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Tetracarbonylhydridoferrates, $MHFe(CO)_4$: Versatile Tools in Organic Synthesis and Catalysis

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I. Introduction

Soon after the discovery of the first transition-metal carbonyl complex $Ni(CO)_4$ by Mond et al.,[1] $Fe(CO)_5$ was observed independently by both Berthelot[2] and Mond.[3] Since that time, this easily available compound has played an important role in the development of metal carbonyl chemistry,[4,5] and its use as a reagent in chemical synthesis is now well documented.[6]

The properties of alkaline solutions of $Fe(CO)_5$ have attracted the interest of many chemists. Indeed, it was soon recognized that, in strongly alkaline solutions, $Fe(CO)_5$ can be transformed into water-soluble compounds.[7,8] These solutions have been dealt with by several authors and shown to contain iron carbonyl metalates.[9-19]

At present, two series of carbonylferrates are known,[5,20] namely, hydridocarbonylferrates and dianionic carbonylferrates:

$$HFe(CO)_4^- \quad HFe_2(CO)_8^- \quad HFe_3(CO)_{11}^- \quad HFe_4(CO)_{13}^-$$

$$Fe(CO)_4^{2-} \quad Fe_2(CO)_8^{2-} \quad Fe_3(CO)_{11}^{2-} \quad Fe_4(CO)_{13}^{2-}$$

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This review is devoted especially to the simplest hydridocarbonylferrate, $HFe(CO)_4^-$. This complex, which is isoelectronic with the well-known $HCo(CO)_4$,[21] appears as a very versatile reagent since it can behave, a priori, as a transition-metal hydride (Fe–H bond), as a nucleophile or a reductant (negative charge), and as a carbonylation reagent (carbonyl ligands). After a brief presentation of the methods of preparation of $HFe(CO)_4^-$ and its main spectroscopic properties, emphasis will be given to its use in stoichiometric reactions for organic synthesis and to its involvement in catalytic reactions. A more general review on anionic transition-metal hydrides recently appeared in the literature.[22] Some reducing properties of $HFe(CO)_4^-$ were also reviewed 10 years ago.[23]

II. Preparation Procedures

II.1. Discovery

The first observations of alkaline solutions of $Fe(CO)_5$ were made in Hieber's laboratory,[10] but the true reaction was best described by Krumholz et al. (eq 1).[9,12,14]

$$2Fe(CO)_5 + 3Ba(OH)_2 \rightarrow [Fe(CO)_4H]_2Ba + 2BaCO_3 + 2H_2O \quad (1)$$

Aqueous solutions of the potassium salt $KHFe(CO)_4$ were prepared according to eq 2.

$$Fe(CO)_5 + KOH + Ba(OH)_2 \rightarrow KHFe(CO)_4 + BaCO_3 + H_2O \quad (2)$$

Anhydrous $KHFe(CO)_4$ was isolated as a brownish, amorphous, highly hygroscopic, oxygen-sensitive substance, contaminated with some amounts of the bibasic salt $K_2Fe(CO)_4$.[14] The dissociation constants of the corresponding acid $H_2Fe(CO)_4$ in water have been estimated as $K_1 = 4 \times 10^{-5}$ and $K_2 = 4 \times 10^{-14}$. Different values have been more recently determined by the same authors:[24]

$$H_2Fe(CO)_4 \rightleftarrows H^+ + HFe(CO)_4^- \quad pK_A = 4.0\ (20\ °C) \quad (3)$$

$$HFe(CO)_4^- \rightleftarrows H^+ + Fe(CO)_4^{2-} \quad pK_A = 12.68\ (20\ °C) \quad (4)$$

II.2. Preparation Procedures

The preparation of $[M]^+[HFe(CO)_4]^-$ is known to occur either from $Fe(CO)_5$ directly or through $Na_2Fe(CO)_4$.

II.2.1. From $Fe(CO)_5$ Directly

The most straightforward method involves reaction of $Fe(CO)_5$ with an alkaline base in aqueous or alcoholic solution (eqs 5 and 6).[25-27]

$$Fe(CO)_5 + 3OH^- \rightarrow HFe(CO)_4^- + CO_3^{2-} + H_2O \quad (5)$$

$$Fe(CO)_5 + 2OH^- \rightarrow HFe(CO)_4^- + HCO_3^- \quad (6)$$

These pale yellow solutions are generally used as prepared. Although the stability of these solutions has been the subject of controversy,[5] it is my experience that they are reasonably stable, at room temperature under argon, provided that all traces of oxidizing agents are rigorously excluded. Anhydrous solutions in aprotic solvents can also be easily obtained from the above solutions.[28,29] Moreover, $[M]^+[HFe(CO)_4]^-$ (where M^+ represents large cations such as R_4N^+,[30] PPN^+,[31,32] or PPh_4^+[33]) can be isolated as solid compounds or attached to a polymer matrix via an exchange process with the chloride form of the Amberlyst A-26 resin.[34]

The deuterio derivatives $NaDFe(CO)_4$ or $[PPN][DFe(CO)_4]$ can be prepared in the same way.[27,35]

Finally, in the presence of excess base, an equilibrium (eq 7) exists, so that $HFe(CO)_4^-$ is always present, even in strongly basic solutions.[18]

$$HFe(CO)_4^- + OH^- \rightleftarrows Fe(CO)_4^{2-} + H_2O \quad (7)$$

The reaction of $Fe(CO)_5$ with a sodium alkoxide, RONa, in the corresponding alcohol has also been used to prepare $NaHFe(CO)_4$.[36,37] In this case, the presence of traces of water is probably necessary.[38]

The reaction of $Fe(CO)_5$ with $NaBH_4$ in refluxing butanol (eq 8) also leads to $HFe(CO)_4^-$, via the unstable formyl complex.[39]

$$Fe(CO)_5 + H^- \rightarrow [HC(O)Fe(CO)_4]^- \rightarrow HFe(CO)_4^- + CO \quad (8)$$

Finally, $HFe(CO)_4^-$ can be generated by reaction of $Fe(CO)_5$ with a tertiary amine in aqueous methanol under carbon monoxide pressure.[40] It is also formed, at high temperature, by the reaction of $Fe(CO)_5$ with trimethylamine in anhydrous methanol under CO/H_2 pressure.[40,41]

II.2.2. By Protonation of $Na_2Fe(CO)_4$

The preparation of the Collman's reagent, $Na_2Fe(CO)_4$, by reaction of $Fe(CO)_5$ with Na(Hg) or with benzophenone–sodium in aprotic media is a well-known reaction.[42] Careful acidification of solutions of this highly oxygen-sensitive compound by acetic or formic acid in aprotic media, followed by filtration of the sodium carboxylate, affords anhydrous solutions of $NaHFe(CO)_4$.[43] $NaDFe(CO)_4$ solutions may be prepared in a similar manner.[44]

II.2.3. Titration of $HFe(CO)_4^-$

A gravimetric titration can be performed by formation of the $[Ni(o\text{-}Phen)_3][HFe(CO)_4]$ derivative.[40]

A modification of Iwanaga's method[45] for the titration of $Co(CO)_4^-$ has been developed for the determination of $HFe(CO)_4^-$ concentrations in liquid samples. $HFe(CO)_4^-$ titrates as a 4-electron reductant against 1.00 mM methylene blue in a 50% solution of acetic acid in toluene.[43]

II.2.4. Mechanism of Formation

A great deal of interest has been devoted to the mechanism of formation of $HFe(CO)_4^-$ from reaction of $Fe(CO)_5$ with aqueous hydroxide ions.[46-54]

The first step of the reaction involves attack of the hydroxide ion on a carbonyl ligand to give a metallocarboxylic acid (eq 9).

$$Fe(CO)_5 + OH^- \rightarrow [(CO)_4FeCO_2H]^- \quad (9)$$

The mode of decarboxylation of this intermediate has been a controversial subject for some time, but now it seems to be generally accepted that the reaction proceeds via the dianion $[(CO)_4FeCO_2]^{2-}$ (eq 10).[51,52]

Although the transient generation of $[Fe(CO)_4]^{2-}$ has not been observed spectroscopically, this species has

$$[(CO)_4FeCO_2H]^- \xrightarrow[-H_2O]{OH^-} [(CO)_4FeCO_2]^{2-} \xrightarrow[-CO_2]{} [Fe(CO)_4]^{2-} \xrightarrow{H_2O} [HFe(CO)_4]^- \quad (10)$$

recently been trapped by reactions with CH_2X_2 during the treatment of $Fe(CO)_5$ with NaOH under phase-transfer conditions.[53,54]

III. Main Structural and Spectroscopic Properties

III.1. Structure

Smith and Bau have determined the X-ray crystal structure of the $HFe(CO)_4^-$ anion as its bis(triphenylphosphine)iminium derivative.[55] It appears as a distorted trigonal bipyramid with the hydrogen atom in an axial position (Fe–H = 1.57 (12) Å). The equatorial carbonyl ligands are bent toward the hydrogen atom (C_{ax}–Fe–C_{eq} = 99.1°). Calculation within a MINDO framework has shown that this bending is due to increased Fe–C bond strength in the axial carbonyl ligand as the bending occurs.[56]

III.2. Spectroscopic Properties

III.2.1. Infrared, Raman, and Mössbauer Spectra

The IR spectrum of $HFe(CO)_4^-$ has been described in a variety of solvents and with a variety of associated cations.[32,35,57,58] According to a C_{3v} symmetry, $HFe(CO)_4^-$ exhibits three absorption bands: a weak band near 2000–2010 cm^{-1} ($A_1^{(2)}$ band), a shoulder near 1910–1930 cm^{-1} ($A_1^{(1)}$ band), and a strong band in the 1880–1900-cm^{-1} region (E band).[32] The Fe–H band is obscured by the more intense ν_{CO} absorptions.[35] The difference in the spectral properties of $HFe(CO)_4^-$ with the nature of the associated cation M^+ has been rationalized in terms of ion-pairing phenomena.[32]

The Mössbauer[58] and Raman[59] spectra of $HFe(CO)_4^-$ have also been reported.

III.2.2. NMR Spectra

The ^1H NMR spectra of all the hydridocarbonylferrates have been reported.[22] For $NaHFe(CO)_4$, the proton chemical shift is −8.74 ppm (THF solution) and this complex is distinguishable from $NaHFe_2(CO)_8$ (δ −8.47) or from $NaHFe_3(CO)_{11}$ (δ −14.87) under the same conditions.[44]

The ^{13}C NMR spectrum of $[PPN]^+[HFe(CO)_4]^-$ in CD_2Cl_2 shows a signal at 220.8 ppm for the average carbonyl chemical shift.[60] This signal appears in the same low-field range (as compared to 203.2 ppm for $H_2Fe(CO)_4$) as those for $[Fe(CO)_4Me]^-$ and $[Fe(CO)_4C(O)Me]^-$.[61]

IV. Stoichiometric Reactions

IV.1. Reactions with Carbon–Carbon Double Bonds

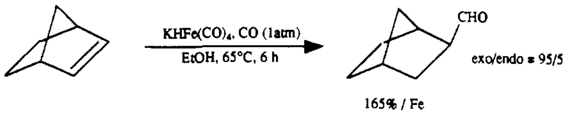
IV.1.1. Simple Olefins

IV.1.1.1. Isomerization. Alkaline solutions of $Fe(CO)_5$ slowly isomerize terminal alkenes to internal ones. For example, when 1-hexene is shaken with such a solution for 24 h at room temperature, 90% is isomerized to 2- and 3-hexenes.[17] The isomerization–deuteration of 1-butene with $DFe(CO)_4^-$ has also been studied. The results confirmed that, at least at room temperature, the $HFe(CO)_4^-$-promoted isomerization of alkenes is slower than with solutions of Rh, Pd, or Pt compounds.[62]

IV.1.1.2. Reduction. Watanabe et al. initially reported that $KHFe(CO)_4$ was not active in the reduction of monoolefins in ethanol at 30 °C, regardless of whether the atmosphere was nitrogen, carbon monoxide, or hydrogen.[28] However, they later showed that $KHFe(CO)_4$ does react with 1-pentene and 1-hexene at higher temperatures.[63] At 60 °C, both olefins are slowly reduced to the corresponding alkane with the side formation of ≤1% ethyl caproate and ethyl enanthate, respectively (eq 11).

$$C_4H_9CH{=}CH_2 + KHFe(CO)_4 \xrightarrow[60\ °C,\ 25\ h]{EtOH,\ CO\ (1\ atm)} C_6H_{14} + \underset{<1\%}{C_6H_{13}COOEt} \quad (11)$$

IV.1.1.3. Carbonylation. As shown above, the carbonylation of simple alkenes by $HFe(CO)_4^-$ itself does not succeed. This observation was confirmed by Pettit et al. in the case of ethylene.[46] However, a recent publication from our laboratory has shown that $KHFe(CO)_4$ can effect the stoichiometric hydroformylation of a strained olefin, namely norbornene, under very mild conditions and with a very high stereoselectivity (eq 12).[64] The reaction can be achieved under an argon atmosphere, but higher reaction rates and yields are obtained under a carbon monoxide atmosphere.

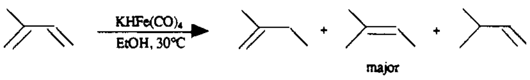


(12)

This one-step, highly stereoselective synthesis of *exo*-norbornanecarboxaldehyde competes very favorably with the previously reported stereoselective methods.[65]

IV.1.2. Conjugated Olefins

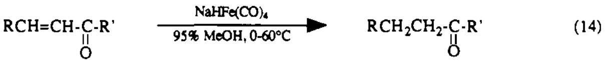
IV.1.2.1. Reduction. IV.1.2.1.1. Reduction of 1,3-Dienes. The reaction of $KHFe(CO)_4$ with isoprene has been studied by Watanabe et al.[28]



(13)

For reactions performed under a nitrogen atmosphere, the overall yield of monoolefins reached 100% with respect to iron. Under a carbon monoxide atmosphere, yields up to 200%/iron were obtained by a very slow reaction (12 days). In addition, the relative distribution of the three monoolefins strongly depended on experimental conditions. The authors also showed that $KHFe(CO)_4$ was not a catalyst for the hydrogenation of 1,3-dienes under hydrogen pressure.[28]

IV.1.2.1.2. Reduction of α,β-Unsaturated Carbonyl Compounds. The possible use of $Fe(CO)_5$ in basic medium for the reduction of α,β-unsaturated ketones (eq 14) has been disclosed by Noyori et al.[27] Although



$$RCH{=}CH\text{-}\underset{\displaystyle O}{\overset{\|}{C}}\text{-}R' \xrightarrow[95\%\ MeOH,\ 0\text{-}60°C]{NaHFe(CO)_4} RCH_2CH_2\text{-}\underset{\displaystyle O}{\overset{\|}{C}}\text{-}R' \quad (14)$$

the exact nature of the reducing agent was not clear at

TABLE I. Reduction of α,β-Unsaturated Carbonyl Compounds with $NaHFe(CO)_4$[27]

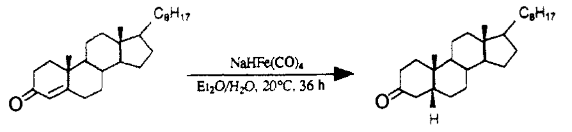
substrate	reactn temp, °C	reactn time, h	product	yield, %
benzalacetone	20	12	benzylacetone	>98
benzalacetophenone	20	12	benzylacetophenone	>98
crotonophenone	0	3	butyrophenone	>98
methyl vinyl ketone	0	3	ethyl methyl ketone	>98
mesityl oxide	60	24	isobutyl methyl ketone	96
2-cyclohexenone	20	10	cyclohexanone	96
2-methyl-2-cyclohexenone	60	24	2-methylcyclohexanone	35
3-methyl-2-cyclohexenone	60	24	3-methylcyclohexanone	52
2-cyclooctenone	20	12	cyclooctanone	>98
crotonaldehyde	0	2	butyraldehyde	>98
cinnamaldehyde	20	12	3-phenylpropionaldehyde	98
methyl cinnamate	20	48	methyl 3-phenylpropionate	90
dimethyl maleate	0	12	dimethyl succinate	96
dimethyl fumarate	0	12	dimethyl succinate	92

that time, it has been shown later by Collman et al. that the reagent used by Noyori was relatively pure $NaHFe(CO)_4$.[44]

α,β-Unsaturated ketones, aldehydes, esters and lactones are selectively reduced in high yields under mild conditions. Some selected examples are reported in Table I.

The reaction of $KHFe(CO)_4$ with an excess of ethyl acrylate in ethanol has been thoroughly studied in our laboratory. It has been found that the reduction to ethyl propionate exceeds the stoichiometry with respect to iron (270%), even under an argon atmosphere. However, no catalytic process is involved in this reaction which occurs, in a second step, by reduction of a $Fe(CO)_4$(acrylate) complex under the action of potassium ethoxide in ethanol.[66]

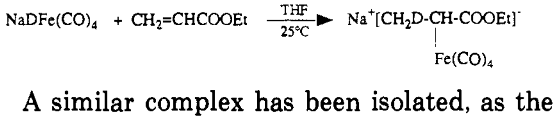
With regard to the stereochemistry of the reduction, 4-cholesten-3-one is selectively converted into coprostanone with a cis stereochemistry at the A/B ring junction (eq 15).[27]



(15)

The use of $DFe(CO)_4^-$ appears as a convenient way to introduce, specifically, deuterium at the β-position of a carbonyl group (Scheme I).[27]

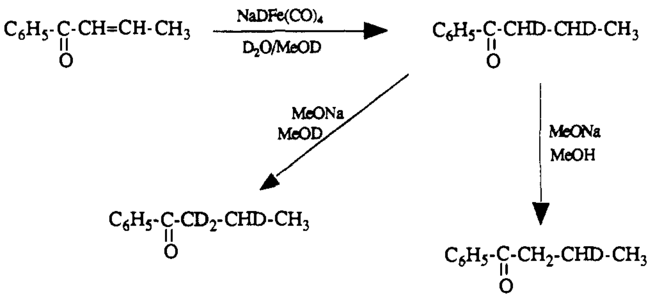
From a mechanistic point of view, Collman et al. have shown that the addition of $NaDFe(CO)_4$ to ethyl acrylate *in THF* (eq 16) is fully regioselective and irreversible.[44]



$$\mathrm{NaDFe(CO)_4 + CH_2{=}CHCOOEt \xrightarrow[25^\circ C]{THF} Na^+[CH_2D\text{-}\underset{\textstyle Fe(CO)_4}{\underset{|}{C}H}\text{-}COOEt]^-} \qquad (16)$$

A similar complex has been isolated, as the PPN^+ salt, from the reaction of ethyl acrylate with $KHFe(CO)_4$ in ethanol and its structure determined by X-ray diffraction.[67]

SCHEME I

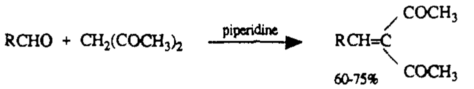


Collman et al. have confirmed[44] the previous observation of Watanabe et al.[68] that the addition of $HFe(CO)_4^-$ to ethyl acrylate *in THF* is inhibited by at least 100-fold by a carbon monoxide atmosphere. This observation has led both groups to suggest a dissociative mechanism (eq 17).

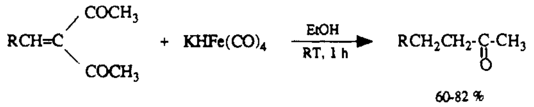
$$HFe(CO)_4^- \rightleftarrows HFe(CO)_3^- + CO \qquad (17)$$

However, the mechanism of addition of $HFe(CO)_4^-$ to the C=C double bond of α,β-unsaturated compounds seems to be strongly dependent on the nature of the solvent. Indeed, it has been shown that, in ethanol, the reduction of ethyl acrylate by $KHFe(CO)_4$ is not inhibited by carbon monoxide, even under 20 bar of pressure. A radical or concerted process has been suggested.[66]

A surprising reaction was observed when $KHFe(CO)_4$ was allowed to react with Knoevenagel condensates.[69] Indeed, a reductive deacylation was observed (eq 19).



$$\mathrm{RCHO + CH_2(COCH_3)_2 \xrightarrow{piperidine} \underset{60\text{-}75\%}{RCH{=}C(COCH_3)_2}} \qquad (18)$$

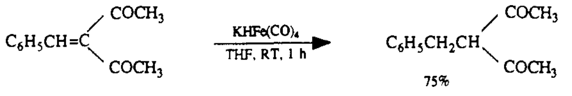


$$\mathrm{RCH{=}C(COCH_3)_2 + KHFe(CO)_4 \xrightarrow[RT,\ 1\ h]{EtOH} \underset{60\text{-}82\ \%}{RCH_2CH_2\text{-}\underset{\|}{\overset{}{C}}\text{-}CH_3}} \quad (\text{C=O}) \qquad (19)$$

R = alkyl, aryl, furfuryl

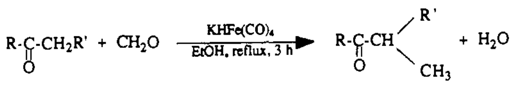
The overall reaction appears to be of interest as it may be useful for the synthesis of methyl ketones with three carbon atoms more than the starting aldehyde.

The nature of the solvent plays an important role in the reaction. Indeed, in THF or acetone, the expected reduction product is obtained (eq 20).[70]



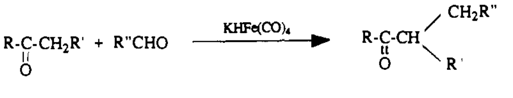
$$\mathrm{C_6H_5CH{=}C(COCH_3)_2 \xrightarrow[THF,\ RT,\ 1\ h]{KHFe(CO)_4} \underset{75\%}{C_6H_5CH_2CH(COCH_3)_2}} \qquad (20)$$

The α,β-unsaturated carbonyl derivative to be reduced can be generated in situ from a carbonyl compound and formaldehyde. The overall reaction results in the methylation of the carbonyl derivative with formaldehyde (eq 21).[71] Depending on the amount of formaldehyde, mono- or dimethylated derivatives may be obtained. Selected examples are reported in Table II.



$$\mathrm{R\text{-}\underset{\underset{\textstyle O}{\|}}{C}\text{-}CH_2R' + CH_2O \xrightarrow[EtOH,\ reflux,\ 3\ h]{KHFe(CO)_4} R\text{-}\underset{\underset{\textstyle O}{\|}}{C}\text{-}CH(R')(CH_3) + H_2O} \qquad (21)$$

The reaction has been further extended to the alkylation by other aldehydes (eq 22).[36] Some examples are given in Table III.



$$\mathrm{R\text{-}\underset{\underset{\textstyle O}{\|}}{C}\text{-}CH_2R' + R''CHO \xrightarrow{KHFe(CO)_4} R\text{-}\underset{\underset{\textstyle O}{\|}}{C}\text{-}CH(CH_2R'')(R')} \qquad (22)$$

TABLE II. Reaction between $KHFe(CO)_4$, Formaldehyde, and a Carbonyl Compound[71]

carbonyl compd	product	yield, %
acetophenone[a]	propiophenone	70
	isopropyl phenyl ketone	20
acetophenone[b]	isopropyl phenyl ketone	90
propiophenone	isopropyl phenyl ketone	85
cyclohexanone[a]	2-methylcyclohexanone	60
	2,6-dimethylcyclohexanone	15
cyclohexanone[b]	2,6-dimethylcyclohexanone	70
benzyl methyl ketone	3-phenylbutan-2-one	80
dodecanal	2-methyldodecanal	55

[a] Ketone:CH_2O = 1. [b] Ketone:CH_2O = 0.5.

TABLE III. Reaction between $KHFe(CO)_4$, an Aldehyde, and a Carbonyl Compound[36]

carbonyl compd	aldehyde	product	yield, %
acetophenone	acetaldehyde	1-phenylbutan-1-one	35
deoxybenzoin	acetaldehyde	1,2-diphenylbutan-1-one	37
butyraldehyde	butyraldehyde	2-ethylhexanal	60
acetone	benzaldehyde	1-phenylbutan-3-one	70
butan-2-one	benzaldehyde	1-phenylpentan-3-one	70
octan-2-one	benzaldehyde	1-phenylnonan-3-one	60
cyclohexanone	benzaldehyde	2-benzylcyclohexanone	75
		2,6-dibenzylcyclohexanone	10
acetophenone	benzaldehyde	1,3-diphenylpropan-1-one	80

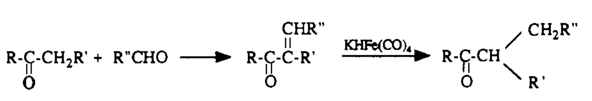
TABLE IV. Reaction of $KHFe(CO)_4$ with Aldehydes and Active Methylene Compounds[36]

methylene compd	aldehyde	product	yield, %
diethyl malonate	formaldehyde[a]	diethyl methylmalonate	72
phenylacetonitrile	formaldehyde[a]	2-phenylpropionitrile	67
phenylacetonitrile	benzaldehyde	2,3-diphenylpropionitrile	75
ethyl cyanoacetate	benzaldehyde	benzylcyanoacetic acid	90
ethyl acetoacetate	benzaldehyde	1-phenylbutan-3-one	50
diethyl malonate	benzaldehyde	diethyl benzylmalonate	40

[a] Aqueous 40% solution.

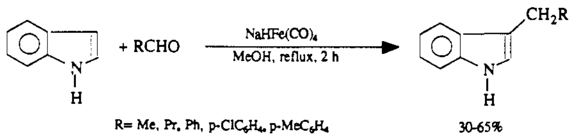
The same reaction has also been applied to the alkylation of active methylene compounds (Table IV).[36]

The suggested reaction scheme involves the condensation of the aldehyde with the carbonyl (or active methylene) compound, catalyzed by the basic medium, to give the corresponding α,β-unsaturated compound intermediate, which is irreversibly reduced by $KHFe(CO)_4$ (eq 23) as previously described (α,β-unsaturated nitriles are reduced in a similar manner).[36]



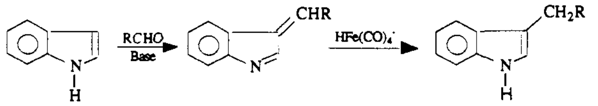
$$R\text{-}C(=O)\text{-}CH_2R' + R''CHO \longrightarrow R\text{-}C(=O)\text{-}C(=CHR'')\text{-}R' \xrightarrow{KHFe(CO)_4} R\text{-}C(=O)\text{-}CH(CH_2R'')(R') \quad (23)$$

IV.1.2.1.3. Reductive Alkylation of Indoles. Indoles can be reductively alkylated (eq 24) by the same procedure as that used for the alkylation of carbonyl compounds.[37]



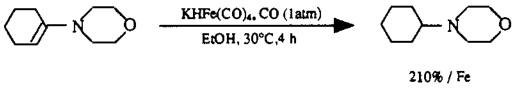
(24)

The proposed mechanism involves the formation of 3-alkylidene- (or arylidene-) indolenines, followed by irreversible reduction with $MHFe(CO)_4$ (eq 25).[37]



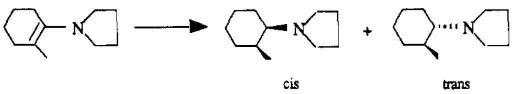
(25)

IV.1.2.1.4. Reduction of Enamines. The reaction of enamines with ethanolic solutions of $KHFe(CO)_4$, $KHFe_2(CO)_8$, and $KHFe_3(CO)_{11}$ has been studied.[72,73] These three reagents were shown to reduce enamines at 30 °C with absorption of carbon monoxide to give the corresponding saturated tertiary amines, e.g., eq 26.



(26)

The reaction also proceeds under a nitrogen atmosphere, but the yield does not exceed 100% with respect to iron. The authors have observed that the reduction of the pyrrolidine enamine of 2-methylcyclohexanone gives a different cis to trans ratio of *N*-(2-methylcyclohexyl)pyrrolidine (eq 27) and that this ratio was characteristic of the hydridocarbonylferrate used.[73]



(27)

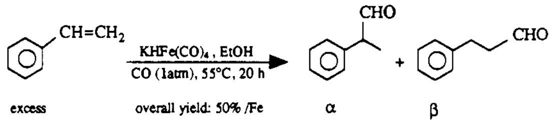
On the basis of careful examination of the rate of formation of the tertiary amines, of the variation of the cis to trans ratio with time, and of the absorption of carbon monoxide with time, the reaction mechanism is thought to involve reduction of iminium salts (eqs 28 and 29).

$$R_2NCH{=}CHR' + H^+ \text{ (moist ethanol)} \rightarrow R_2N^+{=}CHCH_2R' \quad (28)$$

$$R_2N^+{=}CHCH_2R' + HFe_x(CO)_y^- \rightarrow R_2NCH_2CH_2R' + \text{“}Fe_x(CO)_y\text{”} \quad (29)$$

Since the reduction by $KHFe(CO)_4$ is more than stoichiometric, a second reducing species must be generated from "$Fe_x(CO)_y$", carbon monoxide, and a hydroxide ion. It has been proposed that the second reducing species is not $HFe(CO)_4^-$, but rather $HFe_2(CO)_8^-$ or $HFe_3(CO)_{11}^-$.[73]

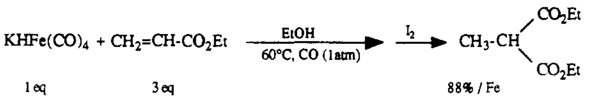
IV.1.2.2. Carbonylation. IV.1.2.2.1. Stoichiometric Hydroformylation of Styrene. The reaction of styrene with $KHFe(CO)_4$ in ethanol yields a mixture of 2- and 3-phenylpropanal (eq 30).[63]



(30)

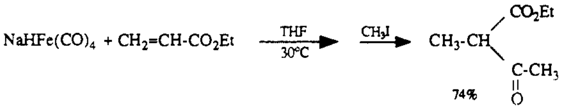
The α-isomer is formed predominantly (α:β = 79:21). As it was shown that isomerization between the two isomeric acylferrate intermediates was probably not significant, the ratio of these isomeric aldehydes was considered to correspond to the direction of the addition of $HFe(CO)_4^-$ to styrene.[63] The authors suggested that the aldehydes were formed in situ by the reaction of $KHFe(CO)_4$ with the acylferrate intermediates, a possibility that was actually shown later to occur.[74]

IV.1.2.2.2. Functionalization of Ethyl Acrylate. As previously mentioned, $HFe(CO)_4^-$ regioselectively adds to ethyl acrylate in THF (eq 16). Contrary to the reaction with styrene, the corresponding alkylferrate does not lead spontaneously to carbonylation products, even under carbon monoxide pressure.[66] Carbonylation occurs only upon reaction with iodine (eq 31) or with reactive alkyl halides (eq 32).[63,68]



$$KHFe(CO)_4 + CH_2{=}CH{-}CO_2Et \xrightarrow[60°C,\ CO\ (1\,atm)]{EtOH} \xrightarrow{I_2} CH_3{-}CH(CO_2Et)_2 \quad (31)$$

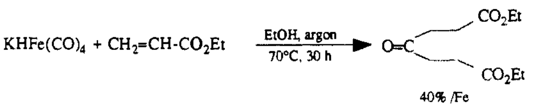
1 eq 3 eq 88% / Fe



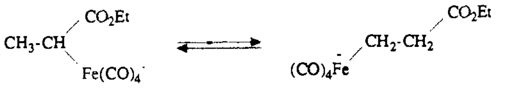
$$NaHFe(CO)_4 + CH_2{=}CH{-}CO_2Et \xrightarrow[30°C]{THF} \xrightarrow{CH_3I} CH_3{-}CH(CO_2Et)(C(=O){-}CH_3) \quad (32)$$

74%

The reaction of $KHFe(CO)_4$ with an *excess* of ethyl acrylate in ethanol has recently been shown to be more complicated than previously described.[66] Indeed, besides the expected reduction product, ethyl propionate, a carbonylation product, diethyl 4-oxopimelate, was formed in 40% yield with respect to iron, whether the atmosphere was carbon monoxide or argon (eq 33).



This result has been rationalized[66] in terms of a slow isomerization of the α-alkylferrate to its β-isomer (eq 34), followed by reaction with excess ethyl acrylate, according to a previously described mechanism involving two sequential migratory–insertion steps.[75]



IV.2. Reactions with Carbon–Carbon Triple Bonds

IV.2.1. Unactivated Alkynes

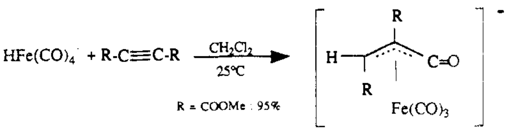
The first reaction of aqueous basic $Fe(CO)_5$ solutions with acetylene was reported by Reppe et al.[15] In addition, these authors isolated a complex formulated as $Fe_2C_{10}H_4O_8$, but no structure was given. However, Wender et al. reported later that this complex could also be obtained from the reaction of $NaHFe(CO)_4$ with acetylene (eq 35).[19,76]

$$NaHFe(CO)_4 + C_2H_2 \xrightarrow[(2)\ H_3O^+]{(1)\ H_2O,\ room\ temp,\ 1\ atm,\ 9\ h} \underset{71\%}{Fe_2C_{10}H_4O_8} \quad (35)$$

Such complexes are now known to occur with different alkynes, and they are believed to have structures similar to that shown in Figure 1.[77,78]

IV.2.2. Activated Alkynes

In aprotic solvents, $HFe(CO)_4^-$ reacts with activated acetylenic compounds such as dimethyl acetylenedicarboxylate by trans addition of the hydride to the acetylenic bond (eq 36).[31,79]



Since this reaction is not inhibited by a carbon monoxide atmosphere, it has been suggested that the active species may be different from the hydridotricarbonylferrate ($HFe(CO)_3^-$) species, which is proposed for the addition of $HFe(CO)_4^-$ to ethyl acrylate in THF.[68] The reaction is not inhibited by radical scavengers, such as duroquinone, so that the mechanism of addition is not clearly understood.[31]

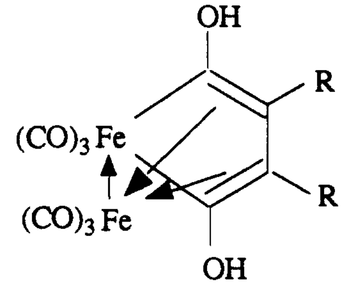


Figure 1.

IV.3. Reactions with Carbonyl and Thiocarbonyl Groups

IV.3.1. Reaction with Ketones and Aldehydes

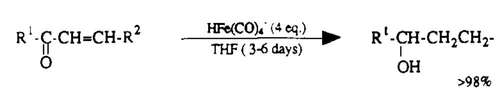
Wender et al. were the first to recognize that, under the conditions of the catalytic conversion of an olefin to the next higher alcohol (see Section V), the reaction proceeds first through a hydroformylation step followed by the reduction of the aldehyde to the corresponding alcohol.[17] As evidence, they showed that benzaldehyde is very slowly reduced to benzyl alcohol under ambient conditions (eq 37).[18]

$$C_6H_5CHO + NaHFe(CO)_4 \xrightarrow[120\ h]{H_2O} \underset{33\%/Fe}{C_6H_5CH_2OH} \quad (37)$$

Moreover, it is generally understood that when $HFe(CO)_4^-$ is associated with an alkali metal cation, PPN^+, or a tetraalkylammonium cation, it does not react with carbonyl compounds.[80,81] However, some significant activity has been observed by Marko that involves the reduction of aldehydes with $HFe(CO)_4^-$ associated with the triethylammonium, Et_3NH^+, cation (eq 38).[81] Ketones, on the other hand, are not reduced under these conditions.

$$3RCHO + 4[Et_3NH^+HFe(CO)_4^-] \xrightarrow[25\ °C]{EtOH} 3RCH_2OH + Fe(CO)_5 + [Et_3NH^+HFe_3(CO)_{11}^-] + 3Et_3N \quad (38)$$

In agreement with the above results and as indicated previously, $KHFe(CO)_4$ reacts with α,β-enones to give the corresponding saturated ketone,[27] which does not undergo further reduction. However, it has been found by Yamashita et al. that, *in THF*, $KHFe(CO)_4$ can effect the slow reduction of α,β-unsaturated ketones to the corresponding saturated alcohols (eq 39).[82]

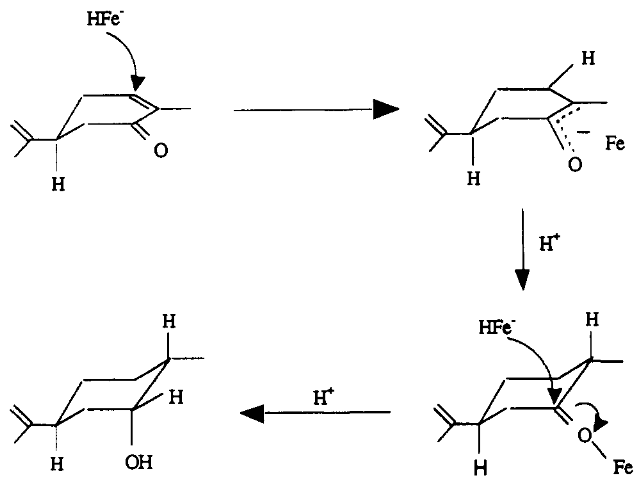


$$R^1{-}C(=O){-}CH{=}CH{-}R^2 \xrightarrow[THF\ (3\text{-}6\ days)]{HFe(CO)_4^-\ (4\ eq.)} \underset{>98\%}{R^1{-}CH(OH){-}CH_2CH_2{-}R^2} \quad (39)$$

This reaction proceeds stereospecifically. Indeed (+)- and (−)-carvone gave exclusively (−)- and (+)-neodihydrocarveol, respectively. The proposed reaction mechanism is given in Scheme II.

Finally, it has been recently reported that $[PPN^+][HFe(CO)_4^-]$ is capable of reducing ketones and aldehydes under acidic conditions (CF_3CO_2H in refluxing THF with a 3:3:2 mole ratio of $HFe(CO)_4^-$, CF_3CO_2H, and organic substrate).[83] However, the author is

SCHEME II[a]



[a] HFe⁻ = $HFe(CO)_4^-$.

TABLE V. Reduction of Organosulfur Compounds with $HFe(CO)_4^-$ in DME[84]

substrate	product	yield, %
$(C_6H_5)_2CS$	$(C_6H_5)_2CH_2$	60
$(4\text{-}CH_3C_6H_4)_2CS$	$(4\text{-}CH_3C_6H_4)_2CH_2$	61
$(4\text{-}CH_3OC_6H_4)_2CS$	$(4\text{-}CH_3OC_6H_4)_2CH_2$	77
adamantanethione	adamantane	74
$CH_3CSNHC_6H_5$	$C_2H_5NHC_6H_5$	51

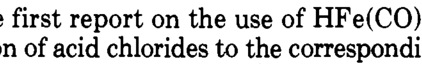
TABLE VI. Reduction of Acid Chlorides by $[Me_4N]^+[HFe(CO)_4]^-$[30]

acid chloride	reactn time, h	aldehyde yield, %
acetyl chloride	3.0	100
isobutyryl chloride	1.75	99
pivaloyl chloride	1.5	80
benzoyl chloride	1.25	91
p-bromobenzoyl chloride	1.0	80
2-furoyl chloride	4.0	90

doubtful whether $HFe(CO)_4^-$ is the actual reducing species.

IV.3.2. Reaction with Thioketones and Thioamides

$KHFe(CO)_4$ is a good reagent for the desulfurization of thioketones and thioamides in 1,2-dimethoxyethane (DME) (eq 40).[84] With $DFe(CO)_4^-$ (from $Fe(CO)_5$ and KOD) as the reagent, the corresponding deuterated compound is obtained. Some examples are reported in Table V.



(40)

IV.3.3. Reaction with Carboxylic Acid Chlorides

The first report on the use of $HFe(CO)_4^-$ for the reduction of acid chlorides to the corresponding aldehydes is attributed to Pettit et al.[30] Acid chlorides react with $[Me_4N]^+[HFe(CO)_4]^-$ at room temperature in aprotic solvents to give the corresponding aldehyde, according to eq 41.

$$2RC(O)Cl + 3HFe(CO)_4^- \xrightarrow[\text{room temp}]{CH_2Cl_2} 2RCHO + HFe_3(CO)_{11}^- + 2Cl^- + CO \quad (41)$$

Some selected examples are reported in Table VI.

TABLE VII. Reduction of Organic Halides with $HFe(CO)_4^-$ in DME/EtOH Mixtures[80]

substrate	product	yield, %
2-bromo-4′-phenylacetophenone	4-phenylacetophenone	82
2,4′-dibromoacetophenone	4-bromoacetophenone	66
2-bromo-4′-methoxyacetophenone	4-methoxyacetophenone	85
1-adamantyl bromomethyl ketone	1-adamantyl methyl ketone	64
9-bromofluorene	fluorene	84
α-bromocamphor	camphor	59

The proposed reaction mechanism involves a nucleophilic attack of $HFe(CO)_4^-$ (eq 42).

$$HFe(CO)_4^- + RC(O)Cl \xrightarrow{-Cl^-} RC(O)FeH(CO)_4 \rightarrow RCHO + \text{“}Fe(CO)_4\text{”} \quad (42)$$

$$2\text{“}Fe(CO)_4\text{”} + HFe(CO)_4^- \rightarrow HFe_3(CO)_{11}^- + CO \quad (43)$$

The same reaction has also been performed with $HFe(CO)_4^-$ attached to a polymeric matrix via an anion-exchange process with the chloride form of the Amberlyst A-26 resin.[34] In this case, a 1:3 acid chloride to $HFe(CO)_4^-$ ratio was used in refluxing solvents (THF, acetone, hydrocarbons, CH_2Cl_2). The advantages of this procedure are the ease in which the reagent can be dried, the ease in which the reaction products can be isolated, and the fact that the iron-containing byproducts are left on the polymeric support.

IV.4. Reactions with Organic Halides

IV.4.1. Alkyl Halides

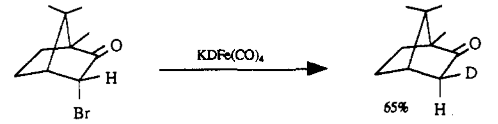
Darensbourg et al. have recently reported a study of the reactivity of anionic transition-metal hydrides complexes (as PPN⁺ salts) toward alkyl bromides.[85] The results indicate that $[PPN]^+[HFe(CO)_4]^-$ is unreactive toward *n*-BuBr and *t*-BuBr in THF at 26 °C (benzyl bromide reacts extremely slowly), whereas some other anionic transition-metal hydrides do react with these organic compounds. However, in more polar solvents, $HFe(CO)_4^-$ does react with alkyl halides. Reduction, elimination, and carbonylation reactions have been reported.

IV.4.1.1. Reduction. Under a nitrogen atmosphere, $KHFe(CO)_4$ is a mild reagent for the dehalogenation of alkyl halides (eq 44).[80] Some selected examples are reported in Table VII.

$$RX + KHFe(CO)_4 \xrightarrow[\text{room temp, 1-3 days}]{EtOH/DME} RH \quad (44)$$

The chemoselectivity of the reagent is particularly interesting since, under the conditions used, the reaction can be carried out in the presence of olefin, ketone, anhydride, methoxy, and aromatic bromide functional groups.[80]

The stereospecificity of the reaction was shown by the reaction of $DFe(CO)_4^-$ with bromocamphor (endo, eq 45), which led to camphor-3-*exo*-*d* without any detectable traces of the endo isomer.



(45)

The reaction of $HFe(CO)_4^-$ with alkyl halides was thus proposed to occur via S_N2 displacement of the

SCHEME III

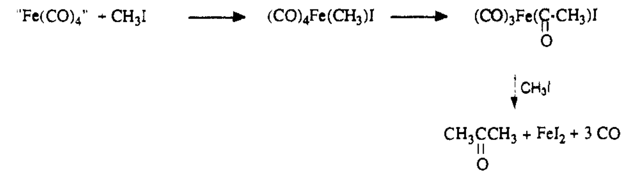


TABLE VIII. Debromination of *vic*-Dibromoalkanes by Polymer-Supported $HFe(CO)_4^-$ [88]

substrate[a]	product	yield, %
1,2-dibromooctane	1-octene	80
1,2-dibromoundecane	1-undecene	75
1,2-dibromooctadecane	1-octadecene	77

[a] Reaction carried out for 6 h in refluxing THF with a 6:1 ratio of iron to substrate.

halide followed by reductive elimination, the latter step occurring with retention of configuration.[80]

The same kind of reaction has also been performed with the polymer-supported form of $HFe(CO)_4^-$.[86]

A thorough study of the reaction of $[Et_4N]^+[HFe(CO)_4]^-$ with methyl iodide has recently been reported by Whitmire et al.[87] The authors studied the kinetics of the reaction in acetonitrile. In all cases, methane resulted in 85–100% yield. A second-order rate constant (first order in iron and in CH_3I) has been determined. On the basis of a study of the reaction of $[Et_4N]^+[HFe(CO)_4]^-$ with 6-bromo-1-hexene and (bromomethyl)cyclopropane, the authors proposed a primarily S_N2 type process (with some electron-transfer component). The reaction mechanism is therefore described by eq 46.

$$HFe(CO)_4^- + CH_3I \rightarrow HFe(CO)_4(CH_3) \rightarrow CH_4 + \text{“}Fe(CO)_4\text{”} \quad (46)$$

Interestingly, the formation of acetone (25–44% yield) was also observed during the reaction. Its formation has been rationalized by a mechanism independent of the nucleophilic attack of $HFe(CO)_4^-$ on methyl iodide. It has been shown that CH_3I reacts with the unsaturated "$Fe(CO)_4$" species (no acetone formation was observed when the reaction was conducted under a carbon monoxide atmosphere) to yield acetone, according to Scheme III.

IV.4.1.2. Elimination Reactions. The reaction of $HFe(CO)_4^-$ with *vic*-dibromoalkanes leads to the corresponding alkenes in good yields.[86,88] Some examples are reported in Table VIII.

IV.4.1.3. Carbonylation Reactions. The first carbonylation reaction of an alkyl halide with $HFe(CO)_4^-$ (eq 47) was reported by Watanabe et al.[26]

$$C_3H_7I + KHFe(CO)_4 \xrightarrow[30\ °C,\ 6\ h]{EtOH,\ CO\ (1\ atm)} \xrightarrow{I_2/EtOH} \underset{50\%}{C_3H_7CHO} + \underset{18\%}{C_3H_7CO_2Et} \quad (47)$$

The aldehyde is apparently formed in situ whereas ethyl butanoate is formed during the oxidation step.[26]

The synthesis of aldehydes from primary alkyl bromides and iodides has also been performed with the polymer-supported form of $HFe(CO)_4^-$ (eq 48, P = polymer).[86] The reaction is conducted in THF under an argon atmosphere with Fe:RX = 3. Some representative examples are reported in Table IX. As no additional ligand is needed to promote the carbon monoxide insertion, it has been suggested that the migratory insertion was induced by the halide ion formed. Indeed, the authors have previously shown that the nucleophilicity of halogen ions is strongly enhanced if they are bonded on the resin.

$$\underset{X = I,\ Br}{RCH_2X} \xrightarrow[THF,\ reflux,\ 4\ h]{P\text{-}C_6H_4CH_2NMe_3^+HFe(CO)_4^-} RCH_2CHO \quad (48)$$

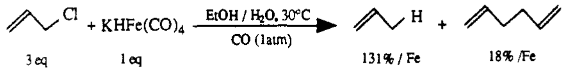
TABLE IX. Reaction[a] of Polymer-Supported $HFe(CO)_4^-$ with Alkyl Halides[86]

alkyl halide	product	yield, %
n-$C_7H_{15}Br$	n-$C_7H_{15}CHO$	90
n-$C_8H_{17}Br$	n-$C_8H_{17}CHO$	90
n-$C_8H_{17}I$	n-$C_8H_{17}CHO$	95
$C_6H_5CH_2CH_2Br$	$C_6H_5CH_2CH_2CHO$	80
$EtOCO(CH_2)_3Br$	$EtOCO(CH_2)_3CHO$	85

[a] Reactions conducted for 4 h in refluxing THF with $HFe(CO)_4^-$:RX = 3.

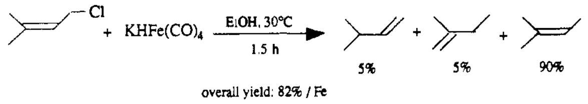
IV.4.2. Allyl and Benzyl Halides

The reactivity of $HFe(CO)_4^-$ with allyl halides has been only briefly studied.[89] The reaction of allyl chloride leads to propene, with 1,5-hexadiene as a side product (eq 49).



(49)

With 1-chloro-3-methyl-2-butene, a mixture of isomeric butenes results (eq 50), the distribution of which is almost independent of the reaction conditions (atmosphere, presence of water, reaction time, etc.).



(50)

The reduction by $HFe(CO)_4^-$ has also been recognized as a side reaction during the carbonylation of benzyl bromide by $Fe(CO)_4^{2-}$ under phase-transfer conditions (eq 51).[90]

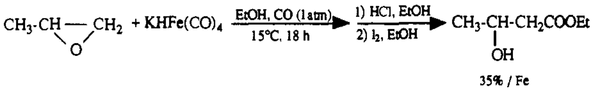
$$Bu_4N^+HFe(CO)_4^- + C_6H_5CH_2Br \xrightarrow[-Bu_4NBr]{CH_2Cl_2,\ CO} C_6H_5CH_3 + Fe(CO)_5 \quad (51)$$

IV.4.3. Aryl Halides

The reaction of $HFe(CO)_4^-$ with aryl halides has been reported only recently.[91] Aryl iodides are reduced to the corresponding arenes in high yields while bromo- and chlorobenzene are unreactive. High chemoselectivities have been observed. Since these reactions have been shown to be catalytic under carbon monoxide (1 atm), they are dealt with in more detail among the catalytic reactions (Section V).

IV.5. Reactions with Olefin Oxides

One of the first reactions in which the reactivity of iron carbonylates toward organic substrates was tested was their reaction with olefin oxides.[26] The reaction of ethanolic solutions of $KHFe(CO)_4$ with propylene oxide was reported to occur according to eq 52.



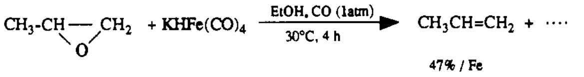
(52)

TABLE X. $KHFe(CO)_4$-Mediated[a] Reductive Alkylation of Primary Amines with Aldehydes[96]

amine	aldehyde	product	yield, %
aniline	formaldehyde	*N,N*-dimethylaniline	~100
aniline	acetaldehyde	*N,N*-diethylaniline	~100
aniline	propionaldehyde	*N,N*-dipropylaniline	~100
aniline	butyraldehyde	*N,N*-dibutylaniline	~100
aniline	benzaldehyde	*N,N*-dibenzylaniline	85
N-ethylaniline	formaldehyde	*N,N*-ethylmethylaniline	~100
N-methylaniline	acetaldehyde	*N,N*-ethylmethylaniline	~100
benzylamine	formaldehyde	benzyldimethylamine	~100
benzylamine	acetaldehyde	benzyldiethylamine	91

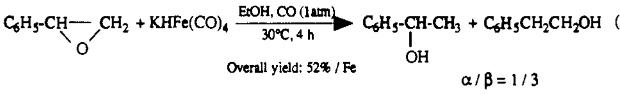
[a] At 28–33 °C for 24–48 h, under carbon monoxide (1 atm).

The same reaction was observed with ethylene oxide at 0 °C, but ethyl 2-hydroxypropionate was obtained in lower yields. It was later recognized that these reactions also gave the corresponding olefins (eq 53).[92]



(53)

When the reaction was carried out with styrene oxide, no carbonylation products were obtained, even under treatment with iodine.[93] Instead, a mixture of phenylethanols resulted (eq 54), together with styrene (16%/Fe) and ethylbenzene (4%/Fe) as side products.



(54)

Finally, $KHFe(CO)_4$ does not react with internal olefin oxides such as 2,3-butylene oxide or cyclohexene oxide.[93]

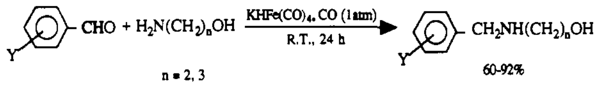
IV.6. Reduction of Imines and Iminium Salts

The reduction of imines and iminium salts by $HFe(CO)_4^-$ occurs during the reductive alkylation of amines with carbonyl compounds. The use of $HFe(CO)_4^-$ for the reductive alkylation of primary amines (eq 55) has been disclosed at the same time by two groups.[94,95]

$$\mathrm{RCHO} + \mathrm{R'NH_2} \xrightarrow[\mathrm{EtOH/H_2O,\ reflux}]{\mathrm{MHFe(CO)_4}} \mathrm{RCH_2NHR'} \qquad (55)$$

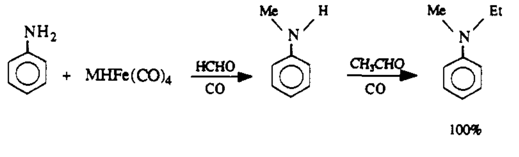
Depending on the amine to aldehyde ratio, both mono- and dialkylation reactions can be performed in high yields.[94] Similar results have been obtained under a carbon monoxide atmosphere (Table X).[96]

Application of this reaction to the reductive N-benzylation of alkanolamines with benzaldehyde derivatives has been recently reported (eq 56).[97]



(56)

The reaction can also be applied to the one-pot synthesis of unsymmetrically N,N-disubstituted anilines (eq 57).[96]



(57)

TABLE XI. Reductive Alkylation[a] of Secondary Amines with Carbonyl Compounds[73]

amine	carbonyl compd	reactn time, h	yield, %/Fe
morpholine	cyclohexanone	48	140
dibutylamine	butyraldehyde	24	50
pyrrolidine	acetophenone	48	110
morpholine	propionaldehyde	24	41

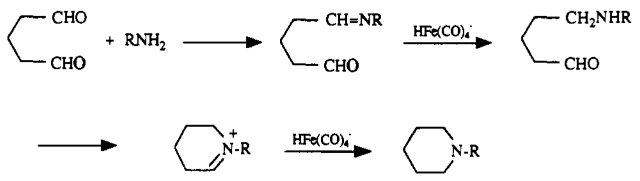
[a] Conditions: temperature, 30 °C; solvent, EtOH; $KHFe(CO)_4$:amine:carbonyl compound = 1:3:3.

TABLE XII. Syntheses[a] of N-Substituted Piperidines from Glutaraldehyde and Primary Amines[100]

amine	reactn time, h	R	yield, %
aniline	5	phenyl	78
p-toluidine	7.5	*p*-tolyl	81
p-methoxyaniline	6.5	*p*-methoxyphenyl	79
p-chloroaniline	7.5	*p*-chlorophenyl	89
o-toluidine	20	*o*-tolyl	77
o-methoxyaniline	18	*o*-methoxyphenyl	82
1-naphthylamine	13	1-naphthyl	80
benzylamine	5	benzyl	90
α-methylbenzylamine	5	α-methylbenzyl	85
phenethylamine	5	phenethyl	55
furfurylamine	5	furfuryl	72
cyclohexylamine	9.5	cyclohexyl	51
1-hexylamine	7	hexyl	60
2-aminoethanol	5.5	2-hydroxyethyl	41
glycine methyl ester	5	CH_2COOCH_3	45

[a] At room temperature under carbon monoxide. $HFe(CO)_4^-$:glutaraldehyde:amine = 1.0:1.0:1.0.

SCHEME IV

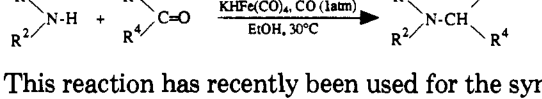


These reactions are believed to proceed via the corresponding imine (eq 58).[94]

$$\mathrm{R^1NH_2} + \mathrm{R^2CHO} \rightarrow \mathrm{R^1N{=}CHR^2} \xrightarrow{\mathrm{HFe(CO)_4^-}} \mathrm{R^1NHCH_2R^2} \qquad (58)$$

This hypothesis has been confirmed by showing that $HFe(CO)_4^-$ reduces *N*-benzylidene-*p*-toluidine to *N*-benzyl-*p*-toluidine in quantitative yield.[94]

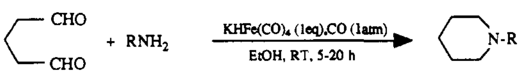
$HFe(CO)_4^-$ is also an efficient reagent for the reductive alkylation of secondary amines with either aldehydes or ketones (eq 59),[73] a reaction similar to the Leuckart–Wallach alkylation.[98] Some examples are reported in Table XI.



(59)

This reaction has recently been used for the synthesis of pentane-1,5-diamines in moderate yields.[99]

The principle of these alkylation reactions has been extended to the synthesis of N-substituted piperidines from glutaraldehyde and primary amines (eq 60).[100] Some examples are reported in Table XII.

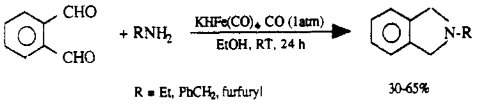


(60)

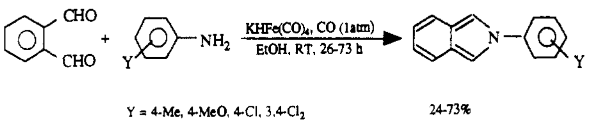
The proposed reaction mechanism involves the reduction of both imines and iminium salts by $HFe(CO)_4^-$ (Scheme IV).

This N-heterocyclization reaction has been further developed.[101,102] For example, Shim et al. have shown that ethanolic $KHFe(CO)_4$, combined with adipaldehyde, is a very efficient reagent for the synthesis of perhydroazepines.[102] A large variety of both aromatic and aliphatic primary amines react with this reagent under carbon monoxide to give the corresponding N-substituted perhydroazepines in good to excellent yields.

On the basis of same principle, the synthesis of 2-substituted isoindolines has been performed from phthalaldehyde and primary amines.[103] Aliphatic amines give selectively the isoindolines (eq 61), whereas aromatic amines lead to mixtures of isoindoles and isoindolines. In some cases, however, the reaction is selective for the production of isoindoles (eq 62).



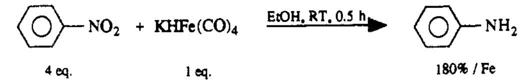
(61)



(62)

IV.7. Reactions with Nitro and Nitroso Compounds

The conversion of nitrobenzene to aniline by alkaline aqueous $Fe(CO)_5$ solutions has been known for some time, even as early as 1925.[104] It was later shown that these reactions involved $HFe(CO)_4^-$. The reaction of $KHFe(CO)_4$ with nitro and nitroso compounds in ethanol proceeds vigorously and exothermally, at room temperature, to give the corresponding amine in good yields (eq 63).[105]



(63)

When the reaction is conducted with nitrobenzene, the amount of aniline formed corresponds to 1.8 mol/mol of $KHFe(CO)_4$. During the reaction, $KHFe(CO)_4$ is oxidized to a di- or trivalent iron species. Nitrocyclohexane is also reduced to cyclohexylamine (140% with respect to iron) under similar conditions. The hydridotetracarbonylferrate species exhibits a high reactivity with nitrosobenzene (aniline, 210%) and a moderate one with azobenzene.[105]

The polymer-supported $HFe(CO)_4^-$ procedure proved to be very convenient for the reduction of aromatic nitro compounds.[88] The reagent is prepared in a chromatographic column containing the resin (Amberlyst A26). The nitro compound, in anhydrous THF, is then passed through the column for 0.5 h. The produced amine is isolated by simply removing the solvent (Table XIII).

The reaction was later investigated by Petit et al., who recognized that $HFe(CO)_4^-$ can act as a 12-electron reductant, with formation of Fe^{2+} salts.[106] These considerations led them to show that, under certain conditions, the reduction of aromatic nitro compounds with carbon monoxide and water could be made truly catalytic. These reactions are dealt with in Section V.

TABLE XIII. Reduction of Nitroarenes by Polymer-Supported $HFe(CO)_4^-$[88]

substrate[a]	product	yield, %
p-$ClC_6H_4NO_2$	p-$ClC_6H_4NH_2$	92
p-$C_6H_5C_6H_4NO_2$	p-$C_6H_5C_6H_4NH_2$	85
p-$CH_3OC_6H_4NO_2$	p-$CH_3OC_6H_4NH_2$	75
p-$OHCC_6H_4NO_2$	p-$OHCC_6H_4NH_2$	80
p-$H_2NC_6H_4NO_2$	p-$H_2NC_6H_4NH_2$	75

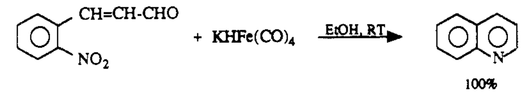
[a] $HFe(CO)_4^-$:nitroarene = 2.

TABLE XIV. $KHFe(CO)_4$-Mediated Synthesis[a] of Quinolines[107]

		condensation[b]			
nitro compd	carbon compd	KOH[c]	time, h	product	yield, %
o-nitrobenzaldehyde	acetaldehyde	0.49	10	quinoline	33
o-nitrobenzaldehyde	acetone	0.06	3	quinaldine	55
o-nitrobenzaldehyde	acetophenone	0.06	23	2-phenylquinoline	17

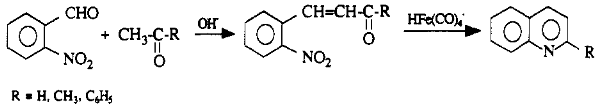
[a] At room temperature under argon for 1-3 h. [b] o-Nitrobenzaldehyde was treated with carbonyl compounds; the condensates obtained in situ then were reduced. [c] Molar ratio of potassium hydroxide to carbonyl compound.

Continuing with the stoichiometric uses of $KHFe(CO)_4$, Watanabe et al. have found that $KHFe(CO)_4$ reacts with o-nitrocinnamaldehyde in ethanol to give quinoline quantitatively (eq 64).[107]



(64)

The successive treatment of o-nitrobenzaldehyde, first with a carbonyl compound in the presence of KOH and then with $KHFe(CO)_4$, constitutes a one-pot, two-step synthesis of quinolines (eq 65). Some selected examples are given in Table XIV.



(65)

Finally, it has been recently reported that $[PPN^+][HFe(CO)_4^-]$ can be used to reduce nitrobenzene to aniline under acidic conditions (CF_3CO_2H in THF at 25 °C with a 5:4:1 molar ratio of $HFe(CO)_4^-$, CF_3CO_2H, and $C_6H_5NO_2$, respectively).[83] Under these conditions, the reduction of nitrobenzene can be selectively performed in the presence of aldehydes, alkyl halides, and acid halides. However, the nature of the actual reducing species is not clear.

IV.8. Reduction of Azides

A simple and convenient method for the reduction of organic azides to amines using $HFe(CO)_4^-$ (eq 66) has

$$RN_3 \xrightarrow[\text{EtOH, room temp}]{\text{KHFe(CO)}_4\text{, CO (1 atm)}} RNH_2 + N_2 \qquad (66)$$

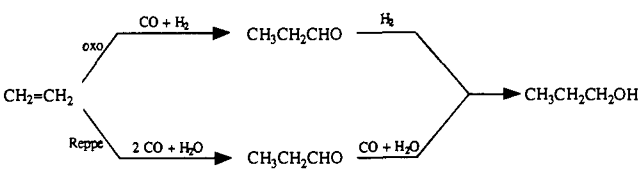
been reported. Some examples are given in Table XV.[108] The authors assume that these reactions proceed via an organic nitrene intermediate. At −40 °C, the reagent is also efficient for the reduction of benzoyl azide to benzamide.[108]

TABLE XV. Reduction[a] of Organic Azides with $KHFe(CO)_4$[108]

R	product	yield, %
phenyl	aniline	77
p-chlorophenyl	*p*-chloroaniline	100
o-chlorophenyl	*o*-chloroaniline	78[b]
p-methylphenyl	*p*-toluidine	84
p-methoxyphenyl	*p*-anisidine	85
n-hexyl	*n*-hexylamine	70

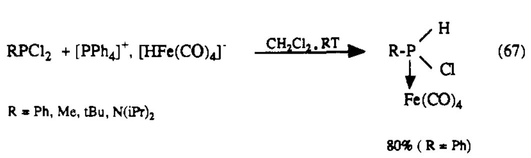
[a] Reactions conducted for 12 h at room temperature. [b] Reaction time 24 h.

SCHEME V



IV.9. Reaction with Dichlorophosphines

The reaction of $HFe(CO)_4^-$ (as Ph_4P^+ salt) with dichlorophosphines has been shown to be a convenient, one-step preparation of halophosphines stabilized by complexation (eq 67).[109]



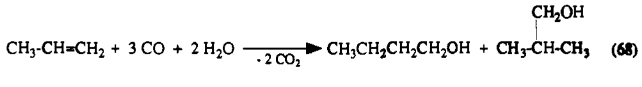
Further investigations by the same authors have shown that these reactions are strongly dependent on reaction conditions (ratio of reagents, order of addition, and nature of the phosphorus substituents) and that diphosphene complexes can be obtained.[110]

V. Catalytic Reactions

V.1. Reppe Alcohol Synthesis

The hydroformylation (oxo) reaction is a very important reaction of high industrial application.[111,112] In 1953, Reppe and Wetter disclosed what is commonly referred to as the "Reppe modification of the hydroformylation reaction" (Scheme V).[15]

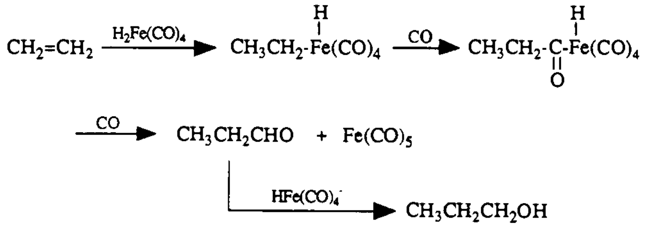
In the Reppe modification, the conversion is achieved without the use of molecular hydrogen per se. The olefin is converted to the next higher alcohol by reaction with carbon monoxide and water in the presence of $Fe(CO)_5$ and a Lewis base (*N*-butylpyrrolidine). This reaction is the basis of the BASF process for the production of butanols from propene.[112,113] At 90–110 °C and 10–15 bar of carbon monoxide pressure, the reaction yields a mixture of butanols (85% *n*-butyl alcohol, 15% isobutyl alcohol) with an overall selectivity of 90% in alcohols (eq 68).



$$CH_3\text{-}CH{=}CH_2 + 3\,CO + 2\,H_2O \xrightarrow[-2\,CO_2]{} CH_3CH_2CH_2CH_2OH + CH_3\text{-}\overset{CH_2OH}{\overset{|}{C}H}\text{-}CH_3 \quad (68)$$

Mechanistic investigations led von Kutepow and Kindler to propose that the catalytically active species was a trinuclear hydridoiron carbonyl complex $[R_3NH]^+[HFe_3(CO)_{11}]^-$.[114] However, some years later, Wada and Matsuda presented evidence that indicated that the catalytic species was the hydridotetracarbonylferrate complex $[R_3NH]^+[HFe(CO)_4]^-$.[115] These authors have shown that, under carbon monoxide pressure, the trinuclear species proposed earlier was rapidly transformed (IR analyses) into the mononuclear one (eq 69) that is not stable under atmospheric pressure (eq 70).[40]

SCHEME VI



$$[Et_3NH]^+[HFe_3(CO)_{11}]^- \xrightarrow[100\,°C]{CO\ (>20\ bar)} [Et_3NH]^+[HFe(CO)_4]^- \quad (69)$$

$$[Et_3NH]^+[HFe(CO)_4]^- \xrightarrow[70°C]{CO\ (1\ bar)} [Et_3NH]^+[HFe_3(CO)_{11}]^- + CO + H_2 \quad (70)$$

The observation that reduced pressures (6–10 bar) increased the hydroxymethylation rate was accounted for by assuming that the liberation of carbon monoxide formed a coordinatively unsaturated $HFe(CO)_3^-$ species (eq 17). In the absence of olefin, the unsaturated species may be converted to $HFe_3(CO)_{11}^-$, but in the presence of an olefin, it enters into the hydroxymethylation cycle.

However, the most pertinent observations were pointed out by Pettit et all, who found that the formation of alcohols was very dependent on the pH of the reaction medium.[46,47] They have shown that, under conditions similar to those of Reppe (KOH as base, 100 °C, 14 bar of ethylene, 20 bar of carbone monoxide), the hydroxymethylation reaction occurs only when the pH has decreased from initially 12.0 (conditions under which $HFe(CO)_4^-$ is the only carbonylmetal species present) to 10.7. This decrease of pH is attributed to the reaction of carbon monoxide with KOH to produce the corresponding formate. They concluded that, at pH 10.7, the conjugated acid begins to be formed in significant amounts (eq 71) and undergoes reaction with ethylene.[47]

$$Fe(CO)_5 + OH^- \xrightarrow{-CO_2} HFe(CO)_4^- \xrightarrow{H_2O} H_2Fe(CO)_4 \quad (71)$$

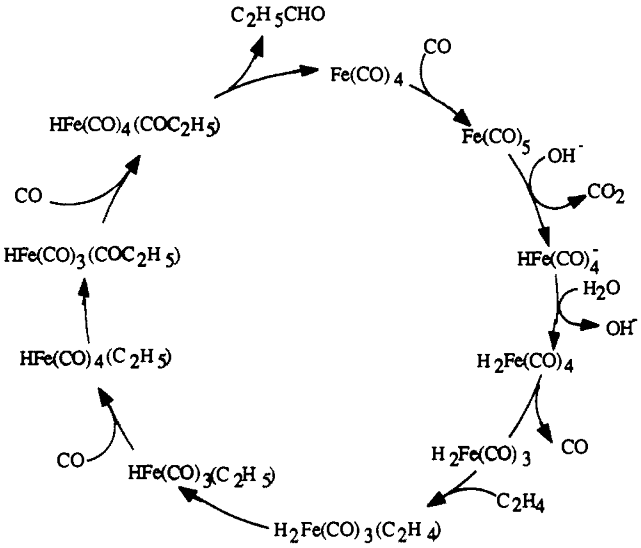
Thus they consider that the mechanism of the Reppe modification of the hydroformylation reaction (Scheme VI) parallels that of the normal process.[116]

The need for a carbonyl group dissociation from $H_2Fe(CO)_4$ was later recognized.[117] More recently, theoretical CNDO investigations by Chinese workers have shown that the proposal of Pettit et al. was reasonable.[118] A carbonyl group dissociation appears as the key step (Scheme VII).

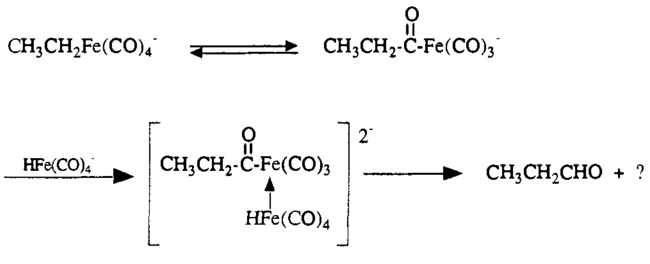
Therefore, it appears that $HFe(CO)_4^-$ is involved both as a precursor for $H_2Fe(CO)_4$ and as a catalyst for the reduction of propanal to propanol.

However, a very elegant study by Barborak and Cann has shown that $HFe(CO)_4^-$ can be involved in a bimo-

SCHEME VII



SCHEME VIII



lecular process during the aldehyde liberation step.[74] Indeed, $HFe(CO)_4^-$ reacts with alkyltetracarbonylferrate complexes to yield the corresponding aldehydes (eq 72).

$$HFe(CO)_4^- + CH_3CH_2Fe(CO)_4^- \xrightarrow{THF} CH_3CH_2CHO \quad (72)$$

On the basis of further experiments, it was proposed that $HFe(CO)_4^-$ reacts with an unsaturated acyliron carbonyl species (Scheme VIII).[74]

This possibility of a binuclear process seems to concur with the recent work of King et al.[119] These authors have reported a detailed kinetic study of the Reppe alcohol synthesis. The main conclusions are that (i) the reaction rate is second order with respect to $Fe(CO)_5$, (ii) the reaction is inhibited by carbon monoxide, and (iii) the IR spectra indicate that both $Fe(CO)_5$ and $HFe(CO)_4^-$ are present under the reaction conditions.

On the basis of these observations, King et al. proposed a detailed mechanism in which the aldehyde liberation step is rate-determining (eq 73, rds = rate-determining step). The regeneration of the mononuclear species is proposed to occur via eqs 74–76.

$$CH_3CH_2C(O)Fe(CO)_3^- + HFe(CO)_4^- \xrightarrow{rds} CH_3CH_2CHO + Fe_2(CO)_7^{2-} \quad (73)$$

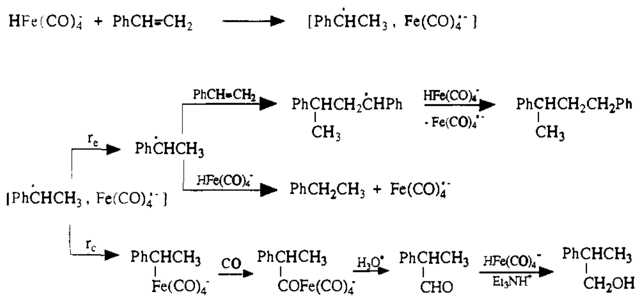
$$Fe_2(CO)_7^{2-} + CO \rightleftarrows Fe_2(CO)_8^{2-} \quad (74)$$

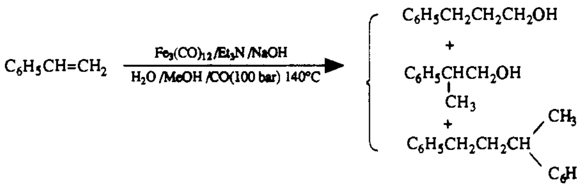
$$Fe_2(CO)_8^{2-} + H_2O \rightleftarrows HFe_2(CO)_8^- + OH^- \quad (75)$$

$$HFe_2(CO)_8^- \rightarrow Fe(CO)_5 + HFe(CO)_3^- \quad (76)$$

The special case of the Reppe hydroformylation of styrene has been studied by Marko et al.[120] Styrene is hydrogenated to ethylbenzene and hydroformylated to 2- and 3-phenylpropanol by CO and H_2O in the presence of a catalytic system consisting of $Fe_3(CO)_{12}$ (or $Fe(CO)_5$), Et_3N, and NaOH (eq 77).

SCHEME IX



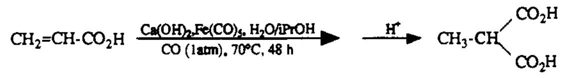


$$C_6H_5CH{=}CH_2 \xrightarrow[H_2O/MeOH/CO(100\ bar)\ 140°C]{Fe_3(CO)_{12}/Et_3N/NaOH} \left\{ \begin{array}{l} C_6H_5CH_2CH_2CH_2OH \\ + \\ C_6H_5CH(CH_3)CH_2OH \\ + \\ C_6H_5CH_2CH_2CH(CH_3)C_6H_5 \end{array} \right. \quad (77)$$

This reaction, which is believed to involve $HFe(CO)_4^-$ as an active species, is very sensitive to the H_2O to MeOH ratio. The hydrogenation to ethylbenzene is favored by adjusting this ratio to 1:2. On the contrary, optimum conditions for hydroformylation (and subsequent hydrogenation of the aldehydes) lie within a narrow range around Et_3N:NaOH = 6:4 and H_2O:MeOH = 3:1. However, the turnover number never exceeds 3. The formation of 1,3-diphenylbutane (eq 77) as byproduct led the authors to propose the intervention of radical pair intermediates, as shown in Scheme IX.[120]

V.2. Catalytic Hydrocarboxylation of Acrylic Acid

It has been recently shown in our laboratory that $HFe(CO)_4^-$ catalyzes the regioselective hydrocarboxylation of acrylic acid to methylmalonic acid under very mild conditions (eq 78).[121,122]



$$CH_2{=}CH\text{-}CO_2H \xrightarrow[CO\ (1\ atm),\ 70°C,\ 48\ h]{Ca(OH)_2, Fe(CO)_5, H_2O/iPrOH} \xrightarrow{H^+} CH_3\text{-}CH(CO_2H)_2 \quad (78)$$

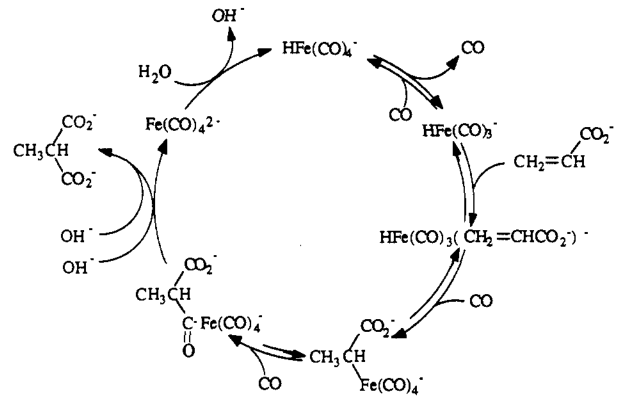
acrylic acid/$Fe(CO)_5$ = 46 64% (Conv. 68%)

The only side reaction (<5%) is the reduction of the substrate to propionic acid (no traces of succinic acid could be detected).

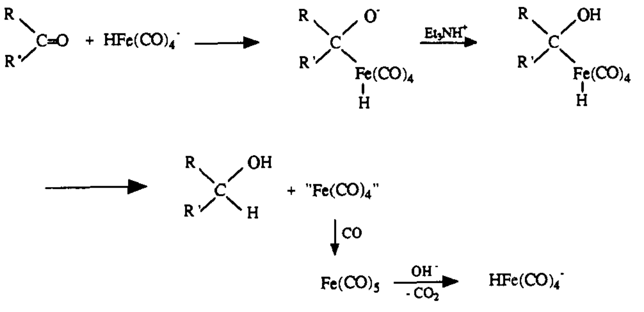
Although various hydroxides can be used as the base, calcium hydroxide proved to be the best suited one because it buffers the pH of the solution near 12.6. This, in turn, allows the maximum $HFe(CO)_4^-$ (vs $[Fe(CO)_4]^{2-}$) concentration to persist throughout the reaction. As the reaction is inhibited by carbon monoxide pressure, the catalytically active species is believed to be the coordinatively unsaturated $HFe(CO)_3^-$. The proposed catalytic cycle is presented in Scheme X.

This reaction is the first example of a regioselective, catalytic hydrocarboxylation of acrylic acid to the branched diacid. Only a Ni-catalyzed hydrocarboxylation of acrylic acid to succinic acid had been reported earlier.[123]

SCHEME X



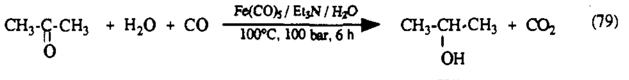
SCHEME XI



V.3. Catalytic Reduction of Aldehydes and Ketones

The catalytic reduction of aldehydes by $HFe(CO)_4^-$ has been recognized as the second step of the Reppe synthesis of alcohols. Sternberg[18] and Pettit[46,47] have shown that the hydroformylation and the reduction steps demand somewhat different reaction conditions, i.e., the second step is favored by increasing the pH of the medium. Marko et al. have studied the particulars of the reduction/hydrogenation of carbonyl compounds in detail.[82]

Acetone is catalytically reduced to isopropyl alcohol by carbon monoxide and water in the presence of iron pentacarbonyl and Et_3N at 100 °C under 100 bar of carbon monoxide, according to eq 79.



$$CH_3\text{-}\underset{\underset{O}{\|}}{C}\text{-}CH_3 + H_2O + CO \xrightarrow[100\,°C,\ 100\ bar,\ 6\ h]{Fe(CO)_5/Et_3N/H_2O} CH_3\text{-}\underset{\underset{OH}{|}}{CH}\text{-}CH_3 + CO_2 \quad (79)$$

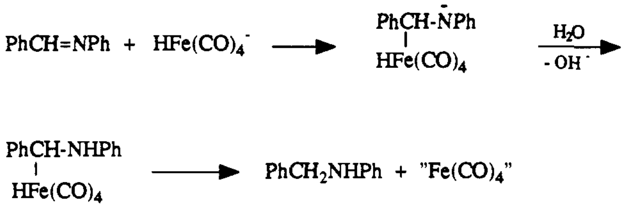
acetone/Fe(CO)$_5$ = 10 73%

One of the main features of this reaction is that Et_3N is a much more efficient base than NaOH. On the basis of information obtained from a comparative study of the stoichiometric reduction of aldehydes and ketones with either $[Et_3NH]^+[HFe(CO)_4]^-$ or $NaHFe(CO)_4$, the mechanism described in Scheme XI has been proposed.[82]

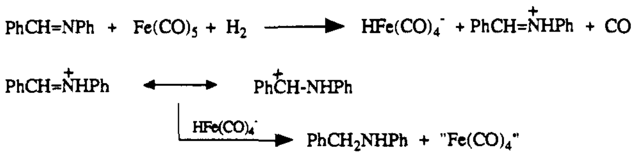
Aldehydes are much more reactive in the first step. The crucial step is the protonation by the relatively strong acid Et_3NH^+ since MeOH and water are not sufficiently acidic to effect the protonation, thus explaining the low rate of hydrogenation in the absence of Et_3N.

The hydrogenation of aldehydes and ketones with molecular hydrogen using $Fe(CO)_5$ as the catalyst precursor in a tertiary amine as the solvent is also believed to involve $[R_3NH]^+[HFe(CO)_4]^-$ as the active specie.[124]

SCHEME XII



SCHEME XIII



V.4. Catalytic Reduction of Schiff Bases

$HFe(CO)_4^-$ is regarded as the catalytically active species in the reduction of Schiff bases such as *N*-benzylideneaniline.[125] The reduction is achieved by carbon monoxide and water in the presence of $Fe(CO)_5$ and a base at 100 °C under 100 bar of carbon monoxide pressure (eq 80). Contrary to what has been found for the reduction of carbonyl compounds, NaOH and Et_3N are equally effective for imines hydrogenation.

$$PhCH{=}NPh + CO + H_2O \xrightarrow[100\ °C,\ 100\ bar,\ 3\ h]{Fe(CO)_5/Et_3N/H_2O/MeOH} \underset{79\%}{PhCH_2NHPh} + CO_2 \quad (80)$$

$$\text{imine:Fe(CO)}_5 = 20 \qquad Et_3N{:}Fe(CO)_5 = 10$$

The proposed mechanism (Scheme XII)[125] is similar to that of the reduction of carbonyl compounds under similar conditions.

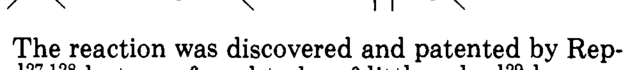
Since the reaction can be performed with NaOH as well as Et_3N, it appears that the presence of $[Et_3NH]^+$ is no longer necessary, thus suggesting that the intermediate amide ion is protonated by a water (or methanol) molecule.

The hydrogenation of imines is also possible by using molecular hydrogen in the presence of $Fe(CO)_5$ as the catalyst precursor in an alcoholic solution (150 °C, 100 bar of H_2).[126] As the reaction can be performed without adding any base, it is suggested that the substrate itself (although a weak base) ensures a sufficient concentration of $HFe(CO)_4^-$. The iminium cation thus formed is very susceptible to nucleophilic attack by $HFe(CO)_4^-$ and leads almost immediately to the amine (Scheme XIII).

The above hypothesis was confirmed by showing that $H_2Fe(CO)_4$ reacts instantaneously with benzylideneaniline at room temperature.[126]

V.5. Aminomethylation Reaction

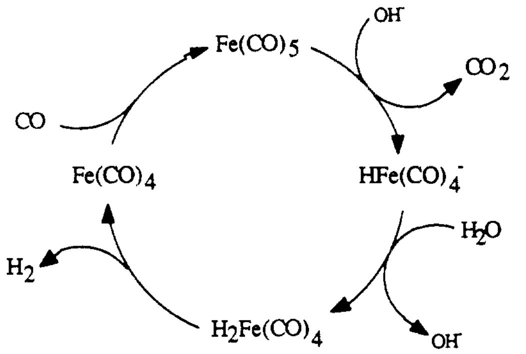
In the presence of aqueous bases, $Fe(CO)_5$ allows the hydroformylation of ethylene and the reduction of imines. This suggests that this catalytic system might conceivably be operating to give direct aminomethylation of olefins according to eq 81.



$$>C{=}C< + 3\,CO + H_2O + HN< \longrightarrow H\text{-}\overset{|}{\underset{|}{C}}\text{-}\overset{|}{\underset{|}{C}}\text{-}CH_2\text{-}N< + 2\,CO_2 \quad (81)$$

The reaction was discovered and patented by Reppe[127,128] but was found to be of little value[129] because

SCHEME XIV



of the slow reaction rates, poor yields, and conversion of the catalyst into inactive iron carbonates.[130] Rhodium-iron[129] and later ruthenium-iron[131,132] mixed-metal catalysts have been found to be much more efficient, but these reactions are beyond the scope of this review.

V.6. Water-Gas Shift Reaction

The water-gas shift reaction is an important way to produce dihydrogen from water and carbon monoxide according to eq 82.[133,134]

$$CO(g) + H_2O(g) \rightleftarrows CO_2(g) + H_2(g) \qquad (82)$$

$$\Delta G°_{298} = -6.82 \text{ kcal/mol}$$

$$\Delta H°_{298} = -9.84 \text{ kcal/mol}$$

$$\Delta S°_{298} = -10.1 \text{ cal/(deg mol)}$$

Commercially, this reaction may be carried out at temperatures over 300 °C with heterogeneous catalysts consisting of iron and chromium oxides[135] or other mixtures of oxides such as Cu/Zn or Co/Mo.[136]

The same reaction can also proceed at lower temperatures with water being present as a liquid. In this case, the reaction is only slightly exothermic and exhibits a large positive entropy change (eq 83).[133]

$$CO(g) + H_2O(l) \rightleftarrows CO_2(g) + H_2(g) \qquad (83)$$

$$\Delta G°_{298} = -4.76 \text{ kcal/mol}$$

$$\Delta H°_{298} = +0.68 \text{ kcal/mol}$$

$$\Delta S°_{298} = +18.3 \text{ cal/(deg mol)}$$

The possible use of $Fe(CO)_5$ as a homogeneous catalyst for the water-gas shift reaction was suggested by Reppe as early as 1953. These suggestions were based on even earlier work, the publication of which had been delayed by World War II.[137] A great deal of time has been devoted to the study of this reaction,[46,47,133,138] and it now appears well accepted that a simplified catalytic cycle may be represented (see Scheme XIV).[139]

Under high pressure in a 75:25 methanol/water mixture, the hydrogen production was shown to be first order in iron pentacarbonyl, independent of carbon monoxide pressure, and sensitive to pH of the reaction medium.[133,138] However, at low carbon monoxide pressures, $Fe(CO)_5$ loses its catalytic activity by reducing water to hydrogen in a stoichiometric reaction, leaving iron(II) carbonate as the final product.[133] The overall activation energy is 22 kcal/mol. The turnover number is 2000 mol of H_2/mol of $Fe(CO)_5$ per day at 180°C.[140] This relatively low turnover number for $Fe(CO)_5$ makes it unlikely that it could become a practical catalyst even under optimized conditions. Indeed, intensive work in this area has led Pearson et al. to show conflicting pH requirements for the two steps involved in the catalytic process.[140]

However, the $Fe(CO)_5$-based catalytic system appears to be an exemplary model system, and it is worth studying from that point of view.[141,142]

V.7. Catalytic Reduction of Aromatic Nitro Compounds

The reduction of nitro and nitroso compounds by $HFe(CO)_4^-$ in ethanol was first reported by Watanabe et al.[105] These reactions were dealt with in the section on stoichiometric reductions.

These authors, however, have noted that the reducing power of the ferrate corresponded to 1.8 equiv of nitrobenzene. In terms of electron transfer, the reduction of nitrobenzene to aniline corresponds to 6 electrons/molecule, and so it appears that $HFe(CO)_4^-$ acts as an 11-electron-transfer agent.[106]

Pettit et al. have recognized that, in basic medium, $HFe(CO)_4^-$ can provide 10 electrons upon complete depletion of the CO ligands and a further 2 electrons by final oxidation to Fe^{2+}, according to eqs 84–86.[106]

$$Fe(CO)_5 \xrightarrow[-CO_2]{OH^-} HFe(CO)_4^- \rightarrow Fe(CO)_4 + H^+ + 2e^- \qquad (84)$$

$$Fe(CO)_n \xrightarrow[-CO_2]{OH^-} HFe(CO)_{n-1}^- \rightarrow Fe(CO)_{n-1} + H^+ + 2e^- \qquad (85)$$

$$Fe \rightarrow Fe^{2+} + 2e^- \qquad (86)$$

In this manner, a total of 12 electrons is available from $HFe(CO)_4^-$. Pettit et al. reasoned that the reaction could be made catalytic in the presence of excess base, under CO pressure, to convert $Fe(CO)_4$ to $Fe(CO)_5$ and to prevent the irreversible oxidation of Fe^0 to Fe^{2+}.

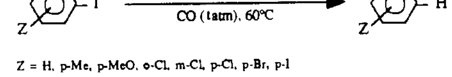
Nitrobenzene could be reduced to aniline at room temperature under 115 bar of carbon monoxide (eq 87).

$$C_6H_5NO_2 \xrightarrow[25\ °C,\ 115\ bar,\ 10-12\ h]{Fe(CO)_5/diglyme/H_2O/Et_3N} C_6H_5NH_2 \qquad (87)$$

However, the nitro derivative must be pumped slowly (10–12 h) into the reactor to prevent irreversible loss of the catalytic activity by excessive stripping of CO ligands. Although the reaction is effectively catalytic, the catalytic system appears very fragile and of little practical value.[106]

V.8. Catalytic Reduction of Aryl Iodides

Potassium tetracarbonylhydridoferrate, generated in situ by reaction of $Fe(CO)_5$ with K_2CO_3 in wet methanol, selectively reduces aryl iodides to the corresponding arenes. In the presence of excess K_2CO_3 (2 equiv/equiv of ArI), the reaction is catalytic under atmospheric carbon monoxide pressure (eq 88).[143]



(88)

Z = H, p-Me, p-MeO, o-Cl, m-Cl, p-Cl, p-Br, p-I

The chemoselectivity of this reagent has been emphasized by showing that these catalytic reductions can be performed in the presence of several other reducible compounds such as bromo- and chlorobenzene, cyclohexanone, benzonitrile, and cyclooctene, without modification (<1%) of any of them.[143]

The mechanism of these reactions has been investigated, both by IR analysis during the reaction and by an electrochemical study of the behavior of the reagent itself.[144,145]

IR analysis of the reaction medium during the reduction of iodobenzene *under argon* showed the appearance of absorption bands assigned to $[HFe_2(CO)_8]^-$, which then evolved to give a unique, large band characteristic of the tetranuclear dianionic complex $[Fe_4(CO)_{13}]^{2-}$. The latter species is apparently unreactive toward iodobenzene. When the reaction is conducted under carbon monoxide in the presence of excess K_2CO_3, the same absorption bands can be transiently observed but rapidly evolve to regenerate $[HFe(CO)_4]^-$.

Electrochemical oxidation of methanolic $KHFe(CO)_4$ solutions under argon (IR analyses) converted $[HFe(CO)_4]^-$ first into $[HFe_2(CO)_8]^-$ and ultimately, into the tetranuclear complex $[Fe_4(CO)_{13}]^{2-}$. These results may be rationalized by eqs 89–91.[144,145]

$$HFe(CO)_4^- \rightarrow HFe(CO)_4^\bullet + e^- \qquad (89)$$

$$2HFe(CO)_4^\bullet \rightarrow H_2Fe_2(CO)_8 \xrightarrow{\text{base}} HFe_2(CO)_8^- \qquad (90)$$

$$2HFe_2(CO)_8^- \rightarrow Fe_4(CO)_{13}^{2-} + 2e^- + 2H^+ + 3CO \qquad (91)$$

When the same electrochemical oxidation is performed under carbon monoxide, the evolution of IR absorption bands during several hours duplicates those observed during the reduction of iodobenzene under carbon monoxide.

The above observations suggest that the reduction of aryl iodides involves a monoelectronic transfer from $HFe(CO)_4^-$ to ArI to give the corresponding radical anion, which then generates an aryl radical (eqs 92–94). Abstraction of an hydrogen atom from either methanol or, more probably, potassium methoxide then would lead to the reduction product ArH (eq 95).[146]

$$HFe(CO)_4^- + ArI \rightarrow [ArI^{\bullet -}, HFe(CO)_4^\bullet] \qquad (92)$$

$$[ArI^{\bullet -}, HFe(CO)_4^\bullet] \rightarrow [Ar^\bullet, HFe(CO)_4^\bullet, I^-] \qquad (93)$$

$$[Ar^\bullet, HFe(CO)_4^\bullet, I^-] \rightarrow Ar^\bullet + HFe(CO)_4^\bullet + I^- \qquad (94)$$

$$Ar^\bullet + MeO^- \rightarrow ArH + CH_2O^{\bullet -} \qquad (95)$$

However, the side formation of small amounts of carbonylation products[144,145] also suggests the formation of aryltetracarbonyliron species (eqs 96–99).

$$[Ar^\bullet, HFe(CO)_4^\bullet, I^-] \rightarrow ArFe(H)(CO)_4 + I^- \qquad (96)$$

$$ArFe(H)(CO)_4 \rightarrow ArH + \text{“}Fe(CO)_4\text{”} \qquad (97)$$

$$ArFe(H)(CO)_4 + CO \rightarrow ArC(O)Fe(H)(CO)_4 \qquad (98)$$

$$ArC(O)Fe(H)(CO)_4 \rightarrow \text{carbonylation products} \qquad (99)$$

The regeneration of the active species from $HFe_2(CO)_8^-$ (formed according to eq 90) under carbon monoxide may be explained by eq 100, as established by Collman et al.[44] Furthermore, it has been shown that $Fe_4(CO)_{13}^{2-}$ is also converted to $HFe(CO)_4^-$ (eq 101) when reacted at 60 °C with K_2CO_3 in wet methanol under carbon monoxide (1 atm).[145]

TABLE XVI. Carbonylation of Iodobenzene[a] by the Bimetallic $Fe(CO)_5/Co_2(CO)_8$ System[147]

$Fe(CO)_5$, mmol	$Co_2(CO)_8$, mmol	C_6H_5I conv, %	C_6H_5COOH, %	$(C_6H_5)_2CO$, %	$(C_6H_5)_2$, %
	0.5	20	15		
1.8		55	2	2	15
1.8	0.5	73	65	4.5	2.5

[a] Reactions conducted on 20 mmol of C_6H_5I in a biphasic (8 M $NaOH(aq)/C_6H_6/EtOH$) system with 3 mmol of Bu_4NBr for 23 h at 60 °C under carbon monoxide (1 atm).

$$HFe_2(CO)_8^- + CO \rightarrow HFe(CO)_4^- + Fe(CO)_5 \qquad (100)$$

$$Fe_4(CO)_{13}^{2-} \xrightarrow[\text{CO (1 atm), 60 °C}]{K_2CO_3/MeOH} HFe(CO)_4^- \qquad (101)$$

V.9. Catalytic Carbonylation of Aryl Iodides

The carbonylation of iodobenzene to benzoic acid has been recently reported to be catalyzed, under very mild conditions (eq 102), by a bimetallic $HFe(CO)_4^-/Co(CO)_4^-$ system.[147]

$$C_6H_5I \xrightarrow[\text{Bu}_4\text{NBr, CO (1 atm), 60 °C, 23 h}]{Fe(CO)_5/Co_2(CO)_6,\ NaOH(aq)/C_6H_6/EtOH} \xrightarrow{H^+} C_6H_5COOH \qquad (102)$$

A synergistic effect between iron and cobalt carbonyl species was disclosed (Table XVI).

Although the mechanism of these reactions has not yet been elucidated fully, it is suggested that they involve, first, an electron transfer from $HFe(CO)_4^-$ to C_6H_5I, leading to the corresponding radical anion (see eq 92). The resulting phenyl radicals (see eq 93) are then believed to be intercepted by $Co(CO)_4^-$ in an $S_{RN}1$ type reaction, as previously proposed for the catalytic carbonylation of aryl halides by $NaCo(CO)_4/NaH/RONa$ systems.[148] In agreement with these hypotheses, the carbonylation of bromobenzene (which on its own is unreactive with the bimetallic system) can be brought about in the presence of iodobenzene.[147]

Under slightly different conditions (absence of ethanol in the biphasic medium), $HFe(CO)_4^-$ alone can promote a slow carbonylation of iodobenzene to a mixture of benzoic acid and benzophenone, the latter being the major product. In this case as well, the reaction is more efficient when carried out with the bimetallic $Fe(CO)_5/Co_2(CO)_8$ system (eq 103).[149]

$$C_6H_5I \xrightarrow[\substack{\text{Bu}_4\text{NBr, CO (1 atm), 60 °C, 23 h} \\ C_6H_5I:Fe(CO)_5:Co_2(CO)_8\ =\ 20:1.8:0.5}]{Fe(CO)_5/Co_2(CO)_8,\ NaOH(aq)/C_6H_6} \xrightarrow[\text{conv 95\%}]{H^+} \underset{50\%}{C_6H_5C(O)C_6H_5} + \underset{30\%}{C_6H_5COOH} \qquad (103)$$

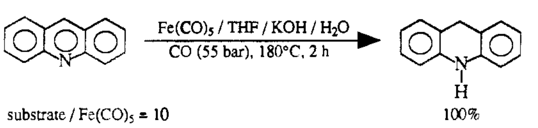
Although the reaction conditions have not yet been optimized, several symmetrically substituted benzophenones (4,4′-dimethoxybenzophenone, 55%; 4,4′-dimethylbenzophenone, 57%; 2,2′-dimethylbenzophenone, 47%) can be isolated in reasonable yield.[149]

This reaction is the only example of a catalytic, *direct* conversion of an aryl halide to the corresponding benzophenone.

V.10. Hydrogenation of Model Coal Constituents

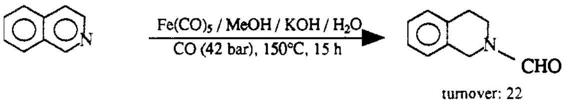
The various synthetic fuel products derived from coal or oil shale require additional hydroprocessing to decrease their nitrogen and sulfur content. At the beginning of the 1980s, iron pentacarbonyl was reported as an economically viable agent for the desulfurization and liquefaction of coal.[150–153]

It has thus appeared important to study the hydrogenation of polynuclear aromatic and heteroaromatic compounds with this catalyst precursor. In 1982, Fisch et al. studied the homogeneous reduction of polynuclear models with a wide variety of transition-metal carbonyl complexes under water–gas shift reaction or synthesis gas conditions.[154] $Fe(CO)_5$ acting as a catalyst precursor for the reduction of anthracene to 9,10-dihydroanthracene was among one of the few examples that was found to be active. However, rather poor yields were obtained. The polynuclear heteroaromatic nitrogen compounds were found to exhibit a greater reactivity while a high regioselectivity was observed (eq 104).

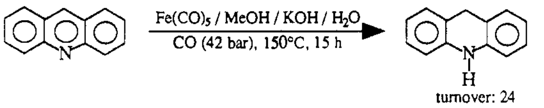


(104)

In a separate study, Kaesz et al. also found that nitrogen heterocycles were more reactive than polynuclear aromatics such as anthracene (naphthalene and phenanthrene were found to be unreactive).[155] At 150 °C under water–gas shift reaction conditions ($CH_3OH/H_2O/KOH$, CO (42 atm)) isoquinoline and acridine are reduced by using catalytic amounts of $Fe(CO)_5$ with turnovers of more than 20 (eqs 105 and 106).



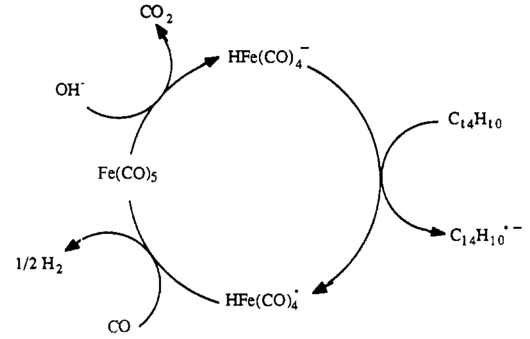
(105)



(106)

At higher temperatures (300 °C), a turnover of 35 could be obtained in the case of isoquinoline. In a search for conditions under which the hydrogenation of anthracene could be improved, the authors found that the presence of heterocycles (terpyridine) enhanced the yield of 9,10-dihydroanthracene (at 300 °C) up to turnovers of nearly 3. Phase-transfer agents and 18-crown-6 were also found to improve the hydrogenation of anthracene up to nearly 17 turnovers. Under the best conditions, the reduction of quinoline could be performed with a turnover of 87.[156] Mechanistic investigation of the above reactions led the authors to propose that $HFe(CO)_4^-$ is the catalytically active species and to suggest the catalytic cycle represented in Scheme XV.

SCHEME XV



V.11. Steam Gasification of Coal

Sodium tetracarbonylhydridoferrate has been found to be an excellent catalyst precursor for the catalytic steam gasification of coal at 650–800 °C.[157–161] A comparison of the efficiency of various $M^+HFe(CO)_4^-$ complexes (M = alkali metal) showed the following order of catalytic activity: Na > Li > K > Rb > Cs. X-ray diffraction studies have shown that $NaHFe(CO)_4$ is converted into Fe_3O_4 and Na_2CO_3 during the reaction.[159] It is thus believed that the catalytic activity is due to a synergistic effect of the binary (Fe–Na) system. The possibility of a reduction of Fe_3O_4 by carbon "complexed" with sodium has been recently proposed (eqs 107–109).[161]

$$3Fe + 4H_2O \rightarrow 4H_2 + Fe_3O_4 \qquad (107)$$

$$Fe_3O_4 + C \xrightarrow{Na} 3FeO + CO \qquad (108)$$

$$Fe_3O_4 + 4C \xrightarrow{Na} 3Fe + 4CO \qquad (109)$$

V.12. Catalytic Homologation of Methanol

The efficiency of $Fe(CO)_5$ as a catalyst precursor for the homologation of methanol was disclosed by Chen and Feder in 1981.[162] In the presence of trimethylamine, $Fe(CO)_5$ was found to catalyze the selective conversion of methanol to ethanol (eq 110) under 300 bar of CO/H_2 and at temperatures above 180 °C.[163,164]

$$CH_3OH + H_2 + 2CO \xrightarrow[MeOH]{Fe(CO)_5/Me_3N} CH_3CH_2OH + CO_2 \qquad (110)$$

The main advantage of this catalytic system is that it produces ethanol without coproduction of water, unlike cobalt systems, which operate according to eq 111.

$$CH_3OH + 2H_2 + CO \rightarrow CH_3CH_2OH + H_2O \qquad (111)$$

With the iron–amine system, the product purification is simpler (no water azeotrope).[165]

On the basis of a thorough study of the variables, the authors proposed a reaction mechanism based on a methyl group transfer between NMe_4^+ and $HFe(CO)_4^-$ as the rate determining step (eqs 112–119).[162] The contribution of methyl formate to the methyl-transfer mechanism has not been ruled out and is considered to be a possibility.[43]

$$Fe(CO)_5 + Me_3N + H_2 \rightleftarrows HNMe_3^+ + HFe(CO)_4^- + CO \qquad (112)$$

$$MeOH + CO \underset{}{\overset{base}{\rightleftarrows}} HCO_2Me \qquad (113)$$

$$HCO_2Me + NMe_3 \rightleftarrows NMe_4^+ + HCO_2^- \qquad (114)$$

$$HFe(CO)_4^- + NMe_4^+ \xrightarrow{rds} HFe(CO)_4Me + NMe_3 \qquad (115)$$

$$HFe(CO)_4Me + CO \rightleftarrows HFe(CO)_4(COMe) \qquad (116)$$

$$HFe(CO)_4(COMe) + CO \rightarrow MeCHO + Fe(CO)_5 \qquad (117)$$

$$MeCHO + H_2 \xrightarrow{HFe(CO)_4^-} MeCH_2OH \qquad (118)$$

$$HCO_2^- + HNMe_3^+ \xrightarrow{Fe(CO)_5} H_2 + CO_2 + NMe_3 \qquad (119)$$

The main side reaction is the formation of CH_4 (up to 30%), which may occur via reductive elimination from $HFe(CO)_4Me$. The high selectivity of the overall reaction (no production of propanol) is believed to be derived from eq 115, where an S_N2 attack of $HFe(CO)_4^-$ on NMe_4^+ yielding $HFe(CO)_4Me$ is postulated. A corresponding reaction could be imagined to give $HFe(CO)_4Et$. However, in such S_N2 reactions, the rate of methyl transfer is reported to be 10–150 times faster than ethyl transfer, depending on the exact nature of the leaving group.[166]

More recently, Tanaka et al. have reported that cyclic *N*-methylamines gave superior performances in comparison to the acyclic amines and proposed a catalytic cycle that does not involve the hydridotetracarbonylferrate.[167]

V.13. Miscellaneous

V.13.1. Synthesis of Formate Esters

$[PPN^+][HFe(CO)_4^-]$ has been shown to be an active catalyst precursor for the conversion of CO_2, H_2, and alcohols into formate esters (eq 120).[168]

$$CO_2 + H_2 + ROH \xrightarrow{[catalyst]} HCO_2R + H_2O \qquad (120)$$

$$R = Me, Et$$

V.13.2. Fischer–Tropsch Synthesis

$KHFe(CO)_4$ supported on H–Y zeolite or silica gel has been used for the Fischer–Tropsch synthesis. These systems exhibit a high selectivity to light olefins without following the Schulz–Flory distribution.[169] Although the characterization of the catalyst has not been performed, these results have been tentatively explained by assuming that very fine K–Fe_n species are formed on H–Y zeolite or silica gel when $KHFe(CO)_4$ is decomposed in the hydrogen flow at 260–350 °C.

V.13.3. Synthesis of Diesters

$KHFe(CO)_4$ has been recently reported to be a "catalyst" for the synthesis of diesters from malonyl or succinyl dichloride and alcohols.[170] Under the reaction conditions, the addition of an acid-trapping agent, such as *N*,*N*-dimethylaniline, is not necessary.

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