$_3$P(C$_6$H$_5$)$_3$Fe(CHO)$^-$ and (OC)$_4$LM(CHO)$^-$ (M = Cr, W; L = CO, P(C$_6$H$_5$)$_3$] formed by treatment of the appropriate metal carbonyl with KHB(O-i-Pr)$_3$.

TABLE 1

YIELDS OF $(OC)_4Fe(CHO)^-$ FROM $Fe(CO)_5$

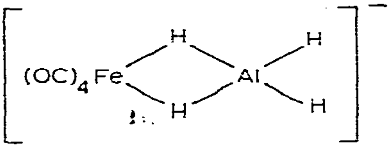
Hydride donor[a]	% Yield[b] of $(OC)_4Fe(CHO)^-$
KH	0[c]
KH (18-crown-6)	0
$KHB(OCH_3)_3$	98[d]
$LiHB(C_2H_5)_3$	69
$NaHB(C_2H_5)_3$	23[e]
$KHB(C_2H_5)_3$	65
$LiHAl(OCH_3)_3$	5
$NaHAl(OCH_2CH_2OCH_3)_2OC_2H_5$	5
$NaH_2Al(OCH_2CH_2OCH_3)_2$	9
$NaBH_4$	5[e]
$LiAlH_4$	5
$BH_3 \cdot THF$	0[c]

[a] Reactions run at 25°C in THF under N_2 with one hydride per $Fe(CO)_5$ except as noted in [c] and [e]. [b] Yields ± 10% by NMR with benzene as internal standard. Trichloroethylene was used in certain cases when aromatics in mineral oil from KH interfered with benzene standard. [c] No reaction after 48 h even with excess of hydride. [d] Isolated as $N(PPh_3)_2^+$ salt in 50% yield. [e] Incomplete reaction after 48 h even with 4 fold excess of hydride.

the crude reaction mixture with an internal standard showed a quantitative yield of formyl complex I; a 50% yield was isolated as the bis(triphenylphosphine)iminium salt.

Attempts to use potassium hydride as the reducing agent with a catalytic amount of trimethylborate present (10 or 50 mole percent) gave only a stoichiometric amount of the formyl complex (10% and 50% respectively). Even though $B(OCH_3)_3$ or $B(C_2H_5)_3$ were required on a stoichiometric basis for the formation of the formyl complex, neither was present in the isolated crystals of $[P(C_6H_5)_3]_2N^+(OC)_4Fe(CHO)^-$. The yield of the formyl complex did not depend on whether $KBH(OCH_3)_3$ or $KBH(C_2H_5)_3$ were pre-formed or were generated in situ by the addition of $B(OCH_3)_3$ or $B(C_2H_5)_3$ to a mixture of KH and $Fe(CO)_5$. Decreased yields of the formyl complex were observed when $Fe(CO)_5$ was present in excess *.

Hydride sources with more than one active hydride per molecule ($NaBH_4$, $LiAlH_4$, $NaAlH_2(OCH_2CH_2OCH_3)_2$) gave only traces of the iron formyl complex I, even when one hydride per iron was present. By contrast, the monohydride agents $KBH(OCH_3)_3$, $LiBH(C_2H_5)_3$, and $KBH(C_2H_5)_3$ could even be used in a two or three fold excess without decreasing the yield of the formyl complex. Perhaps the ineffectiveness the multihydride reducing agents is due to their ability to form chelates such as II. However, it would seem likely that the multihydride



(II)

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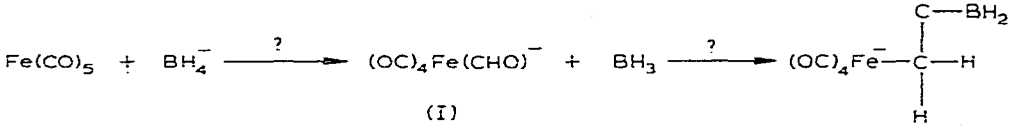
* This could be due to attack by $(OC)_4Fe(CHO)^-$ on $Fe(CO)_5$ to produce binuclear species.

reagents, like the monohydride reagents, would prefer to initially transfer hydride to $Fe(CO)_5$ to form formyl complex I, eq. 3. With the multihydride re-



$$Fe(CO)_5 + BH_4^- \xrightarrow{?} \underset{(I)}{(OC)_4Fe(CHO)^-} + BH_3 \xrightarrow{?} (OC)_4\overset{-}{Fe}-\underset{H}{\overset{C-BH_2}{C}}-H \qquad (3)$$

ducing agents, but not with the monohydride reducing agents, the boron or aluminum by-product (BH_3 in eq. 3) would be an electrophilic reducing agent which might well be effective in the further reduction of the nucleophilic formyl complex I, eq. 3. This reduction, if it were found to occur, would serve as a model for steps thought to occur in the conversion of coal to methane and methanol in the presence of transition metal catalysts [1,2].

Reactions of other metal carbonyls with hydride sources

Attempts to isolate a substituted iron formyl complex by the reaction of $Fe(CO)_4P(C_6H_5)_3$ with $KBH(OCH_3)_3$ failed *. The IR spectrum of the crude reaction mixture showed after 24 h a strong band at 1737 cm^{-1}, suggesting the formation of $Fe(CO)_4^{2-}$ or the unknown $Fe(CO)_3(PPh_3)^{2-}$. A pyrophoric grey white precipate was removed by filtration and tentatively identified as $K_2Fe(CO)_4$ [11] from its IR spectrum (1737 cm^{-1} band, no PPh_3 bands) and the characteristic IR bands of $(CO)_4Fe(COCH_3)^-$ on reaction with CH_3COCl [12]. The formation of $K_2Fe(CO)_4$ suggests that backbonding to the phosphine ligand in the substituted formyl complex is not sufficiently strong to retard phosphine dissociation and prevent hydride migration. The resulting iron hydride $HFe(CO)_4^-$ would be deprotonated by excess hydride agent to give $Fe(CO)_4^{2-}$.

Group VIB metal carbonyls, $M(CO)_6$ (M = Cr, Mo, and W), reacted with various hydride sources in THF, but no formyl complexes were isolated *. The reaction of a two-fold excess of $LiBH(C_2H_5)_3$ with $W(CO)_6$ in THF at 25°C gave a mixture of products with no $W(CO)_6$ remaining *. Attempted isolation of a tungsten formyl complex from the reaction mixture by procedures analogous to those used for isolation of the acetyl complex [13] $(OC)_5W(COCH_3)^-$ gave only $HW_2CO_{10}^-$ and $W(CO)_6$. Methylation of the reaction mixture in THF with CH_3SO_3F or in water with $CH_3O^+BF_4^-$ followed by dry column chromatography (Silica Gel, hexane, under N_2) gave $(OC)_5WC(OCH_3)C_2H_5$ **, a product presumably resulting from ethide transfer rather than hydride transfer from $LiBH(C_2H_5)_3$. No evidence was obtained for $(OC)_5WC(OCH_3)H$ formation.

(Methycyclopentadienyl)manganesetricarbonyl showed no reaction after treatment with a two-fold excess of $LiBH(C_2H_5)_3$ for one week at room temperature.

Effect of the cation on the IR spectrum and the decomposition rate of $(OC)_4Fe(CHO)^-$

The synthesis shown in eq. 3 provides an easy route for the preparation of

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* Casey and Newman observed the expected formyl complex by NMR [14].

** A mildly air sensitive, yellow oil idenitified by the similarity of its IR spectrum (in THF, cm^{-1}): 2073w 1970m(sh), 1930s; and its NMR spectrum (in C_6H_6, TMS standard, δ (ppm)): 0.60 (3H, t, J 8 Hz), 2.82 (2H, q, J 8 Hz), 3.85 (3H, s) to that of $(OC)_5WC(OCH_3)CH_3$ [13].

TABLE 2

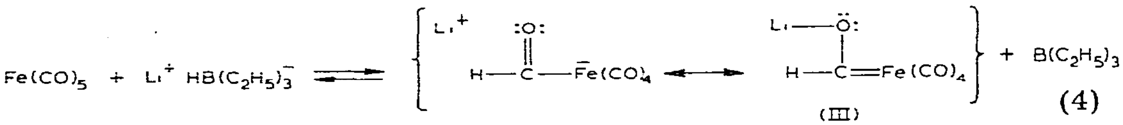
VARIATION OF FORMYL IR BAND AND HALF-LIFE OF $(OC)_4Fe(CHO)^-$ WITH CATION

Counterion	Formyl IR band (cm^{-1})	Half-life (days) [a]
Li^+	1560	11 [b]
Na^+	1575	12 [b]
K^+	1577	14 [b]
$N(PPh_3)_2^+$	1600	32 [c]

[a] Temperature −22°C. [b] In THF; one eq. $B(C_2H_5)_3$ present. [c] In CH_2Cl_2, no $B(C_2H_5)_3$ present.

$(OC)_4Fe(CHO)^-$ with several different cations. Table 2 shows the variation in the formyl band in the infrared spectrum and the rate of decomposition of the formyl complex with the cation present.

Referring back to the data in Table 1, it can be seen that iron pentacarbonyl is a stronger Lewis acid toward hydride than several common boron and aluminum Lewis acids ($B(C_2H_5)_3$, $B(OCH_3)_3$, and $Al(OCH_3)_3$). A possible factor favoring hydride residing on carbon in $Fe(CO)_5$ rather than choosing to coordinate to boron or aluminum could be the ability of the formyl group to interact with the cation through the formyl oxygen; the cation does not have such a favorable opportunity available with the hydride residing on the boron or aluminum, eq. 4. The pairing of the cation through the formyl oxygen is supported by the variation of the formyl IR frequency with the cation (Table 2). The decrease in the formyl frequency as the cation is varied in the order $PPh_3N^+ > K^+ > Na^+ > Li^+$ is consistent with the expected greater ion pairing ability of the smaller cations and the greater contribution of resonance form III to the structure with the smaller cations present. The shift to lower frequencies of the formyl C=O absorption with smaller cations is mirrored by a large shift of the formyl carbon resonance to lower field in the carbon-13 NMR [8].



$$\mathrm{Fe(CO)_5} + \mathrm{Li^+\,HB(C_2H_5)_3^-} \rightleftharpoons \left\{ \mathrm{Li^+}\ \mathrm{H{-}C({=}O){-}\overset{-}{Fe}(CO)_4} \longleftrightarrow \mathrm{H{-}C(O{-}Li){=}Fe(CO)_4}\ \text{(III)} \right\} + \mathrm{B(C_2H_5)_3} \qquad (4)$$

The iron formyl band from the crude reaction mixtures did not show a dependence on the boron or aluminum Lewis acid which remained after hydride transfer. For example, the same frequency of 1580 cm^{-1} for the formyl group was observed after the reduction of $Fe(CO)_5$ with $KHB(C_2H_5)_3$ or $KHB(OCH_3)_3$. Likewise reduction with $LiHB(C_2H_5)_3$ or $LiHAl(OCH_3)_3$ gave $Li^+(OC)_4Fe(CHO)^-$ showing a formyl band at 1560 cm^{-1}. Thus it appears that the cation rather than the neutral boron or aluminum Lewis acid is preferred for coordination with the basic formyl oxygen, eq. 5.

$$\mathrm{H{-}C(O{-}Z){=}Fe(CO)_4} + \mathrm{MY_3} \rightleftharpoons \mathrm{H{-}C(O{-}\overset{-}{M}Y_3){=}Fe(CO)_4} + \mathrm{Z^+} \qquad (5)$$

(Z = Li, Na, K ; MY_3 = $B(C_2H_5)_3$, $B(OCH_3)_3$, $Al(OCH_3)_3$)

The rate of decomposition of the formyl complex also does not seem to be sensitive to the presence of boron Lewis acids. For example, the half-life of $K^+(OC)_4Fe(CHO)^-$ was the same within experimental error with $B(OCH_3)_3$ or $B(C_2H_5)_3$ present. Likewise the rate of decomposition of $[P(C_6H_5)_3]_2N^+$ $(OC)_4Fe(CHO)^-$ was unaffected by the presence of $B(OCH_3)_3$.

It has previously been shown [8] that $(OC)_4Fe(CHO)^-$ decomposes to $(OC)_4FeH^-$ presumably by initial loss of CO to give the unsaturated complex IV followed by hydride migration to give $(OC)_4FeH^-$, eq. 6. The acceleration of the

$$(OC)_4Fe(CHO)^- \overset{-CO}{\rightleftharpoons} \underset{(IV)}{[(CO)_3Fe(CHO)^-]} \rightarrow (OC)_4FeH^- \qquad (6)$$

decomposition process by the smaller cations could be due to the increased ability of the smaller cations to ion pair through the formyl oxygen as shown in eq. 4. The resultant lowering of the electron density on the metal and decreased backbonding to the terminal carbonyls would increase their lability and the rate of decomposition, eq. 6. The ease with which the cation can be varied both in the formation reaction, eq. 2, and the decomposition reaction, eq. 6, of $(OC)_4Fe(CHO)^-$ and the convenient location of NMR (δ ~15) and IR (~1575—1600 cm^{-1}) signals of $(OC)_4Fe(CHO)^-$ make this a system well suited to mechanistic studies dealing with the effects of ion pairing in inter- and intra-molecular hydride transfer reactions.

Experimental

Infrared spectra were obtained on a Perkin—Elmer 521 IR spectrometer using 0.10 mm CaF_2 solution cells. NMR spectra were recorded on Varian EM-360 or Varian A56/60 NMR spectrometers, using benzene or trichloroethylene which had been stored over Linde 4A molecular sieves as an internal standard. All reactions, isolations, and spectral determinations were carried out under nitrogen since solutions of $(OC)_4Fe(CHO)^-$ are highly air sensitive.

$LiHAl(OCH_3)_3$ was prepared by the addition of methanol to a standard 1 *M* THF solution $LiAlH_4$ (Aldrich Chemical Co). $NaHB(C_2H_5)_3$, $NaHB(OCH_3)_3$, $KHB(OCH_3)_3$, and $KHB(C_2H_5)_3$ were generated in situ by addition of $B(C_2H_5)_3$ or $B(OCH_3)_3$, to KH or NaH [10]. $LiHB(C_2H_5)_3$ was purchased (Aldrich) as a 1 *M* THF solution or generated from LiH and $B(C_2H_5)_3$. KH was purchased as a mineral oil dispersion (Aldrich). Tetrahydrofuran was freshly distilled from sodium and benzophenone under nitrogen. Dichloromethane and ether (dry) were degassed prior to use. All other reagents were used without purification.

Half-lives of $(OC)_4Fe(CHO)^-$ salts shown in Table 2 were determined by NMR on aliquots from solutions stored in Schlenk tubes under nitrogen with glass stoppers. The procedure for the preparation of the $K^+(OC)_4Fe(CHO)^-$ solution with $B(OCH_3)_3$ present is given below. The solutions of Li^+ and Na^+ salts were prepared by the same procedure using LiH or NaH dispersions and $B(C_2H_5)_3$. The K^+ salt solution with $B(C_2H_5)_3$ present was prepared in an analogous fashion from $Fe(CO)_5$ using KH and a 1 *M* THF solution of $B(C_2H_5)_3$ (Aldrich).

Reactions of other hydride donors with $Fe(CO)_5$ and the reactions other metal carbonyls with various hydride donors were carried out by procedures similar to the procedure below for the reaction of $Fe(CO)_5$ and $KHB(OCH_3)_3$.

Reaction of $Fe(CO)_5$ with $KHB(OCH_3)_3$

Into a dry 25 ml erlenmeyer flask was placed 178 mg (1 mmol) of a 22.5% oil dispersion of KH, and a magnetic stir bar. The flask was sealed with a rubber septum and flushed with nitrogen. To this flask was added 10 ml of freshly distilled THF, 114 μl (1 mmol) of $B(OCH_3)_3$, and 134 μl,(1 mmol) of $Fe(CO)_5$ by syringe. The solution was then stirred for 10 min, 89 μl (128.5 mg) of trichloroethylene was added by syringe, as a standard, and the yield was determined by NMR.

Preparation and isolation of $[P(C_6H_5)_3]_2N^+(OC)_4Fe(CHO)^-$

Into a dry Schlenk tube was placed 575 mg (1 mmol) of bis(triphenylphosphine)iminium chloride (PPN^+Cl^-) and a magnetic stir bar. The tube was sealed with rubber septum and degassed. A THF solution of $K^+(OC)_4Fe(CHO)^-$ was prepared as described above, and after 30 min it was added through needle tubing to the PPN^+Cl^-. The solution was stirred for 1/2 h, and the solvent and residual $Fe(CO)_5$ were removed under vacuum. The brownish crystals were dissolved in a minimum amount (about 8 ml) of degassed CH_2Cl_2 and the solution was filtered. The product was precipitated with degassed ether (about 60 ml) and separated by filtration. The resulting crystals were dissolved in a minimum amount of CH_2Cl_2 (about 5 ml), diethyl ether (7 ml) was added, and the flask was stored at —20°C. Over the course of seven days 368 mg (50% yield) of yellow needles were obtained in several batches. (A small amount of ether was added to the filtrate after each collection.) The product was characterized by elemental analysis. Found: C, 66.87; H, 4.32; N, 1.88. $C_{41}H_{31}NP_2FeO_5$ calcd.: C, 66.95; H, 4.25; N, 1.90%) and by a comparison of its IR and NMR spectra with those previously reported [8].

Variation of IR spectrum and rate of decomposition with cation (Table 2)

The generation of $(OC)_4Fe(CHO)^-$ with Li^+, Na^+, and K^+ as the cation was accomplished by the use of the appropriate alkali metal hydride and a trialkylborane or borate ester prepared or purchased as noted above. The sodium salt has also been prepared by formylation of $Na_2Fe(CO)_4$ [8]. Solutions of bis(triphenylphosphine)iminium salt were prepared from the isolated salt. Half-lives for the decomposition of $(OC)_4Fe(CHO)^-$ in THF with different counterions present were determined by following the disappearance of the formyl NMR signal and assuming first order kinetics in the decomposition process.

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