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Radical chemistry of iron carbonyls

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Abstract. It is shown that catalytic carbonylation of various compounds using iron carbonyl complexes is based on two types of reactions [redox disproportionation of iron carbonyl induced by Lewis bases and oxidative addition of Brønsted and Lewis acids to (hydrido)carbonylferrate anions] comprising single-electron initiation steps and subsequent radical chain reactions. The role of iron carbonyl radical anions as catalysts for carbonylation processes with controlled reduction potential of the medium is noted. Characteristic features of the radical chemistry of iron and other transition metal carbonyls is analysed. The bibliography includes 262 references.

I. Introduction

The chemistry of transition element carbonyls has been developed for more than a century since the initial discovery in 1890 of complexes of transition metals with CO ligands, first, nickel tetracarbonyl [1] and then iron pentacarbonyl.[2, 3] The discovery of the Fischer – Tropsch process for hydrocarbon synthesis from synthesis gas ($CO + H_2$) [4–7] and hydroformylation of organic compounds made a major impact on the development of this field of chemistry.[8] Metal carbonyls are used as catalysts in all these processes. The development of homogeneous catalytic systems for the Reppe synthesis and the replacement of synthesis gas by water gas ($CO + H_2O$) [9] may be regarded as the major achievements of these studies. As far as carbon monoxide is a key component of the $CO + H_2$ and $CO + H_2O$ gas mixtures, the mechanism of catalysis by transition element-based catalysts should be governed by the chemistry of metal carbonyls. Owing to the structural and chemical similarities between a metal surface with adsorbed CO molecules and carbonyl metal complexes, the latter can be regarded as simple models of catalytic processes, because studies of heterogeneous transformations are often extremely labour-consuming (see for example Refs 5 – 7, 10 and 11).

It is quite possible that in the nearest future the humankind will solve the energy problem by using renewable sources of energy instead of oil and gas; however there is no substitute for hydrocarbons in the industrial organic synthesis. The problem of alternative sources of raw materials for petrochemical industry will inevitably arise as the world oil supply gradually diminishes.[5, 6, 12] Hydrocarbons and other organic products obtained from CO may be such an alternative. In spite of some successful examples of application of CO conversion processes, in most cases they cannot compete with the petrochemical ones for economic reasons. The main problem is lack of inexpensive and selective catalysts for operation under mild conditions. The search for such catalysts requires a detailed investigation of the reactions of various coordination compounds with CO. The iron carbonyl complexes are regarded as the most promising ones, as they are readily available, stable and highly catalytically active in a variety of transformations.

In the early 1930s, Hieber and co-workers started to study the properties of iron carbonyls, particularly their reactions with Lewis bases (cited from [13, 14]). They have shown that the two-electron redox disproportionation is the predominant pathway of these reactions. This process results in the formation of Fe^{2+} salts with carbonyl-ferrate dianions (CFA) and (or) with their protonated analogues, hydridocarbonyl-ferrate monoanions (HCFA).

$$Fe_n(CO)_m + k\,L \longrightarrow \begin{cases} [FeL_k]^{2+}[Fe_p(CO)_{q-1}]^{2-} & \text{CFA} \\ [FeL_k]^{2+}[HFe_p(CO)_{q-1}]_2^- & \text{HCFA} \end{cases}$$

$n = 1$, $m = 5$; $n = 2$, $m = 9$; $n = 3$, $m = 12$; $p = 1$, $q = 5$; $p = 2$, $q = 9$; $p = 3$, $q = 12$; $p = 4$, $q = 14$; $2 \leqslant k \leqslant 6$; L is a nucleophilic ligand (a neutral Lewis base).

Besides, these reactions may yield the products of substitution of nucleophilic ligands for the CO groups. Rearrangements of the metal core accompanied by the change in the number of metal

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atoms in a cluster also may take place in these reactions. Numerous iron carbonyl complexes containing various functional groups have been obtained nowadays.[15,16]

Studies of the mechanisms of transformations of iron carbonyls are crucial for elucidation of their catalytic activity. The mechanisms are usually described by schemes that include 16-electron coordinatively unsaturated species. Thus, the following sequence of reactions was suggested for substitution processes:[2,5,14–16]

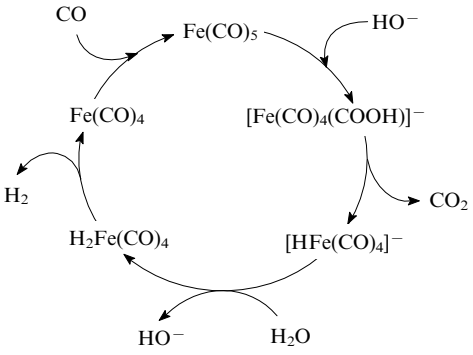
$$Fe_n(CO)_m \longrightarrow Fe_n(CO)_{m-1} + CO,$$

$$Fe_n(CO)_{m-1} + L \longrightarrow Fe_n(CO)_{m-1}L.$$

$n = 1, m = 5; n = 2, m = 9; n = 3, m = 12$; L is a nucleophilic ligand.

The catalytic scheme of water–gas shift reaction (Scheme 1) suggested by Pettit and co-workers[17,18] is another example of transformations catalysed by iron carbonyl complexes. The same scheme with only minor variations was also used by the same authors for the description of the mechanism of Reppe synthesis. The most general and complete version of this scheme has been published by King *et al.*[19,20] The nucleophilic addition of a base to a carbonyl ligand takes place at the first stage of the catalytic cycle, which is followed by decarboxylation and the formation of hydridocarbonylferrate anion. The Scheme contains two redox reactions.

Scheme 1



The substitution of nucleophilic ligands for the CO groups during the activation of iron carbonyls by trimethylamine oxide proceeds in a similar way (Scheme 2).[21–24]

Scheme 2

$$Fe_n(CO)_m + Me_3N{\rightarrow}O \longrightarrow Fe_n(CO)_{m-1}C(O)\cdots ONMe_3 \longrightarrow$$

$$\longrightarrow Fe_n(CO)_{m-1} + CO_2 + Me_3N,$$

$$Fe_n(CO)_{m-1} + L \longrightarrow Fe_n(CO)_{m-1}L.$$

The three abovementioned schemes are unified by a common paradigm, which has been formed over more than a century, concerning the major role of 16-electron intermediate species in the transformations of metal carbonyls. The paradigm is formulated as the Tolman rule,[25] which states that the predominant pathway of these reactions consists of consecutive formation of 18-, 16- and 18-electron complexes (18e → 16e → 18e).

The formation of 16-electron coordinatively unsaturated species, for example $Fe(CO)_4$, is postulated on the basis of their detection by IR spectroscopy in the gas phase[26,27] and in noble gas matrices at 4–20 K.[28–31] However, only recently, was the existence of $Fe(CO)_4$ in a solution registered by femtosecond IR spectroscopy during UV photolysis of iron pentacarbonyl. The lifetime of such species is 660 ps (6.6×10^{-10} s).[32,33] Obviously, special experimental conditions of flash photolysis and the so short lifetime of iron tetracarbonyl cast doubt upon its participation in the processes in the liquid phase.

II. Iron carbonyl radical anions

Alongside with neutral and charged iron carbonyl complexes containing an even number of electrons, iron derivatives with an odd number of electrons may also exist. We are talking about iron carbonyl radical anions (ICRA) $[Fe_n(CO)_m]^{-\bullet}$ ($n = 1$, $m = 5$; $n = 3$, $m = 12$) and $[Fe_n(CO)_{m-1}]^{-\bullet}$ ($n = 1$, $m = 5$; $n = 2$, $m = 9$; $n = 3$, $m = 12$; $n = 4$, $m = 14$), which may be generated by various methods.

Electrochemical single-electron reduction of iron carbonyls in various solvents leading to the formation of ICRA has been studied by polarography using dropping mercury electrodes[34–39] and by cyclic voltammetry using platinum,[37–41] gold[42,43] and glassy-carbon electrode.[39]

Iron carbonyl radical anions were also obtained by chemical methods: either by reactions of iron carbonyls with strong reducing agents such as alkali metals or sodium benzophenone ketyl,[44–46] or by oxidation of carbonylferrate anions by, for example, ferrocenium or silver salts.[46,47] Iron carbonyl radical anions are formed also during UV or ^{60}Co γ-irradiation of the corresponding iron carbonyls or CFA.[43,45,48–52]

The formation of $[Fe(CO)_4]^{-\bullet}$ in noble gas matrices at low temperatures has been observed in the same experiments in which the 16-electron $Fe(CO)_4$ species have been registered.[31,53,54] In order to suppress the formation of mono- and polynuclear iron carbonyl radical anions, a stabilising agent, namely, 0.02% of CCl_4, has been added to the system (the mechanism of stabilisation is discussed in Section VII).[31] The $[Fe(CO)_4]^{-\bullet}$ radical anion in Ne or Ar matrices has C_{3v} symmetry and its IR spectrum exhibits a CO absorption band at 1859.7 cm^{-1} (in Ne) or at 1853.5 cm^{-1} (in Ar).[31,48,53,54]

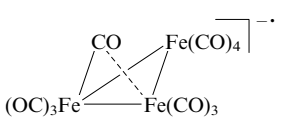
Only the signals of terminal CO groups [ν_{CO} = 2057 (vw),† 2017 (w), 1984 (vw), 1966 (m), 1933 (w), 1922 cm^{-1} (w, sh)][55,56] are present in the IR spectra of $[Fe_3(CO)_{11}]^{-\bullet}$ in THF, while in a solution in aqueous THF in the presence of NaOH, the spectrum changes [ν_{CO} = 2057 (vw), 2019 (vw, sh), 1982 (vw), 1969 (m), 1960 (m, sh), 1933 (w), 1916 cm^{-1} (w, sh)].[57]

The ESR spectra of iron carbonyl radical anions in different solvents at various temperatures were studied in a number of papers.[38,44–46,49,58,59] The ESR spectral parameters of ICRA and their hydrido analogues (*g*-factor and hyperfine splitting constants *a* on the ^1H, ^{13}C and ^{57}Fe nuclei) are given in Table 1.

The iron carbonyl radical anions in which one or several CO groups are replaced by phosphine or phosphite ligands are also known.[37,44,45,60,61]

Low-temperature ESR-spectroscopic studies of ICRA in crystalline matrices and solid solutions have been performed.[47,50–52,62,63]

The most stable iron carbonyl radical anion, $[Fe_3(CO)_{11}]^{-\bullet}$, has been isolated as bis(triphenylphosphine)iminium (PPN^+) and $[PPh_4]^+$ salts and characterised by elemental and X-ray diffraction analysis. The X-ray study has shown that the anion consists of a triangular core of iron atoms with one semibridging and ten terminal CO ligands.[55,56]



The photoelectron spectra of the $[Fe(CO)_4]^{-\bullet}$ radical anion have been reported,[64–66] and its reactivity towards various compounds in the gas phase was studied by mass spectroscopy and ion cyclotrone resonance.[67–70] Besides, clusterisation of ICRA in the

† The following notation is used for the band intensities in the IR spectra: v. is very, w. is weak, s is strong, m. is medium; sh (shoulder) is a signal superimposed as a shoulder on another signal.

Table 1. ESR data of some ICRA and its hydride analogues.

Species	g	a /mT (the number of nuclei)			Temperature /°C	Solvent	Ref.
		^{1}H	^{13}C	^{57}Fe			
$[Fe(CO)_4]^{-\bullet}$ (**1**)	2.0486				−80	THF, MeTHF	43, 49
$[Fe_2(CO)_8]^{-\bullet}$ (**2**)	2.0385			3.7 (2)	−80	THF	46
$[Fe_3(CO)_{11}]^{-\bullet}$ (**3**)	2.0497			5.2 (1)	−80	THF	46
$[Fe_3(CO)_{12}]^{-\bullet}$ (**4**)	2.0016		3.55 (12)	3.1 (3)	−80	THF	46
$[Fe_4(CO)_{13}]^{-\bullet}$ (**5**)	2.0134		16.2 (3), 14.2 (3), 2.5 (6), 7.9 (1)	1.27 (3), 5.8 (1)	−80	THF	46
$[HFe(CO)_4]^{\bullet}$ (**6**)	2.0545	22.60 (1)			−110	n-C_5H_{12}	49
$[HFe_2(CO)_8]^{\bullet}$ (**7**)	2.0122	22.22 (1)	12.37 (2)		−110	n-C_5H_{12}	49
	2.0120	22.2 (1)	12.3 (2)	3.60 (2)	−100	n-C_5H_{12}, cyclo-C_3H_6	58
$[HFe_3(CO)_{11}]^{\bullet}$ (**8**)	2.0641	18.95 (1)	10.0 (3)		−80	n-C_5H_{12}	49
	2.0635	18.4 (1)			−80	THF	58
$[H_3Fe(CO)_3]^{\bullet}$	2.0459	24.9 (2), 2.9 (1)			−80	n-C_5H_{12}	49
$H_3Fe_2(CO)_7]^{\bullet}$	2.0161	16.7 (1), 5.0 (2)			−80	n-C_5H_{12}	49
$[H_2Fe(CO)_3]^{-\bullet}$ (**9**)	2.0529	22.2 (2)			−110	MeTHF	59
$[H_2Fe_2(CO)_7]^{-\bullet}$ (**10**)	2.0435	22.4 (2)			−80	MeTHF	59
$[H_2Fe_3(CO)_{10}]^{-\bullet}$ (**11**)	2.0489	24.2 (2)			−40	MeTHF	59

Note. MeTHF is 2-methyltetrahydrofuran.

reactions of $[Fe(CO)_4]^{-\bullet}$ with iron pentacarbonyl in the gas phase were studied [71–73] and IR spectra of the clusters formed were obtained.[74]

Thus, on the one hand, we have got 16-electron intermediate complexes, formed during iron carbonyl transformations, which are short-lived and ghostly 'as the Cheshire cat smile' (the comparison was made by Poliakoff, one of the founders of this field of chemistry). On the other hand, the relatively stable ICRA resulting from single-electron reduction of iron carbonyls, are regarded at best as by-products of processes involving iron carbonyls.

III. Reactions of iron carbonyls with Lewis bases. Activating complex formation

During investigation of the reactions of iron carbonyls with various Lewis bases in anionic or neutral form, it was found that radical anions are easily generated in an ESR spectrometer cavity even at early stages of reactions at low conversions of the initial complexes.[75–79] Nevertheless, the concentrations of the ICRA were relatively high (10^{-5}–10^{-2} mol litre^{-1}).

Naturally, these data may be interpreted as evidence in favour of single-electron reduction of iron carbonyls similar to the electrochemical reduction or to the action of strong reducing agents such as the sodium mirror and sodium benzophenone ketyl. However, the Lewis bases used (supposed electron donors) may hardly be regarded as reducing agents, because their oxidation potentials are too high (for example, these values for Cl^- and HO^- in acetonitrile are equal to +2.24 and +0.92 V, respectively [80]). These processes have to be interpreted as anomalous reactions proceeding 'against the potential', which are similar to the reactions between *p*-quinones and bases studied by Pedersen.[81]

The concept of the 'activating complex formation' was suggested by Abakumov [82, 83] to explain the mechanisms of this type of reactions. As applied to iron carbonyls, this concept may be formulated as follows: if a donor L^- (a Lewis base in its anionic form) is unable to reduce directly an acceptor C (an iron carbonyl) but forms a complex CL^-, which becomes a reducing agent with respect to the initial iron carbonyl molecule, then a single-electron process becomes possible (Scheme 3).

The Lewis bases used are, most often, quite simple molecules (or ions) containing localised σ-bonds without a π-electronic conjugated system. Elimination of an electron from such a compound results in a significant change in the atomic charge of

Scheme 3

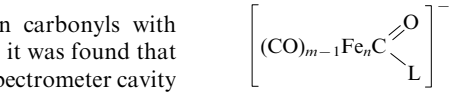
$$L^- + C \not\longrightarrow L^{\bullet} + C^{-\bullet},$$

$$L^- + C \longrightarrow CL^-,$$

$$CL^- + C \longrightarrow CL^{\bullet} + C^{-\bullet}.$$

the 'key' atom. This process is energetically unfavourable. On the contrary, the CL^- complex formed acquires donor properties and electron elimination stabilises the complex due to delocalisation.

The activating complex formation for the reactions of iron carbonyls with Lewis bases consists of the addition of the base to the carbonyl group.



The structure of such adducts is well known (see, for example, the review [84]). The kinetics of formation of hydroxycarbonyl (L = OH) and methoxycarbonyl (L = OMe) iron complexes in solution has been studied.[85–87] The thermodynamic and kinetic aspects of the formation of such derivatives in the gas phase are described in papers.[67, 88–92]

In some cases it is possible to isolate an adduct of an iron carbonyl with Lewis base. This fact was used to confirm the second redox step in Scheme 3. Thus, the salt (PPN)[$Fe(CO)_4$. .C(O)OMe] has been isolated.[86, 93] No ESR signals have been observed for this salt in solution, as for the initial iron pentacarbonyl. The reaction of the salt with iron pentacarbonyl directly in the cavity of an ESR spectrometer reveals that fast reduction of the iron carbonyl yielding ICRA takes place even at temperatures below −80 °C. The type of ESR spectrum and the character of its gradual change are similar to those for the reaction of $Fe(CO)_5$ with sodium methoxide.[77] Therefore, the reaction of iron carbonyl with anionic Lewis bases may be represented as follows:

$$Fe_n(CO)_m + L^- \rightleftharpoons [Fe_n(CO)_{m-1}C(O)L]^-, \quad (1)$$

$$[Fe_n(CO)_{m-1}C(O)L]^- + Fe_n(CO)_m \longrightarrow \longrightarrow [Fe_n(CO)_{m-1}C(O)L]^{\bullet} + [Fe_n(CO)_m]^{-\bullet}, \quad (2)$$

$n = 1, m = 5$; $n = 2, m = 9$; $n = 3, m = 12$.

This scheme of formation of radical anions is general and does not depend on the type of iron carbonyl or Lewis bases. A great number of anionic Lewis bases in the form of sodium derivatives NaL [L = OR, SR, NR_2, CR_2NO_2 (R = H, Alk, Ph)], alkali metal and complex cation salts M^+L^- (M is an alkali metal, PPN, NR_4; L = H, F, Cl, Br, I, CN, SCN, N_3, $MeCO_2$, CF_3CO_2, $MeSO_3$, NO_2) as well as sodium salts of dianions S^{2-}, CO_3^{2-}, SO_4^{2-} have been studied in the reactions with $Fe(CO)_5$, $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$.[76–79] Tetrahydrofuran, 2-methyltetrahydrofuran, diethyl ether, monoglyme, dioxane, methylene chloride, methanol, ethanol and THF–water (10 : 1 by volume) were used as solvents.[78]

Redox disproportionation of iron carbonyls induced by neutral Lewis bases is much more difficult. Particularly, the interaction of $Fe(CO)_5$ with neutral bases (ROH, RSH, R_2NH) yields a set of radicals, which is virtually identical to that formed in the reactions of anionic forms; however the process is considerably slower and takes place only at high temperature.[77] The rate of ICRA generation may be lower due to both a smaller equilibrium constant of the first step of activating complex formation [reaction (3)] and the additional energy expenditure for the generation and separation of charges during the second, redox stage of the process [reaction (4)].

$$Fe_n(CO)_m + L \rightleftharpoons Fe_n(CO)_{m-1}C(O)L, \quad (3)$$

$$Fe_n(CO)_{m-1}C(O)L + Fe_n(CO)_m \longrightarrow \longrightarrow [Fe_n(CO)_{m-1}C(O)L]^{+\cdot} + [Fe_n(CO)_m]^{-\cdot}, \quad (4)$$

$n = 1, m = 5; n = 2, m = 9; n = 3, m = 12.$

Besides the abovementioned reactions, the reactions of iron carbonyls with standard solvents and reagents, such as pyridine, DMF, DMSO, *o*-phenanthroline[77] and trimethylamine oxide[79] were studied by ESR. All these neutral Lewis bases possess electron-donating properties.

A study on the rates of reactions between Lewis bases and $Fe(CO)_5$, $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$ has shown that the rate is the lowest for $Fe(CO)_5$ and the highest for $Fe_3(CO)_{12}$. The difference is a result of the higher reduction potential ($E_{1/2\,red}$) for $Fe_3(CO)_{12}$ (which is in the range from -0.32 to -0.44 V)[38,39] in comparison with that for $Fe(CO)_5$ ($E_{1/2\,red} = -1.77$ V).[39] The electron transfer step [reactions (2) and (4)] proceeds much easier for $Fe_3(CO)_{12}$ for this reason. Probably, the heterogeneity of the $Fe_2(CO)_9$–L (or L^-) system does not affect the process rate in this particular case. The electron transfer from the activated complex formed to the neighbouring iron carbonyl molecule [reactions (2) and (4)] proceeds on the surface of a crystal and is accompanied by charge delocalisation over the crystal, thus reducing the energy required for the process and compensating the diffusion limitations.

Thus, the scheme comprising a complex formation stage followed by the transfer of one electron from the activated complex to another substrate molecule may be regarded as general for the disproportionation reactions of iron carbonyls with Lewis bases.

However, for a long time there has been no answer to the main question: 'Do the radicals take part in the reaction or are they just by-products?' In order to solve this problem, kinetic studies of the reactions of iron carbonyls with various Lewis bases have been performed. The following conclusions may be drawn from the obtained data:

1. The initial stage of the interaction of iron carbonyls with Lewis bases is a reversible bimolecular reaction having the first order with respect to each of the components,[84,86,87,94] which consists of activating complex formation [reaction (1)]. The subsequent processes are multistep.[86,95]

2. A scheme of transformations including (according to the Tolman rule[25]) the formation of 16-electron coordinatively unsaturated species of the $Fe(CO)_4$ type underlay all kinetic calculations.

3. Methods that determine only the parameters of the initial reactants and final reaction products were used in kinetic studies of the multistep processes. (The complexes with the bases formed at the first step of the reaction were an exception.) The absence of the kinetic data on the intermediate catalytically active species makes such schemes look like a 'black box' (*i.e.*, the change of the input parameters results in the change in the output parameters, but there is no way to find out what is going on inside the box).

The radical chain mechanism of the process was first proved by studying the kinetics of accumulation and loss of the intermediate radical species, namely, iron carbonyl radical anions.[96] A well studied reaction of iron dodecacarbonyl with tetraethylammonium ethanetiolate in THF was used as a model. For this reaction, the structures of intermediate radical species[77,97] and final products are known.[98] The reaction was carried out directly in the cavity of an ESR spectrometer in a flow system using the stopped flow method. It was shown[96] that the experimental results on the kinetics of accumulation and loss of intermediate radical anions **3** and **4** correspond well to the calculated ones. These calculations were based on the suggested mechanism of two-step redox formation of ICRA [reactions (1) and (2)].

The iron in complexes with Lewis bases formed in reactions (2) and (4) are in the formal oxidation states (+1) and (−1), respectively.‡ These complexes initiate two chains of transformations caused by substitution reactions in the coordination sphere of the radicals. Whereas Fe(−1) radicals are intrinsically stable and easily detectable, the registration of Fe(+1) radicals is much more challenging, because such complexes (the iron configuration is d^7) are usually extremely unstable. In the case of hard Lewis bases (L), the coordination sphere of the carbonyl complex is destabilised with elimination of CO ligands and oxidation of the iron atom to Fe^{2+}. This gives inorganic compounds of the FeL_2 type (L is an anion) or salts of the $[FeL_k]^{2+}$ cation (L is a neutral base).[13,14] Stabilisation of the coordination sphere of an iron carbonyl complex becomes possible in the case of soft Lewis base L (or in the case of transition of hard base into a soft one, *e.g.*, NO_2^- into NO[76]) or when the η-bonding of ligand L with the metal core increases during the reaction. Sometimes such iron(+1) radicals may be detected by ESR either directly or as spin adducts.[76,99]

The radical complexes $[Fe(CO)_{5-n}L_n]^{+\cdot}$ (n = 1, 2), in which one or two CO groups are replaced by phosphine or phosphite ligands are most stable.[100–103] The complex $[Fe(CO)_3(PPh_3)_2].[PF_6]\cdot 0.5\,CH_2Cl_2$ has been isolated[100] and characterised by X-ray crystallography.[104]

The reactions of iron carbonyls with sodium hydrosulfide and thiolates, which may be regarded as soft Lewis bases, are suitable for the detection of radical complexes of Fe(+1). These bi- and trinuclear radical anions of the $[Fe_2(CO)_6(SR)_2]^{-\cdot}$ and $[Fe_3(CO)_9(SR)_2]^{-\cdot}$ types formed in the reaction with $Fe(CO)_5$ may be detected.[77,97] The number of metal atoms may change as a result of exchange of the CO ligands with the starting iron carbonyl or the L^- ion. These processes take place in the coordination sphere of the initially formed Fe(+1) complexes [reaction (2)].[77,105]

$$[Fe(CO)_4C(O)L]^{\cdot} \longrightarrow [Fe(CO)_4L]^{\cdot} + CO. \quad (5)$$

$$\begin{array}{ccccc} [Fe(CO)_4L]^{\cdot} & \underset{CO}{\overset{Fe(CO)_5}{\rightleftharpoons}} & [Fe_2(CO)_7L]^{\cdot} & \underset{CO}{\overset{Fe(CO)_5}{\rightleftharpoons}} & [Fe_3(CO)_{10}L]^{\cdot} \\ CO \uparrow\downarrow L^- & & CO \uparrow\downarrow L^- & & CO \uparrow\downarrow L^- \\ [Fe(CO)_3L_2]^{-\cdot} & \underset{CO}{\overset{Fe(CO)_5}{\rightleftharpoons}} & [Fe_2(CO)_6L_2]^{-\cdot} & \underset{CO}{\overset{Fe(CO)_5}{\rightleftharpoons}} & [Fe_3(CO)_9L_2]^{-\cdot} \end{array} \quad (6)$$

‡ Strictly speaking, the oxidation stages should be noted as $+(1/n)$ and $-(1/n)$, where n is the number of iron atoms in the corresponding species. One should keep this in mind when regarding the designations used in this review.

In this situation, $Fe(CO)_5$ acts as a peculiar spin trap stabilising the radical Fe(+1) complex by delocalisation of the unpaired electron over the iron carbonyl fragment. The subsequent oxidation, which happens during either disproportionation or catalysis, and substitution by electron transfer (ETC mechanism, see Section VI), yields the final diamagnetic products. The sequences of the reactions (6) represent the case where no transitions of the L^- ligand in the metal coordination sphere take place. The delocalisation of the unpaired electron on the ligand makes possible the reorganisation (reduction, oxycarbonyl bond formation, *etc.*) of this ligand followed by coordination of the modified ligands. The formation of bi- and polynuclear iron complexes with unusually coordinated modified ligands is well known.[106, 107]

As it was mentioned before, the reactions of iron carbonyls with Lewis bases generate unstable (with exception of radical anion **4**, see Table 1) electron-rich ICRA $[Fe_n(CO)_m]^{-\bullet}$. These ICRA are formed during single-electron redox disproportionation [reactions (2), (4)]. The ICRA are transformed into more stable electron-deficient species $[Fe_n(CO)_{m-1}]^{-\bullet}$ by decarbonylation. According to the Sedgwick's rule of closed 18-electron configuration, the transition from 19- to 17-electron complexes takes place during this process: §

$$[Fe_n(CO)_m]^{-\bullet} \longrightarrow [Fe_n(CO)_{m-1}]^{-\bullet} + CO. \quad (7)$$

Usually, the formation of ICRA **2**–**5** is observed in any combination of the starting iron carbonyl and the base.[76–79] Differences are only in the succession of their generation and consumption at various stages of the process. For example, in the reactions of $Fe(CO)_5$ with the bases, the radical anions are generated in the sequence **1**, **2**, **4** and **3**, **5**. The mononuclear radical anion **1** was detected at the initial stages of the reaction of $Fe(CO)_5$ with strong bases, such as NaOMe and NaOEt, in 2-methyltetrahydrofuran at -100 °C.[78] In similar reactions of $Fe_3(CO)_{12}$ the radical anions **3**, **4** are produced first and the radicals **2**, **5** are formed later. Species **2** is generated initially in the heterogeneous system containing $Fe_2(CO)_9$; radical anions **3**–**5** emerge at later stages. Similar succession of ICRA generation was observed during the reduction of iron carbonyls over a sodium mirror.[46] The equilibrium between ICRA **2**–**5** with the trinuclear radical anion **3** as the major component was observed at room temperature when the reaction was performed in a closed system, *e.g.*, in a sealed ampoule. Higher temperature shifts the equilibrium towards the species containing more metal atoms. At the same time the ESR signals of species **2**–**5** appear and become dominant during the generation of penta- and hexanuclear $[Fe_5C(CO)_{14}]^{-\bullet}$ and $[Fe_6C(CO)_{16}]^{-\bullet}$ radical anions in the temperature range from -30 °C to 50 °C.[77]

The coordination sphere of iron carbonyl radical anions **1**–**5** is quite labile and capable of fast ligand and electron exchange. This enables interconversions of radical ion clusters

$$\underset{\mathbf{1}}{[Fe(CO)_4]^{-\bullet}} + Fe(CO)_5 \rightleftharpoons \underset{\mathbf{2}}{[Fe_2(CO)_8]^{-\bullet}} + CO, \quad (8)$$

$$\underset{\mathbf{2}}{[Fe_2(CO)_8]^{-\bullet}} + Fe(CO)_5 \rightleftharpoons \underset{\mathbf{4}}{[Fe_3(CO)_{12}]^{-\bullet}} + CO, \quad (9)$$

$$\underset{\mathbf{4}}{[Fe_3(CO)_{12}]^{-\bullet}} \rightleftharpoons \underset{\mathbf{3}}{[Fe_3(CO)_{11}]^{-\bullet}} + CO, \quad (10)$$

$$\underset{\mathbf{3}}{[Fe_3(CO)_{11}]^{-\bullet}} + Fe(CO)_5 \rightleftharpoons \underset{\mathbf{5}}{[Fe_4(CO)_{13}]^{-\bullet}} + 3\,CO. \quad (11)$$

Donor compounds, particularly the solvent molecules (Solv), may take part in these processes [104]

$$[Fe_3(CO)_{12}]^{-\bullet} + Solv \rightleftharpoons [Fe_2(CO)_7 \cdot Solv]^{-\bullet} + Fe(CO)_5, \quad (12)$$

$$[Fe_2(CO)_7 \cdot Solv]^{-\bullet} + CO \rightleftharpoons [Fe_2(CO)_8]^{-\bullet} + Solv. \quad (13)$$

The reactions (8)–(11) represent a sort of radical-ion 'oligomerisation' of iron pentacarbonyl in solution. The same reaction may take place in the gas phase.[72–74] The reverse process, namely, a catalytic conversion of $Fe_3(CO)_{12}$ into $Fe(CO)_5$ by electron transfer, has been described.[108]

Being labile electron-deficient species, ICRA **1**, **2**, **3** and **5** tend to fill their electronic shells. Therefore, in the reactions of iron carbonyls with Lewis bases they convert into carbonylferrate dianions $[Fe_n(CO)_{m-1}]^{2-}$, containing 18, 34, 48 and 60 cluster valence electrons for n = 1, 2, 3 and 4 respectively. The unstable intermediate complexes of Fe(+1) mentioned above may act as reducing agents for iron carbonyl radical anions.[77]

Thus, in general, the reactions of iron carbonyls with Lewis acids proceed as two-electron disproportionations and afford traditional products of these transformations, the CFA salts.[13, 14]

IV. Reactions of (hydrido)carbonylferrate anions with Brønsted and Lewis acids

The (hydrido)carbonylferrate anion–Brønsted (or Lewis) acid system is the antipode of the previously discussed iron carbonyl–Lewis base system. It is very important to note that most of the carbonylation processes are catalysed by one of these systems.[19, 20, 84, 109, 110] Besides, the interaction of CFA and HCFA with Brønsted and Lewis acids may take place in non-catalytic processes as well, namely, in stoichiometric reactions giving aldehydes, ketones, carboxylic acids, esters and amides,[111] α-diketones,[112] and in the reduction of α,β-unsaturated carbonyl compounds.[113, 114] The iron carbonyl radical species were detected in early investigations of these reactions, but not identified, and this explains the interest in these processes.[113, 115] For example, the radicals are formed during the direct reduction of an alkyl halide (Lewis acid) by HCFA.[116, 117]

$$[HFe(CO)_4]^- + RHal \longrightarrow \underset{\mathbf{6}}{[HFe(CO)_4]^{\bullet}} + RHal^{-\bullet} \longrightarrow$$

$$\longrightarrow Fe(CO)_4 + RH + Hal^-.$$

The formation of a 16-electron intermediate species of the $Fe(CO)_4$ type is traditionally suggested in this reaction, as in Schemes 1 and 2. The existence of this species in solution has been discussed in the Introduction. Besides, the direct reduction of RHal is also thermodynamically unlikely and possible only in the case of aromatic iodides with the smallest negative reduction potentials.[109, 118] Intensive generation of ICRA **2**–**5** in the reactions of CFA and HCFA with Lewis and Brønsted acids has been observed by ESR spectroscopy.[59] These radical anions are identical to those formed in the reactions of iron carbonyls with Lewis bases. The hypothesis of 'activating complex formation', used previously to explain the mechanism of the reactions of iron carbonyls with Lewis bases (see Section 3), has been used to explain this fact too. The only difference between these two cases is that CFA or HCFA play a donor role (B^-), while their complexes (BA) with the acid (A^+) are acceptors. If the donor (CFA or HCFA) cannot directly reduce an acceptor (an acid), but the formation of their complex is still possible, then this complex may take part in a single-electron transfer, which thus becomes achievable (Scheme 4).

Scheme 4

$$B^- + A^+ \not\longrightarrow B^{\bullet} + A^{\bullet},$$

$$B^- + A^+ \longrightarrow BA,$$

$$B^- + BA \longrightarrow B^{\bullet} + BA^{-\bullet}.$$

§ In fact, the electron shells of ICRA **1**–**5** contain 17, 33, 47, 49 and 59 cluster valence electrons respectively. The 18-electron closed shell configuration rule is conventionally accepted for clarity and in order to compare the complexes with different numbers of metal atoms.

According to Scheme 4, the activating complex formation stage corresponds to the well known processes: either the protonation of CFA or HCFA

$$[Fe_n(CO)_{m-1}]^{2-} \underset{-H^+}{\overset{H^+}{\rightleftharpoons}} [HFe_n(CO)_{m-1}]^- \underset{-H^+}{\overset{H^+}{\rightleftharpoons}} H_2Fe_n(CO)_{m-1},$$

$n = 1, m = 5; n = 2, m = 9; n = 3, m = 12; n = 4, m = 14;$

or the oxidative addition of alkyl and acyl halides to them[15, 93, 109, 111, 113, 119–124]

$$[Fe(CO)_4]^{2-} + RX \longrightarrow [RFe(CO)_4]^- + X^-, \quad (14)$$

$$[RFe(CO)_4]^- + R'X \longrightarrow R'RFe(CO)_4 + X^-, \quad (15)$$

R = H: R′ = Alk, AlkC(O); R = R′ = Alk, Ar, AlkC(O), ArC(O); X = Cl, Br, 4-$MeC_6H_4SO_2$ (Ts).

The reactions (14) and (15) are given for well studied mononuclear iron complexes, which are most active in the redox transformations affecting the metal coordination centres.¶

The electron transfer itself happens at the next step during the reduction of the formed neutral complex $R'RFe(CO)_4$

$$[RFe(CO)_4]^- + R'RFe(CO)_4 \longrightarrow [RFe(CO)_4]^{\bullet} + [R'RFe(CO)_4]^{-\bullet}. \quad (16)$$

A similar electron transfer stage for protonated complexes CFA looks as follows:

$$[HFe_n(CO)_{m-1}]^- + H_2Fe_n(CO)_{m-1} \longrightarrow [HFe_n(CO)_{m-1}]^{\bullet} + [H_2Fe_n(CO)_{m-1}]^{-\bullet}. \quad (17)$$

The pure starting compounds without any traces of the oxidation products are required in order to confirm that the electron transfer occurs during this stage of the reaction. This was achieved, for example, by vacuum distillation of complex $H_2Fe(CO)_4$ [R = R′ = H in reaction (16) or $n = 1$, $m = 5$ in reaction (17)] directly into an ampoule located in the cavity of an ESR spectrometer.[59] No ESR signals were observed in a solution of $H_2Fe(CO)_4$ in 2-methyltetrahydrofuran at temperatures below −60 °C. A similar situation has been found in the case of a solution of (PPN)[$HFe(CO)_4$] in MeTHF over a wide range of temperatures up to room temperature. At the same time, the reaction of $H_2Fe(CO)_4$ with (PPN)[$HFe(CO)_4$] in this solvent results in the appearance of ICRA signals at as low as −100 °C. It was shown,[59] that 17-electron radical $[HFe(CO)_4]^{\bullet}$ and 19-electron radical anion $[H_2Fe(CO)_4]^{-\bullet}$, formed at the electron-transfer stage of the reaction, are unstable under these conditions and are quickly converted into $[Fe_2(CO)_8]^{-\bullet}$ by reactions (18) and (19), (20), respectively.

$$\underset{\mathbf{6}}{[HFe(CO)_4]^{\bullet}} + [HFe(CO)_4]^- \longrightarrow \underset{\mathbf{2}}{[Fe_2(CO)_8]^{-\bullet}} + H_2, \quad (18)$$

$$[H_2Fe(CO)_4]^{-\bullet} \longrightarrow [Fe(CO)_4]^{-\bullet} + H_2, \quad (19)$$

$$\underset{\mathbf{1}}{[Fe(CO)_4]^{-\bullet}} + H_2Fe(CO)_4 \longrightarrow \underset{\mathbf{2}}{[Fe_2(CO)_8]^{-\bullet}} + H_2. \quad (20)$$

Radical anions **3**–**5**, **11** containing greater numbers of metal atoms arise in reactions (21) and (9)–(11).

$$[Fe_2(CO)_8]^{-\bullet} + H_2Fe(CO)_4 \longrightarrow \begin{cases} \underset{\mathbf{4}}{[Fe_3(CO)_{12}]^{-\bullet}} + H_2 \\ \underset{\mathbf{11}}{[H_2Fe_3(CO)_{10}]^{-\bullet}} + CO \end{cases} \quad (21)$$

The transformations of $RR'Fe(CO)_4$ complexes (R = H, R′ = Alk, Ac) should be particularly noted. These are the key compounds in many processes involving $[HFe(CO)_4]^-$ (Ref. 106). In this case, reaction (16) is as follows:

$$[HFe(CO)_4]^- + R'HFe(CO)_4 \longrightarrow [HFe(CO)_4]^{\bullet} + [R'HFe(CO)_4]^{-\bullet}. \quad (22)$$

The unstable 19-electron complex $[R'HFe(CO)_4]^{-\bullet}$ formed initially is transformed into the more stable 17-electron species by elimination of R′H or CO [reaction (23)]. In the latter case, the $[R'HFe(CO)_3]^{-\bullet}$ radical anions are formed. They were detected in the reactions of acyl halides R′X (R′ = Ac, Bz) with $[HFe(CO)_4]^-$ (Ref. 59).

$$[R'HFe(CO)_4]^{-\bullet} \longrightarrow \begin{cases} [Fe(CO)_4]^{-\bullet} + R'H \\ [R'HFe(CO)_3]^{-\bullet} + CO \end{cases} \quad (23)$$

It is remarkable that the $[R'Fe(CO)_4]^-$ and $[HFe(CO)_4]^-$ anions do not react with each other. For instance, propionaldehyde is not formed in the reaction between $[EtC(O)Fe(CO)_4]^-$ and $[HFe(CO)_4]^-$; however it is formed in 57% yield when the acetic acid, which partially protonates the $[HFe(CO)_4]^-$, is added to the reaction mixture.[125] This confirms that the process proceeds according to pathway (22). The yield of the target compound, which is approximately half of the theoretical one, points out to the partial protonation of $[HFe(CO)_4]^-$ and its consumption according to reactions (16) (for R = R′ = H) and (18)–(20).

As it was noted before, on the one hand, ICRA are relatively stable species (during the reaction their steady-state concentrations may be fairly high). On the other hand, these ICRA are coordinatively unsaturated electron-deficient systems with labile coordination sphere capable of fast ligand and electron exchange. An important consequence of these two characteristics is the ability of ICRA to add Brønsted or Lewis acids. These reactions are the key stages in a number of reduction and carbonylation processes of various compounds. Initially, the radical anion reacts with an electron acceptor (the corresponding acid):

$$[Fe(CO)_4]^{-\bullet} + RX \longrightarrow [RFe(CO)_4]^{\bullet} + X^-,$$

and then, similarly to reaction (18), species **2** are formed.

$$[RFe(CO)_4]^{\bullet} + [HFe(CO)_4]^- \longrightarrow RH + \underset{\mathbf{2}}{[Fe_2(CO)_8]^{-\bullet}}. \quad (24)$$

The subsequent transformations of the ICRA are of the radical chain type and are accompanied by the increase in the number of metal atoms in the radical complex:

$$[Fe_2(CO)_8]^{-\bullet} + RX \longrightarrow [RFe_2(CO)_8]^{\bullet} + X^-,$$

$$[RFe_2(CO)_8]^{\bullet} + [HFe(CO)_4]^- \longrightarrow RH + \underset{\mathbf{4}}{[Fe_3(CO)_{12}]^{-\bullet}}. \quad (25)$$

Radical anions **3** and **5** are reduced to corresponding CFA by reactions (26) and (27) at the final stages of the interaction of (hydrido)carbonylferrate anions with Brønsted and Lewis acids. The reduction potentials of these CFA make the processes thermodynamically favourable.[42, 126]

$$\underset{\mathbf{3,5}}{[Fe_n(CO)_{m-1}]^{-\bullet}} + [Fe_p(CO)_{q-1}]^{2-} \longrightarrow [Fe_n(CO)_{m-1}]^{2-} + \underset{\mathbf{1,2}}{[Fe_p(CO)_{q-1}]^{-\bullet}}, \quad (26)$$

¶ Tri- and tetranuclear CFA can be alkylated and acylated at the carbonyl group resulting in the formation of the $[Fe_n(CO)_{m-2}(COR)]^-$ (R = Me, Ac; $n = 3$, $m = 12$; $n = 4$, $m = 14$) complexes, which mainly tend to undergo transformations of the carbonyl ligand.[15]

$$[Fe_n(CO)_{m-1}]^{-\bullet} + [HFe(CO)_4]^- \longrightarrow$$
$$\mathbf{3, 5}$$
$$\longrightarrow [Fe_n(CO)_{m-1}]^{2-} + [HFe(CO)_4]^{\bullet}, \quad (27)$$
$$\mathbf{6}$$

$n = 3, m = 12$ (**3**); $n = 4, m = 14$ (**5**); $p = 1, q = 5$ (**1**); $p = 2, q = 9$ (**2**).

The final products of the reaction are diamagnetic compounds, mainly the modified organic ligands and polynuclear CFA and HCFA.

Thus, the reactions of (hydrido)carbonylferrate anions with the Brønsted and Lewis acids, like the reactions of iron carbonyls with Lewis bases, may be described as radical chain processes which include the preliminary activating complex formation and the redox initiation stage.

V. Reactions of iron carbonyls with carbonylferrate anions

It is believed that the nucleophilic displacement of the CO groups in the reactions of diamagnetic iron carbonyls and carbonylferrate anions results in the formation of CFA with an increased number of metal atoms Thus, the reaction of $Fe(CO)_5$ with $[Fe(CO)_4]^{2-}$ yields $[Fe_2(CO)_8]^{2-}$ [reaction (28)]:[42, 43, 113, 127–129]

$$Fe(CO)_5 + [Fe(CO)_4]^{2-} \longrightarrow [Fe_2(CO)_8]^{2-} + CO. \quad (28)$$

The $[Fe_3(CO)_{11}]^{2-}$ anion is formed from $Fe(CO)_5$ and $[Fe_2(CO)_8]^{2-}$ (Ref. 127)

$$Fe(CO)_5 + [Fe_2(CO)_8]^{2-} \longrightarrow [Fe_3(CO)_{11}]^{2-} + 2\,CO,$$

while the reaction of $[Fe_3(CO)_{12}$ with $[Fe(CO)_4]^{2-}$ results in the formation of $[Fe_4(CO)_{13}]^{2-}$ (Ref. 130):

$$Fe_3(CO)_{12} + [Fe(CO)_4]^{2-} \longrightarrow [Fe_4(CO)_{13}]^{2-} + 3\,CO.$$

It was shown [77] that the $[Fe(CO)_4]^{2-}$ and $[Fe_2(CO)_8]^{2-}$ anions easily react with $Fe(CO)_5$ and $Fe_3(CO)_{12}$, ICRA **2**–**5** being formed at the initial steps of the reaction. At the same time, the reactions of tri- and tetranuclear CFA salts, $[Fe_3(CO)_{11}]^{2-}$ or $[Fe_4(CO)_{13}]^{2-}$, with $Fe_3(CO)_{12}$ give first mainly heavier radical anions **3**–**5**. It should be noted that the reaction of $(PPN)_2[Fe_3(CO)_{11}]$ with $Fe_3(CO)_{12}$ is the preparative method for the synthesis of the stable radical anion salt, $(PPN)[Fe_3(CO)_{11}]^{-\bullet}$ (Ref. 131). These data show that in the reactions of carbonylferrate anions with iron carbonyls, single-electron transfer takes place at low degrees of conversion.

$$[Fe_p(CO)_{q-1}]^{2-} + Fe_n(CO)_m \longrightarrow$$
$$\longrightarrow [Fe_p(CO)_{q-1}]^{-\bullet} + [Fe_n(CO)_{m-1}]^{-\bullet} + CO,$$

for $p = 1, q = 5$ and $p = 2, q = 9$: $n = 1, m = 5$; $n = 2, m = 9$; $n = 3, m = 12$; for $p = 3, q = 12$ and $p = 4, q = 14$: $n = 3, m = 12$.

Such process may be regarded as direct single-electron reduction of iron carbonyls,† which is quite natural, taking into account the high reduction potentials of CFA (Fig. 1).[42]

The two-electron reduction potential ($E_{red} = -1.77$ V) [39] for $Fe(CO)_5$ is shown in Fig. 1. This potential, probably, corresponds to the reduction of iron pentacarbonyl in very fast reactions of types (7) (for $n = 1, m = 5$) and (8) followed by the reduction of $[Fe_2(CO)_8]^{-\bullet}$ to the corresponding anion. In the electrochemical terms, this corresponds to the two-electron reduction with an intermediate chemical stage (ECE). The value $E_{1/2\,red} = -2.67$ V has been reported [43] for the reduction potential of $Fe(CO)_5$, which is probably related to the supporting electrolyte used, Bu_4NBF_4 ($E_{1/2\,red} = -2.75$ V [132]).

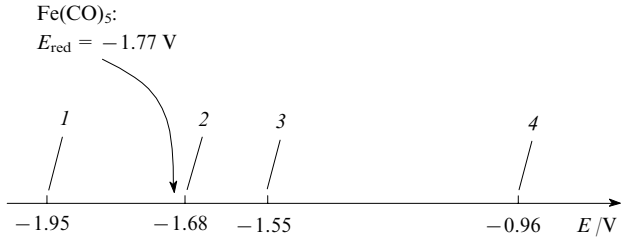


Figure 1. The scale of the redox potentials of the following pairs: $[Fe(CO)_4]^{2-}/[Fe(CO)_4]^{-\bullet}$ (*1*), $[Fe_2(CO)_8]^{2-}/[Fe_2(CO)_8]^{-\bullet}$ (*2*), $[Fe_3(CO)_{11}]^{2-}/[Fe_3(CO)_{11}]^{-\bullet}$ (*3*) and $[Fe_4(CO)_{13}]^{2-}/[Fe_4(CO)_{13}]^{-\bullet}$ (*4*) in THF.[42]

Whereas the interaction of trinuclear $[Fe_3(CO)_{11}]^{2-}$ and $Fe_3(CO)_{12}$ complexes ($E_{1/2\,red}$ from -0.32 to -0.44 V [38, 39]) in an open system results in the formation of trinuclear ICRA **3** and **4**, the reaction of tetracarbonylferrate anion with iron pentacarbonyl proceeds as a radical chain reaction. The reaction gives $[Fe_2(CO)_8]^{2-}$ when the concentrations of the starting compounds are equimolar [see reaction (28)].

$$[Fe(CO)_4]^{2-} + Fe(CO)_5 \longrightarrow 2\,[Fe(CO)_4]^{-\bullet} + CO,$$
$$[Fe(CO)_4]^{-\bullet} + Fe(CO)_5 \longrightarrow [Fe_2(CO)_8]^{-\bullet} + CO,$$
$$[Fe_2(CO)_8]^{-\bullet} + [Fe(CO)_4]^{2-} \longrightarrow [Fe_2(CO)_8]^{2-} + [Fe(CO)_4]^{-\bullet}.$$

With excess iron pentacarbonyl, the process continues further to give trinuclear CFA incapable any more of reducing the starting iron pentacarbonyl at ambient temperature at the final stage of the reaction.

$$[Fe_2(CO)_8]^{2-} + Fe(CO)_5 \longrightarrow [Fe_2(CO)_8]^{-\bullet} + [Fe(CO)_4]^{-\bullet} + CO,$$
$$[Fe_2(CO)_8]^{-\bullet} + Fe(CO)_5 \rightleftharpoons [Fe_3(CO)_{12}]^{-\bullet} + CO,$$
$$[Fe_3(CO)_{12}]^{-\bullet} \rightleftharpoons [Fe_3(CO)_{11}]^{-\bullet} + CO,$$
$$[Fe_3(CO)_{11}]^{-\bullet} + [Fe(CO)_4]^{2-} \longrightarrow$$
$$\longrightarrow [Fe_3(CO)_{11}]^{2-} + [Fe(CO)_4]^{-\bullet},$$
$$[Fe_3(CO)_{11}]^{-\bullet} + [Fe_2(CO)_8]^{2-} \longrightarrow$$
$$\longrightarrow [Fe_3(CO)_{11}]^{2-} + [Fe_2(CO)_8]^{-\bullet}.$$

The radical chain process with single-electron redox steps ends in the formation of diamagnetic complexes. In a closed system, when CO is not removed from the reaction vessel, the iron carbonyl radical anions **2**–**5** are in equilibrium [reactions (9)–(13)].

A series of papers [127, 131, 133–137] dealing with the reactions of CFA with other metal carbonyls and the reactions of anionic carbonyl compounds of various metals with iron carbonyls should be noted. The electron transfer between such complexes and the formation of ICRA at the intermediate stages of the process have been discussed.[127, 134, 135, 137] The charge transfer in the $A_2[Fe_2(CO)_8]$ salts, where A are *N*-methylated pyridine derivatives, PPN, Ph_4P or the organometallic cation $[CpFe(C_6H_6)]^+$ (Cp is cyclopentadienyl), has been described.[138] The electron transfer in this system results in the formation of radical anion **2**, which undergoes subsequent conversions.

$$[Fe_2(CO)_8]^{2-} + A^+ \longrightarrow [Fe_2(CO)_8]^{-\bullet} + A^{\bullet}.$$
$$\mathbf{2}$$

The structures of $[Li_2(THF)_6Fe_2(CO)_8]$ and $[Li_2(THF)_4Fe_2(CO)_8]_n$ complexes in which the iron carbonyl fragment contains two bridging CO ligands with coordinated $Li(THF)_3$ and $Li(THF)_2$ groups have been determined by X-ray

† This scheme of the direct reduction may be regarded as a variant of the redox disproportionation with the preliminary activating complex formation stage, if the 'additional' lone pair of CFA is considered as a donor ligand.

crystallography.[139] A similar structure of the $Fe_2(CO)_8$ fragment was suggested for the $[Fe_2(CO)_8]^{-\bullet}$ radical anion.[7,63] On the contrary, the structure of the corresponding carbonylferrate anion $[Fe_2(CO)_8]^{2-}$ does not contain any bridging groups, two $Fe(CO)_4$ fragments being linked only by the Fe–Fe bond.[133,138,140,141] It should be noted that the lithium salt with the $[Fe(CO)_4]^{2-}$ anion is unknown in a pure state. As the reduction potential of Li^+ ($E_{1/2\,red}$ from −1.42 to −1.82 V)[142,143] is less negative than the redox potential of the $[Fe(CO)_4]^{2-}/[Fe(CO)_4]^{-\bullet}$ pair (see Fig. 1), the reduction of Li^+ occurs. In the case of $[Li_2(THF)_6Fe_2(CO)_8]$ and $[Li_2(THF)_4Fe_2(CO)_8]_n$ complexes, when the redox potential of the $[Fe_2(CO)_8]^{2-}/[Fe_2(CO)_8]^{-\bullet}$ pair (see Fig. 1) falls in the $E_{1/2\,red}$ region of lithium, charge transfer from CFA to Li^+ may take place followed by the rigid fixation of the cation in a contact ion pair. The presence of two different types of lithium atoms in the structure of the polymeric complex also supports this suggestion.

Thus the carbonylferrate anions are quite strong reducing agents, able to take part in the direct single-electron reduction of various substrates, including iron carbonyls. The iron carbonyl radical anions are formed in these processes and the radicals undergo further conversions by a radical chain mechanism.

VI. Nucleophilic substitution and catalytic conversions of iron carbonyls induced by electron transfer

A series of papers on the nucleophilic substitution of CO by phosphine, phosphite and isocyanate ligands in iron carbonyl complexes under the conditions of preliminary chemical or electrochemical reduction of the initial complex to the corresponding radical anion was published in the early 1980s. The trinuclear iron carbonyl complex $Fe_3(CO)_{12}$ (Refs 60, 144–146) and complexes of the $Fe_3(\mu_3\text{-}E)_2L(CO)_8$ type, where L = CO: E = NAr, PPh, S, Se;[147–151] E_2 is 2,3-diazanorbornene;[152] L = $C_3H_2S_2$, E = S[153,154] were the main objects of these studies. The replacement of CO in iron pentacarbonyl by phosphine and phosphite ligands, initiated by sodium benzophenone ketyl, has been described.[155] It appeared that these processes correspond to the known substitution reactions or to the catalytic conversions induced by electron transfer:[156–158]

$$MCO + e \xrightarrow{E_1^\circ} MCO^{-\bullet}, \quad (29)$$

$$MCO^{-\bullet} \longrightarrow M^{-\bullet} + CO, \quad (30)$$

$$M^{-\bullet} + L \longrightarrow ML^{-\bullet}, \quad (31)$$

$$ML^{-\bullet} \xrightarrow{E_2^\circ} ML + e, \quad (32)$$

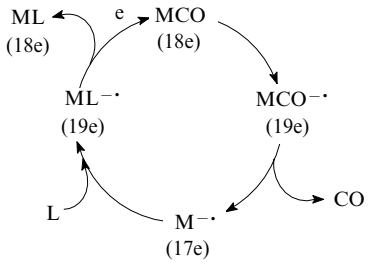
$$ML^{-\bullet} + MCO \longrightarrow ML + MCO^{-\bullet}, \quad (33)$$

MCO is iron carbonyl complex,
L = PR_3, $P(OR)_3$, NCR (R = Alk, Ar).

If the standard elecrochemical potentials of reactions (29) and (32) obey the inequality $E_2^\circ > E_1^\circ$, then the electron-induced nucleophilic substitution, EINS, takes place.[140,155] If $E_1^\circ > E_2^\circ$, then a catalysed reaction called electron-transfer chain catalysis (ETC) takes place.[146,157,158] The catalytic cycle is shown in Scheme 5.

Reactions (29)–(33) and Scheme 5 represent the simplest case of an ETC process without taking into account the interconversions of the intermediate 19-electron ($MCO^{-\bullet}$ and $ML^{-\bullet}$) and 17-electron ($M^{-\bullet}$) radical anions. After the electron addition in reaction (29) the reorganisation of the radical anions accompanied by the change in the number of iron atoms in the metal core and rearrangement of the coordination sphere are possible [see, for example, reactions (6), (8)–(10) in Section III and also the papers [108,159]].

Scheme 5



In spite of the fact that no data on the ETC processes involving intermediate 17-electron radical cations are known for iron carbonyls, similar reactions for the carbonyls of Group VI metals were described in the literature.[160] As applied to the iron carbonyls, these transformations may be described as follows (Scheme 6):

Scheme 6

$$MCO \xrightarrow{E_1^\circ} MCO^{+\bullet} + e,$$

$$MCO^{+\bullet} + L \longrightarrow MCOL^{+\bullet},$$

$$MCOL^{+\bullet} \longrightarrow ML^{+\bullet} + CO,$$

$$ML^{+\bullet} + e \xrightarrow{E_2^\circ} ML,$$

$$ML^{+\bullet} + MCO \longrightarrow ML + MCO^{+\bullet},$$

MCO is iron carbonyl complex,
L = PR_3, $P(OR)_3$ (R = Alk, Ar).

If $E_1^\circ > E_2^\circ$, then electron-induced nucleophilic substitution takes place. For instance, the nucleophilic substitution of the CO group in the $[Fe(CO)_3(PPh_3)_2]^{+\bullet}$ radical cation yielding the $[Fe(CO)_2.(PPh_3)_2(L-L)]^{+\bullet}$ complex, where L–L are 1,2-diketones, *o*-chloranyl, 1,2-naphthoquinone, belongs to this type of reaction.[102,161] If $E_2^\circ > E_1^\circ$, the catalytic ETC process occurs. Only one example of ETC process in which the addition of the nucleophilic anion (EtS^-) is followed by rearrangement of the metal skeleton is known for 17-electron Fe(+1) carbonyl complexes.[96]

$$[Fe_3(CO)_{11}C(O)SEt]^- \xrightarrow[-e]{} [Fe_3(CO)_{11}C(O)SEt]^\bullet, \quad (34)$$

$$[Fe_3(CO)_{11}C(O)SEt]^\bullet \longrightarrow [Fe_2(CO)_7SEt]^\bullet + Fe(CO)_5, \quad (35)$$

$$[Fe_2(CO)_7SEt]^\bullet + [Fe_3(CO)_{11}C(O)SEt]^- \longrightarrow [Fe_2(CO)_7SEt]^- + [Fe_3(CO)_{11}C(O)SEt]^\bullet. \quad (36)$$

Thus, in the ETC processes involving complex iron carbonyl radical ions, ligand exchange takes place in the coordination sphere of a complex with incomplete 17-electron configuration. This is a radical chain process; however its final products are diamagnetic.

VII. Iron carbonyls as reducing agents

It was shown in Section III that disproportionation reactions of iron carbonyls with Lewis bases include a stage of activating complex formation followed by single-electron transfer from the carbonyl complex activated by the electron donor to another molecule of the starting carbonyl. This gives complexes of iron in the oxidation state (+1) and radical anions containing iron in the oxidation state (−1) [see reactions (1)–(4)]. If the reaction mixture contains a third component (Q), more easily reducible than the starting iron carbonyl, then the reduction of only this component is possible.

$$Fe(CO)_5 + L \rightleftharpoons Fe(CO)_4C(O)L, \quad (37)$$

$$Fe(CO)_4C(O)L + Q \rightleftharpoons [Fe(CO)_4C(O)L]^{+\bullet} + Q^{-\bullet}, \quad (38)$$

L is a Lewis base.

The situation represented by reactions (37) and (38) occurs when the reduction potentials of the compound Q are higher than those of iron pentacarbonyl [$E_{1/2\,red} = -1.77$ V in THF *vs.* the saturated calomel electrode (SCE)],[39] as, for example in the case of the nitroso compound Bu^tNO [$E_{1/2\,red} = -1.36$ V (MeCN, SCE)];[162] haloalkanes, *viz.*, CCl_4 [$E_{1/2\,red} = -0.78$ V (dioxane, SCE)][163] and $CHCl_3$ [$E_{1/2\,red} = -1.68$ V (dioxane, SCE)],[163] as well as sulfur [$E_{1/2\,red} = -1.077$ V in DMF *vs.* the Fc/Fc^+ couple (Fc is ferrocene)[164]].

A study of the reaction of $Fe(CO)_5$ with 2-methyl-2-nitrosopropane (Bu^tNO) in THF or toluene in the absence of electron donors has shown that at 20 °C, the induction period of the reaction is rather long (~20 min).[76] The fast accumulation of the $Fe(CO)_3NO^\bullet$ [$Fe(1^+)$] and $Bu^tNO^{-\bullet}$, which are subsequently converted into the stable radicals $(OC)_3(NO)FeN^\bullet(O)Bu^t$ and $Bu^t_2NO^\bullet$, takes place after this period.

$$\begin{aligned} &Fe(CO)_3NO^\bullet + Bu^tNO \longrightarrow (OC)_3(NO)FeN^\bullet(O)Bu^t \\ &Bu^tNO^{-\bullet} \longrightarrow (Bu^t)^\bullet + NO^-, \\ &(Bu^t)^\bullet + Bu^tNO \longrightarrow Bu^t_2NO^\bullet. \end{aligned} \quad (39)$$

The intermediate nitrosyl anion NO^- initiates the already discussed scheme of redox disproportionation of $Fe(CO)_5$ under the action of an anionic nucleophile.

$$\begin{aligned} &Fe(CO)_5 + NO^- \longrightarrow [Fe(CO)_4C(O)NO]^-, \\ &[Fe(CO)_4C(O)NO]^- + Bu^tNO \longrightarrow \\ &\quad \longrightarrow Fe(CO)_3NO^\bullet + 2\,CO + Bu^tNO^{-\bullet}. \end{aligned} \quad (40)$$

After the end of the induction period, the process proceeds as a chain reaction, which is provided by the formation of $Bu^tNO^{-\bullet}$ in reaction (40) and its decomposition [reaction (39)]. In the case of excess $Fe(CO)_5$ relative to Bu^tNO, after complete decomposition of nitroso compound, the resulting $Bu^t_2NO^\bullet$ [$E_{1/2\,red} = -1.63$ V (MeCN, SCE)][165] is reduced to the hydroxylamine anion according to a scheme similar to reaction (38).

The $Fe(CO)_5$–Lewis base system (L = DMF, HMPA, tertiary amines, *etc.*) is widely used as an initiator for radical addition, telomerisation of olefins with haloalkanes and the reduction of polychloro-substituted compounds.[166–171] Haloalkanes (mainly, polyhaloalkanes) are quite reactive in these processes, because they are reduced more easily than iron pentacarbonyl. The scheme of the process initiation may be represented by reactions (37), (38), where L is DMF or HMPA, and Q is an easily reduced haloalkane RX. The resulting $RX^{-\bullet}$ radical anion decomposes to give the $R^\bullet$ radical, which subsequently participates in the radical process, and a halide ion X^-. The latter reacts with $Fe(CO)_5$, as a Lewis base, as described above, thus enhancing the initiation of subsequent transformations. The intermediate species of the single electron redox process, namely, the Fe^+ carbonyl complexes, for example $Cl(OC)_4FeN^\bullet(O)Bu^t$, and alkyl radicals, were identified by spin-trap methods.[99,169–171] In the presence of olefins, diamagnetic Fe^{2+} complexes and the products of addition of haloalkanes to the double C=C bond are the final products of telomerisation. Without olefins the reaction of $Fe(CO)_5$ with polyhalomethanes CCl_3X (X = Cl, Br) in the presence of DMF yields hexachloroethane, which is also evidence for the radical $Cl_3C^\bullet$ generation.[172,173] In the presence of hydrogen donors (alcohols, mercaptans, organosilicon hydrides), the hydrogen atom adds to the $RCCl_2^\bullet$ radical formed upon decomposition of $RCCl_3$. Thus, readily available compounds containing a trichloromethyl group are reduced to dicloro derivatives.[169]

A study[174] of the reaction of $Fe(CO)_5$ with sulfur (S_8) in THF at 20 °C has demonstrated that after the induction period (> 10 min), the ESR spectra exhibit a broadened signal for $S_3^{-\bullet}$ with $g = 2.031$ (according to the literature, $g = 2.032$[175] and 2.033[176]). However, no ICRA are detected. The stable radical anion $S_3^{-\bullet}$, together with S_n^{2-} ($n < 8$), is formed from $S_8^{-\bullet}$ through a relatively complicated disproportionation.[164,177,178] The polysulfide dianions S_n^{2-}, being Lewis bases, initiate the redox process according to reactions (38) and (39), where $Q = S_8$. The identification of the Fe^+ radical carbonyl complexes in this system is difficult, because their signals overlap with the broad signal of $S_3^{-\bullet}$. However, the formation of diamagnetic complexes of the $S_2Fe_2(CO)_6$, $S_2Fe_3(CO)_9$ and $SFe_3(CO)_{10}$ type[179–181] points to the fact that their precursors are the Fe^+ radical ion complexes, which are involved in the transformations similar to reaction (6).

If an unsaturated compound is introduced in the reaction of an iron carbonyl with S_8, the $S_n^{-\bullet}$ radical anions appearing in the system will add to the double bond, forming cyclic polysulfides, various organic sulfur derivatives and their iron carbonyl complexes.[181,182] This process may be used for the low-temperature vulcanisation of resins. It was also reported that $Fe(CO)_5$ in the presence of sulfur is an effective catalyst of lignite and bituminous coal liquefaction under hydrogen[183,184] or water gas ($CO + H_2O$)[185] gasifications.

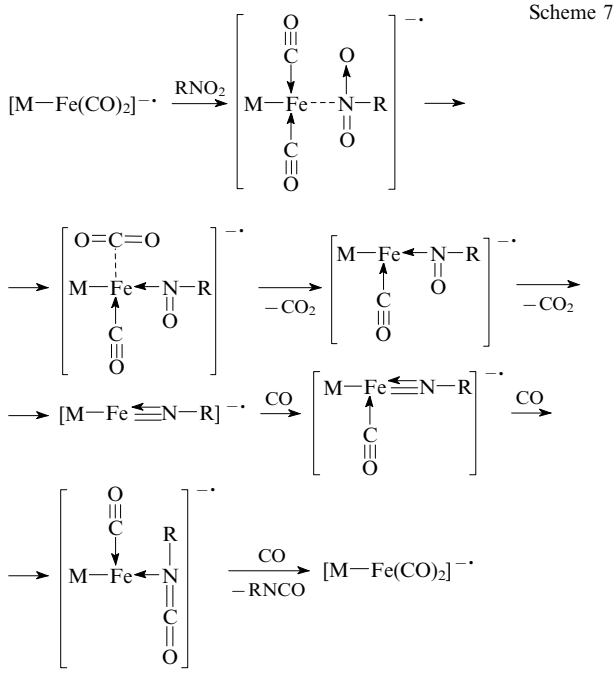
Thus, in the reactions with Lewis bases in the presence of compounds reduced more easily than iron pentacarbonyl, $Fe(CO)_5$ forms an activated complex with a Lewis base and acts as a single-electron reducing agent. The resulting Fe^+ radical carbonyl derivatives are then oxidised either to Fe^{2+}, or to diamagnetic carbonyl complexes of the $L_2Fe_2(CO)_6$, $L_2Fe_3(CO)_9$ and $LFe_3(CO)_{10}$ type, where L is a nucleophilic ligand. Another reaction pathway is determined by the $Q^{-\bullet}$ radical anion formed upon the reduction.

VIII. Catalytic processes involving iron carbonyl radical anions

The catalytic transformations of iron carbonyls in the processes of carbonylation of various compounds are usually described by a scheme constructed according to the Tolman rule for determination of the major reaction pathway *via* complexes with even numbers of electrons in the outer shell (18e → 16e → 18e). However, all attempts to prove this mechanism failed. In fact, catalytic processes of carbonylation with iron carbonyl complexes include reactions of two types: the redox disproportionation of iron carbonyls induced by Lewis bases (see Section III) and the oxidative addition of Brønsted and Lewis acids to the (hydrido)-carbonylferrate anions (see Section IV).[19,20,84,109,110] In both cases, ICRA **2**–**5** are formed. These ICRA are fairly stable and their steady-state concentrations during the reaction may be high (10^{-5}–10^{-2} mol litre^{-1}). At the same time, ICRA **2**, **3** and **5** are coordinatively unsaturated electron-deficient systems with a labile coordination sphere, capable of fast ligand and electron exchange. Usually reactions involving these ICRA follow a radical chain mechanism (see Sections III and IV); therefore these species are, most likely, catalysts of carbonylation. The catalytic activity of ICRA was demonstrated for the first time in the reductive carbonylation of nitro and nitroso compounds[76] and was confirmed later[56,57] with $[Fe_3(CO)_{11}]^{-\bullet}$ as a model compound.[56,57] Radical anion nitrene complexes were found by ESR method in the reactions of Bu^tNO_2 and Bu^tNO with participation of the ICRA (Scheme 7).

Scheme 7 depicts the case where only one molecule of nitro compound is present in the coordination sphere of an iron carbonyl cluster. This molecule is reduced consecutively to nitroso derivative and then to the nitrene complex. If the process is carried out in the catalytic mode with a controlled negative reduction potential of the medium, the intermediate nitrene complexes are carbonylated to give isocyanates and the starting ICRA. The iron

Scheme 7



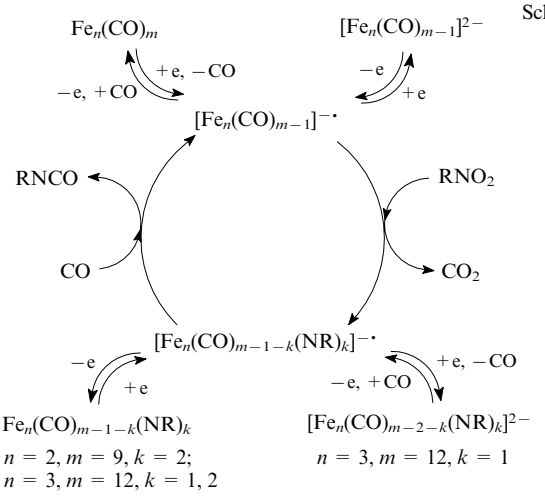
M = $Fe_{n-1}(CO)_{m-3}$.

oxidation state (−1) in the catalytic species remains unchanged in this process. The addition of the second molecule of the nitro compound yields intermediate radical species containing ligands with nitro groups reduced to different extent.[76]

If the reaction is carried out with a stoichiometric component ratio, the reduction of nitrogen-containing ligands may end after the formation of nitrene structures. In the absence of an adequate reduction potential of the medium and with additional supply of carbon monoxide, the nitrogen-containing ligands in intermediate complexes are reduced at the expense of oxidation of Fe(−1) into Fe(+1). Further on, the radical anions lose the unpaired electron to be transformed into well known diamagnetic complexes with d^7 electron configuration of the iron atom, for example, into $Fe_2(CO)_6(NR)_2$, $Fe_3(CO)_9(NR)_2$, $Fe_3(CO)_{10}NR$, *etc.*[186,187] This results in withdrawal of the complex from the catalytic cycle, and the subsequent formation of isocyanates becomes impossible (Scheme 8).

In the presence of proton donors in the reaction mixture, the nitro compounds are reduced to amines.[56,188] The intermediate radical anion nitrene complexes may be stabilised by being

Scheme 8



reduced to diamagnetic anions, $[Fe_3(CO)_9NR]^{2-}$ and $[HFe_3(CO)_9NR]^-$ (Ref. 56).

It is noteworthy that the catalytically active species are 17-electron radical anions; in the process of catalysis, they add a ligand, *e.g.*, CO, and are transformed into 19-electron species. The latter eliminate the product being thus converted into the original electron-deficient form. There is a possibility of the transformation of an electron-rich system into an electron-deficient one upon cluster core rearrangement due to breaking of the Fe−Fe or Fe−N bonds and upon localisation of the excessive electron on the ligand. In these cases, a new bond is formed between the coordinated ligands, for example, CO−NR, or their reduction, for example into the RNH ligand, takes place in the presence of proton donors. These transformations afford various diamagnetic complexes, which may be isolated upon the reaction of iron carbonyls with nitro compounds.[186,189]

Thus, the catalytic cycle of reductive carbonylation of nitro and nitroso compounds catalysed by ICRA includes transformations *via* complexes 17e → 19e → 17e, and the process itself has a radical chain character.

IX. Reactions with possible involvement of iron carbonyl complexes

The concept of the 'activating complex formation' discussed in Section III describes adequately a wide variety of redox processes in organic and organometallic chemistry,[82,83] for example, the reactions of ferrocenium salts with different nucleophilic reagents.[190]

If the neutral complex C in Scheme 2 is replaced by the radical cation $C^{+\bullet}$, we get Scheme 9. This may explain the halide-induced disproportionation of radical cations $[Fe(CO)_3(PR_3)_2]^{+\bullet}$ containing iron atom in the formal oxidation state 1+ into the complexes $Fe(CO)_3(PR_3)_2$ [Fe(0)] and $Fe(CO)_2(PR_3)_2X_2$ [Fe(II)], where X = Cl, Br, I.[100,101,103]

Scheme 9

$$L^- + C^{+\bullet} \not\longrightarrow L^{\bullet} + C,$$

$$L^- + C^{+\bullet} \longrightarrow CL^{\bullet},$$

$$CL^{\bullet} + C^{+\bullet} \longrightarrow CL^+ + C.$$

The 'activating complex formation' produces at the first stage the known[100,101] radical $[Fe(CO)_3(PR_3)_2X]^{\bullet}$ [reaction (41)]. This is followed by an electron transfer from this compound to the starting radical cation and the formation of the coordination sphere of Fe(+2) carbonyl complex [reactions (42) and (43)].

$$[Fe(CO)_3(PR_3)_2]^{+\bullet} + X^- \longrightarrow [Fe(CO)_3(PR_3)_2X]^{\bullet}, \quad (41)$$

$$[Fe(CO)_3(PR_3)_2X]^{\bullet} + [Fe(CO)_3(PR_3)_2]^{+\bullet} \longrightarrow [Fe(CO)_3(PR_3)_2X]^+ + Fe(CO)_3(PR_3)_2, \quad (42)$$

$$[Fe(CO)_3(PR_3)_2X]^+ + X^- \longrightarrow Fe(CO)_2(PR_3)_2X_2 + CO. \quad (43)$$

The mechanism of single-electron redox disproportionation of iron carbonyls induced by Lewis bases, resulting in the formation of ICRA, is quite common and may be applied to a wide variety of bases (see Section III). However, this mechanism has to be proved in every particular case. For instance, some authors[23,24] regard the *N*-oxide-induced ligand substitution in iron carbonyls as a special type of transformations caused by 'oxygen atom transfer reagents' (see Scheme 2 in Introduction). However, it was shown[79] that, in reality, such processes start with the formation of ICRA according either to reactions (1) and (2) ($L^- = OH^-$), if commercial $Me_3NO \cdot 2H_2O$ available as $[Me_3NOH]^+OH^- \cdot H_2O$ is applied, or to reactions (3) and (4) (L = Me_3NO), if the preliminarily dehydrated amine oxide is used. This is followed by nucleophilic displacement of CO in the formed ICRA according

to reactions (29)–(33), which is a typical electron transfer induced catalysis (see Section VI).

The activation of nucleophilic substitution and CO exchange in $Fe(CO)_5$ under the action of salts (such as $CoHal_2$ and $NiHal_2$)[191] or transition metal complexes[192,193] occurs in a similar way. These compounds are able to dissociate yielding negatively charged species, for example, halide ions X^-, which act as Lewis bases. They react with $Fe(CO)_5$ to form complexes $[Fe(CO)_4C(O)X]^-$ [reaction (1)], which subsequently react with the starting $Fe(CO)_5$ molecule according to equation (2), producing iron carbonyl radical anions.[78] It is important to note that in these compounds, the transition metal is in a low oxidation state and is unable to oxidise the emerging radical anions. The activation of such processes by potassium hydride[194] and by the complex hydride derivatives, R_3BH^- (R = H, Alk, AlkO) and AlH_4^- (Refs 194 and 195), which produce the $[Fe(CO)_4C(O)H]^-$ formyl iron complex[196–199] proceeds by a similar way.

The kinetic data on one of the most important carbonylation processes, Reppe olefin hydroformylation in alkaline solutions containing $Fe(CO)_5$,[9] have been interpreted according to the traditional scheme based upon the Tolman rule. Several intermediate 16-electron species, the possible existence of which was not proved, are included in this scheme.

However, the very same data can be consistently interpreted by assuming the formation of ICRA in the iron carbonyl–Lewis base system and their radical chain transformations through complexes 17e → 19e → 17e, which do exist in solution and are easily detectable by ESR spectroscopy. The key stage of the process is the addition of an olefin to the coordinatively unsaturated 17-electron radical anion in the presence of a proton donor. As a result, an alkyl-containing iron carbonyl radical is generated [reaction (44)].

$$RCH{=}CHR' + H^+ + [Fe_n(CO)_{m-1}]^{-\bullet} \longrightarrow \longrightarrow [RCH_2-CHR'-Fe_n(CO)_{m-1}]^{\bullet} \quad (44)$$

R, R′ = Alk; $n = 2$, $m = 9$; $n = 3$, $m = 12$.

The next stage is the addition of CO producing a 19-electron species and the transformation of the latter into the 17-electron radical upon carbonylation of the Fe–Alk bond.

$$[RCH_2-CHR'-Fe_n(CO)_{m-1}]^{\bullet} \xrightarrow{CO} \underset{(17e)}{} \longrightarrow [RCH_2-CHR'-Fe_n(CO)_m]^{\bullet} \longrightarrow \underset{(19e)}{} \longrightarrow [RCH_2-CHR'C(O)Fe_n(CO)_{m-1}]^{\bullet}$$

12 (17e)

The subsequent reaction of radical **12** with $[HFe(CO)_4]^-$ produces an aldehyde and radical anion with an increased number of iron atoms, similarly to the reactions of acyl derivative $[RFe(CO)_4]^{\bullet}$ [reactions (24) and (25)]. The hydridocarbonylferrate anion $[HFe(CO)_4]^-$ is formed in this process as a result of redox disproportionation of $Fe(CO)_5$ in the presence of a proton donor.[19,20,109] In the presence of carbon monoxide, ICRA **2**–**5** interconvert[76–78,96,108] according to reactions (8)–(11). This provides the regeneration of radical anions **2** and **3** and thus determines the catalytic character of the process.

Stoichiometric reduction of various unsaturated compounds (alkenes,[200] 1,3-dienes,[201] α,β-unsaturated carbonyl compounds,[113,114] enamines,[202] a number of nitrogen-containing heterocycles and anthracene[203]) by HCFA occurs in the absence of CO in a proton donor medium. During the reduction, ESR signals that may be assigned to ICRA **2**–**4** were detected. However, the formation of such species was usually attributed to side processes.[113]

An alkyl-containing complex is formed at the first step of the reduction.

$$RCH{=}CHR' + H^+ + [HFe_n(CO)_{m-1}]^- \longrightarrow \longrightarrow RCH_2-CHR'HFe_n(CO)_{m-1}$$

R, R′ = Alk; $n = 1$, $m = 5$; $n = 2$, $m = 9$.

The subsequent process is believed to proceed according to reactions (22) and (23) (see Section IV), *i.e.*, the scheme of single-electron redox disproportionation in the HCFA–Lewis acid system, resulting in the formation of ICRA and reduction products, is implemented. The iron carbonyl radical anions react with the starting compounds [see reactions (44), (24) and (25)]. As a result, the hydrocarbonylferrate anion is completely spent for the reduction of unsaturated compound.

The transformation schemes *via* the 17e → 19e → 17e complexes may be applied also to the explanation of other processes, which involve the iron carbonyl–Lewis base and HCFA–Lewis (or Brønsted) acid systems. However, the validity of using such schemes should be proved in each particular case.

X. Redox disproportionation of transition metal carbonyls

The redox disproportionation induced by Lewis bases is a typical reaction of transition metals carbonyls. As a result of this reaction, the reduction of carbonyls to carbonylmetallate or hydridocarbonylmetallate anions and their oxidation to positively charged complexes take place. The general features of the formation of stable complexes, namely, binary carbonyls containing only the metal atoms and carbonyl ligands, should be considered in the discussion of these processes, because the relationship between the stability and reactivity is important for the choice of potential carbonylation catalysts.

All complexes require the 18-electron configuration of the outer electron shell of a metal atom in order to achieve the thermodynamic stability (the Sidgwick rule). The number of CO ligands coordinated to the metal (not more than 6) is an important factor determining the stability of carbonyl complexes obtained in various processes. The size of the metal atom is another such factor. The larger is the metal atom and the smaller is the number of CO groups required for its coordination, the more pronounced is the tendency of the complex to form cluster structures. This fact is reflected in the concept of close packing of ligands on a metal core surface.[204] For instance, the vanadium atom, which possesses a d^5 electron configuration, forms a stable 17-electron radical, $[V(CO)_6]^{\bullet}$, unable to dimerise. On treatment with a Lewis base (L), this radical easily disproportionates yielding the salt $[VL_n][V(CO)_6]_2$ ($n = 3$, 6), in which the mononuclear anion $[V(CO)_6]^-$ obtains the closed 18-electron configuration.[205]

A stable mononuclear carbonyl $Ni(CO)_4$ with a closed 18-electron shell is known for nickel (electron configuration d^{10}). During the redox disproportionation induced by Lewis bases (L), it transforms into salts of polynuclear carbonyl-containing Ni(−2) anions, $[NiL_n][Ni_p(CO)_q]$ with $p \geqslant 5$ nickel atoms in the anion cluster, for example $[Ni_6(CO)_{11}]^{2-}$, $[Ni_9(CO)_{18}]^{2-}$ or $[Ni_{12}(CO)_{21}]^{4-}$ (Refs 206–208). Platinum, which is located in the Periodic Table in the same group as nickel, but in Period 6, does not form a stable mononuclear carbonyl $Pt(CO)_4$, but produces a polymeric cluster $[Pt(CO)_2]_x$ instead.[209] The same is true for carbonylplatinates, for example for $[Pt_3(\mu\text{-}CO)_3(CO)_3]_n^{2-}$ (Ref. 210).

Group VI metals, Cr, Mo and W, form very stable hexacarbonyls $M(CO)_6$, which disproportionate only under the action of strong bases and under drastic conditions. For instance, the reactions of $M(CO)_6$ with KOH produces $[HM_2(CO)_{10}]^-$ binuclear anions,[211,212] and the reactions of $Cr(CO)_6$ with KOH in the presence of the cryptand 222 (4,7,13,16,21,24-hexaoxa-1,10-

diazabicyclo[8.8.8]hexacosane) result in the formation of the $[HCr(CO)_5]^-$ anion.[213] Dianionic carbonylmetallates, $[M_2(CO)_{10}]^{2-}$ (M = Cr, Mo, W), are also known for these metals.[212,214–216] When less basic nucleophiles are used, the redox disproportionation does not occur. The reactions stop after the formation of complexes at the CO group, for example $[M(CO)_5C(O)L]^-$ [M = Cr: L = N_3, H, NEt_2 (Ref. 214); M = W, L = OMe (Ref. 217)]. The subsequent transformations are accompanied by replacement of the carbonyl group and yield either $[M(CO)_5L]^-$ anions (M = Cr, Mo, W; L = NCS, H, CN, Cl, Br, I) or neutral compounds $M(CO)_5L$ (M = W: L = THF, $NAlk_3$, AlkCN).[216,218]

Group VII metals, Mn, Tc‡ and Re (with the electron configuration d^7), form stable binuclear carbonyls $M_2(CO)_{10}$ with a closed 18-electron shell. Their redox disproportionation induced by Lewis bases (L) produces the $[ML_6][M(CO)_5]_2$ salts (M = Mn, Re).[219–221] The oxidation state of the metal in the pentacarbonylmetallate aniones is −1. In the case of manganese, the formation of complex salts $[Mn(CO)_{6-n}L_n]^+[Mn(CO)_5]^-$ [n = 3 or 6; L is pyridine (Py), amines, *etc.*] is possible.[222]

Stable binuclear $[Co_2(CO)_8]$ and tetranuclear $[Co_4(CO)_{12}]$ carbonyl complexes with 18-electron closed shells are typical of cobalt (the electron configuration d^9).[223,224] Their disproportionation induced by Lewis acids (L) generates the mononuclear $[Co(CO)_4]^-$ anion.

$$\left.\begin{matrix} Co_2(CO)_8 \\ Co_4(CO)_{12} \end{matrix}\right\} \xrightarrow[-CO]{L} [CoL_6][Co(CO)_4]_2$$

The disproportionation of $Co_2(CO)_8$ in the presence of pyridine may give also the trinuclear $[Co_3(CO)_{10}]^-$ anion. Depending on the conditions, the counter-ions are represented by Co^+ and Co^{2+} complexes, such as $[Co(CO)_4Py]^+$, $[Co(CO)_4Py_3]^+$, $[CoPy_3]^{2+}$ and $[CoPy_4]^{2+}$ (Ref. 224).

The cobalt group metals, Rh and Ir, also form dimeric carbonyls $M_2(CO)_8$; however these carbonyls are unstable and are converted into tetranuclear complexes, $M_4(CO)_{12}$.[209,225] The clusters $M_6(CO)_{16}$ are also known for rhodium and iridium.[209,225] The reduction of the carbonyls of these metals results in the formation of the mononuclear anion $[M(CO)_4]^-$; however, the anionic Rh and Ir carbonylmetallate complexes usually exist as polynuclear clusters $[M_p(CO)_q]^{n-}$ with the number of metal atoms $p \geqslant 5$ and the charge n ranging from −1 to −4, for example, $[M_5(CO)_{16}]^-$, $[M_6(CO)_{16}]^{2-}$, $[Ir_{12}(CO)_{26}]^{2-}$, $[Rh_{22}(CO)_{37}]^{4-}$ and $[Rh_{26}(CO)_{32}]^{2-}$ (Refs 204, 209, 225 and 226).

Iron (the electron configuration d^8) forms stable 18-electron carbonyls, $Fe(CO)_5$, $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$, and also a carbidocarbonyl cluster $Fe_5C(CO)_{15}$. The redox disproportionation of iron carbonyls produces the salts of carbonylferrate or hydrocarbonylferrate anions with the number of iron atoms from 1 to 4 (see Introduction). Carbidocarbonyl anionic clusters $[Fe_5C(CO)_{14}]^{2-}$ and $[Fe_6C(CO)_{16}]^{2-}$ are formed in the reactions of iron carbonyls at temperatures around 150 °C.[204,227] These clusters contain the largest number of iron atoms. The redox transformations of these compounds produce complexes with fewer number of iron atoms.[78]

The iron group metals, Ru and Os, have a larger atom size and produce stable trinuclear carbonyls $M_3(CO)_{12}$, while mononuclear pentacarbonyls of these atoms $M(CO)_5$ are unstable. The redox disproportionation of $Ru_3(CO)_{12}$ under the action of KOH produces the $[HRu_3(CO)_{11}]^-$ and $[Ru_6(CO)_{18}]^{2-}$ anionic complexes,[228] and its pyrolisys gives the $Ru_6C(CO)_{17}$ cluster.[209] The thermal destruction of $Os_3(CO)_{12}$ yields new polynuclear carbonyls, $Os_5(CO)_{16}$, $Os_6(CO)_{18}$, $Os_7(CO)_{21}$ and $Os_8(CO)_{23}$.[209] The polynuclear anionic clusters of Ru and Os, for instance $[Ru_{10}C_2(CO)_{24}]^{2-}$ and $[Os_{10}C(CO)_{24}]^{2-}$, are also known (Refs 204, 228 and 229).

Generally, the anionic carbonyl clusters of platinum group metals are able to combine into polynuclear clusters with larger number of metal atoms, up to several dozens or even hundreds. The resulting clusters have a metal core like a crystal lattice with a 'coat' of CO ligands at the surface. This seriously hinders the determination of their structure, because during the X-ray study of such clusters the localisation of carbonyl ligands and determination of their number is problematic due to high absorption of X-rays and strong scattering by metal atoms.[204] Besides, the '18-electron configuration rule', which is valid for mono- and polynuclear complexes of transition metals, does not work for large clusters. The stable forms of these structures are described in terms of the concept of cluster valence electrons (CVE) and cluster core electrons (CCE), which are directly involved in the metal–metal bonding.[204]

Thus, the disproportionation of Group V–VII metals and Fe or Co, which belong to Group VIII of Period 4 of the Periodic Table, produces either stable mononuclear carbonyl complexes or clusters of few metal atoms. Polynuclear cluster structures are more typical of carbonyls of platinum Group VIII metals of Periods 5 and 6.

The reducing ability of metal carbonyls is an important factor, affecting the rate of the redox disproportionation induced by Lewis bases. This ability is determined by the single-electron reduction potential (E°_{red}). There are some difficulties in measuring E°_{red}, caused by chemical transformations of carbonyl complexes during electrolysis. The initially formed electron-rich radical anion of a metal carbonyl tends to transform into an electron-deficient one (transition 19e → 17e) by elimination of CO or by breaking of the metal–metal bond. More energetically favourable radical anion is formed in the former case. The unpaired electron of this radical anion is located in the highest occupied molecular orbital, which is lower than the lowest unoccupied molecular orbital bearing the unpaired electron of the initial 19-electron radical anion. The breaking of the metal–metal bond may be accompanied either by a decrease in the number of metal atoms in the complex or by rearrangement of the cluster core. For example, the initial 19-electron radical anions $[Mn_2(CO)_{10}]^{-\bullet}$ and $[Co_2(CO)_8]^{-\bullet}$ decompose quickly into 18-electron anions $[Mn(CO)_5]^-$ and $[Co(CO)_4]^-$ and 17-electron radicals $[Mn(CO)_5]^\bullet$ and $[Co(CO)_4]^\bullet$ respectively.[134,222,224,230,231] The latter are then easily reduced to the corresponding anions, because their reduction potentials are less negative.[232] As a result, the two-electron reduction of the starting metal carbonyl takes place; in this process, the electrochemical stages are accompanied by a chemical reaction (ECE mechanism).[233]

$$Mn_2(CO)_{10} + 2e \longrightarrow 2[Mn(CO)_5]^-,$$

$$Co_2(CO)_8 + 2e \longrightarrow 2[Co(CO)_4]^-.$$

The two-electron reduction in the ECE-reactions is also typical of $Fe(CO)_5$ (see Section V, Fig. 1 and its caption) and for Group VI metal carbonyls $M(CO)_6$ (M = Cr, Mo, W) [reactions (45)–(48)]. In these cases, as in the previous example, the reduction potential of the formation of binuclear complexes at the second electrochemical stage (48) is less negative than the potential of stage (45).[43,234]

$$M(CO)_6 + e \rightleftharpoons [M(CO)_6]^{-\bullet}, \quad (45)$$

$$[M(CO)_6]^{-\bullet} \longrightarrow [M(CO)_5]^{-\bullet} + CO, \quad (46)$$

$$[M(CO)_5]^{-\bullet} + M(CO)_6 \longrightarrow [M_2(CO)_{10}]^{-\bullet} + CO, \quad (47)$$

$$[M_2(CO)_{10}]^{-\bullet} + e \rightleftharpoons [M_2(CO)_{10}]^{2-}. \quad (48)$$

‡ The chemistry of the carbonyl complexes of radioactive technecium is barely known. Only the reduction of $Tc_2(CO)_{10}$ to $[Tc(CO)_5]^-$ is described.[219]

Another interpretation of this process with the same final product, instead of stages (47), (48), includes further reduction of $[M(CO)_5]^{-\bullet}$ to $[M(CO)_5]^{2-}$ and either the reaction of the latter with the starting complex $M(CO)_6$ (M = Cr)[43] or its dimerisation, resulting in the formation of $[M_2(CO)_{10}]^{2-}$ (M = Cr, Mo, W).[40] However, irrespective of the possible reaction pathway, the two-electron potential of the ECE process may be regarded, with some restrictions, as the potential of single-electron reduction of the metal carbonyl. The ECE process includes fast chemical transformations and the diffusion-controlled first stage [reaction (45)] with the most negative reduction potential.

In some cases, when relatively stable radical anions, *e.g.* $[Fe_3(CO)_{12}]^{-\bullet}$, are formed, it is possible to determine two consecutive single-electron reduction potentials (Table 2).[37–39]

Table 2. Reduction potentials of metal carbonyls.

Starting complex	Product	Potential /V (method) [a]	Number of electrons [b]	Ref.
$V(CO)_6$	$[V(CO)_6]^-$	−0.21 (C)	1	40
$Cr(CO)_6$	$[Cr_2(CO)_{10}]^{2-}$	−2.66 (C)	2	40
		−2.7 (P)	1–2 ?	34
$Mo(CO)_6$	$[Mo_2(CO)_{10}]^{2-}$	−2.59 (C)	2	40
		−2.7 (P)	1 ?	34
$W(CO)_6$	$[W_2(CO)_{10}]^{2-}$	−2.63 (C)	2	40
		−2.9 (P)	1 ?	34
$Fe(CO)_5$	$[Fe_2(CO)_8]^{2-}$	−2.38 (C)	2	40
		−1.67 (C)	2	37
		−1.77 (P)	2	39
		−2.4 (P)	1 ?	34
$Ni(CO)_4$	–	−2.70 (C)	2	40
		−2.80 (C)	2	235
		−2.9 (P)	1 ?	34
$Mn_2(CO)_{10}$	$[Mn(CO)_5]^-$	−1.65 (C)	2	40
		−1.8 (P)	2	34
$Re_2(CO)_{10}$	$[Re(CO)_5]^-$	−2.36 (C)	2	40
		−2.3 (P)	2	34
$Co_2(CO)_8$	$[Co(CO)_4]^-$	−0.75 (C)	2	235
$Fe_3(CO)_{12}$	$[Fe_3(CO)_{12}]^{-\bullet}$	−0.32 (P)	1	39
		−0.26 (C)	1	37
		−0.44 (C)	1	38
$Ru_3(CO)_{12}$	$[Ru_3(CO)_{12}]^{2-}$	−0.815 (P)	1	37
		−0.97 (P)	2	236
		−1.00 (C)	2	236
		−1.49 (P)	2	237
$Os_3(CO)_{12}$	$[Os_3(CO)_{12}]^{2-}$	−1.16 (P)	1	37
		−1,31 (P)	2	236
		−1.54 (C)	2	236

[a] The determination method is either the cyclic voltammetry (C) or polarography (P). [b] The number of electrons, which determines the character (one- or two-electron) of the reduction potential, is indicated. The question mark means that the authors doubt the reliability of the value.

The reduction potentials listed in Table 2 were measured by different methods and under different conditions. These potentials describe the ECE processes, which are irreversible in some cases, but on the basis of these data, some qualitative conclusions about the ability of a carbonyl complex to undergo Lewis base-induced redox disproportionation may yet be drawn. The complexes $M(CO)_6$ (M = Cr, Mo, W), possessing the most negative reduction potentials, are difficult to disproportionate. Therefore, the processes in which metal carbonyls reduce, for example, organic compounds are typical of the carbonyls of these metals. These complexes are used as the initiators of radical addition reactions, the olefin telomerisation with haloalkanes and the reduction of polychlorinated compounds.[166–171, 238] Their transformations in the presence of Lewis bases may be described by reactions (49)–(54) similarly to reactions (37), (38) and (1), (2), (5) for $Fe(CO)_5$.

$$M(CO)_6 + L \longrightarrow M(CO)_5C(O)L, \quad (49)$$

$$M(CO)_5C(O)L + RX \longrightarrow [M(CO)_5C(O)L]^{+\bullet} + RX^{-\bullet}, \quad (50)$$

$$RX^{-\bullet} \longrightarrow R^{\bullet} + X^-, \quad (51)$$

$$X^- + M(CO)_6 \rightleftharpoons [M(CO)_5C(O)X]^-, \quad (52)$$

$$[M(CO)_5C(O)X]^- + RX \longrightarrow [M(CO)_5C(O)X]^{\bullet} + RX^{-\bullet}, \quad (53)$$

$$[M(CO)_5C(O)X]^{\bullet} \longrightarrow [M(CO)_5X]^{\bullet} + CO, \quad (54)$$

M = Cr, Mo, W; X = Cl, Br, I; L is a Lewis base.

The radicals $M(CO)_5Cl^{\bullet}$ (M = Cr, Mo, W), detected by the spin trap method, may be regarded as a proof for the suggested scheme.[99, 166, 168, 169, 171, 238] Other metal carbonyls possessing low reduction potentials such as $Re_2(CO)_{10}$, $Mn_2(CO)_{10}$, $Ni(CO)_4$, are also used as the initiators of similar reactions.[166–171, 238, 239] In the case of binuclear complexes $Re_2(CO)_{10}$, $Mn_2(CO)_{10}$ and $Co_2(CO)_8$, the initiation may proceed as a result of photolytic generation of monomeric radicals $[M(CO)_5]^{\bullet}$ (M = Re, Mn) and $[Co(CO)_4]^{\bullet}$, respectively.

The metal carbonyls possessing high reduction potentials, *e.g.*, $V(CO)_6$, $Co_2(CO)_8$ and $Fe_3(CO)_{12}$, disproportionate easily. It is reasonable to suggest that this process proceeds according to a scheme similar to that proposed for iron carbonyls [see Section III, reactions (1)–(4)]:

$$M_n(CO)_m + L^{0/-} \rightleftharpoons [M_n(CO)_{m-1}C(O)L]^{0/-}, \quad (55)$$

$$[M_n(CO)_{m-1}C(O)L]^{0/-} + M_n(CO)_m \longrightarrow [M_n(CO)_{m-1}C(O)L]^{+\bullet/\bullet} + [M_n(CO)_m]^{-\bullet}. \quad (56)$$

The formation of the adducts $[M_n(CO)_{m-1}C(O)L]^{0/-}$ (see §) in the reactions of metal carbonyls with Lewis bases in the neutral (L^0) or anionic (L^-) form [reaction (55)] is well known and has been discussed in a review.[84] The higher is the reduction potential of the complex, the easier is the redox disproportionation according to equation (56). The detection of carbonyl radical anions in these processes is difficult due to their low stability, although they are known for most metal carbonyls. For instance, the $[Ni(CO)_3]^{-\bullet}$ (Ref. 240), $[Ni_2(CO)_7]^{-\bullet}$ (Ref. 241) and $[M(CO)_5]^{-\bullet}$ (M = Cr,[43, 241] Mo, W[242]) radical anions and the $[M(CO)_5]^{\bullet}$ (M = Mn, Re)[243–245] and $[Co(CO)_4]^{\bullet}$ (Ref. 232) radicals formed upon decomposition of the $[M_2(CO)_{10}]^{-\bullet}$ and $[Co_2(CO)_8]^{-\bullet}$ radical anions respectively, have been studied.

The $[Ru_3(CO)_{12}]^{-\bullet}$ radical anion was detected in the reaction of $Ru_3(CO)_{12}$ with anionic forms of bases: HO^-, MeO^-, EtO^-, EtS^-, Et_2N^-, H^- and Cl^- (Ref. 78). Taking into account the fact that the first stage of this reaction yields the $[Ru_3(CO)_{11}C(O)L]^-$ anion,[87] the scheme of single-electron redox disproportionation may be represented by reactions (57) and (58).

$$Ru_3(CO)_{12} + L^- \rightleftharpoons [Ru_3(CO)_{11}C(O)L]^-, \quad (57)$$

$$[Ru_3(CO)_{11}C(O)L]^- + Ru_3(CO)_{12} \longrightarrow [Ru_3(CO)_{11}C(O)L]^{\bullet} + [Ru_3(CO)_{12}]^{-\bullet}. \quad (58)$$

The CO group of the $[Ru_3(CO)_{12}]^{-\bullet}$ radical anion may be substituted by another ligand (ETC process), similarly to the substitutions in iron carbonyl radical anions [see Scheme 5 and reactions (30), (31) and (33)], as occurs, for example, in the electrochemical generation of this species in the reactions of $Ru_3(CO)_{12}$ with PPh_3.[236] The only difference is in the method of generation of the radical anion. This scheme describes well the

§ The superscript after the slash indicates the alternative charge.

nature of the catalytic action of various Lewis bases in the substitution of CO by phosphine ligands, which was studied in a series of papers.[246–250] The catalytic activity of the $Ru_3(CO)_{12}-Et_4NCl$ system in the reductive carbonylation of nitro compounds[251] may also be related to the generation of the radical anion $[Ru_3(CO)_{12}]^{-\bullet}$, which is a total analogue of ICRA, which are the catalysts of these processes (see Section VIII).

An important feature of the $Ru_3(CO)_{12}$ complex should be noted: the main products of its reactions with such Lewis bases as halide ions are trinuclear complexes with halide ligands, and the yield of the (hydrido)carbonylruthenate anions is negligible.[246, 248, 249] Probably, this is caused by the fact that the rearrangement of the radical product $[Ru_3(CO)_{11}C(O)L]^{\bullet}$ is accompanied by ETC process and, similarly to $Fe_3(CO)_{12}$ [see reactions (34)–(36)], may be represented by the following equations:

$$[Ru_3(CO)_{11}C(O)L]^{\bullet} \longrightarrow [Ru_3(CO)_{11})L]^{\bullet} + CO, \quad (59)$$

$$[Ru_3(CO)_{11}L]^{\bullet} + [Ru_3(CO)_{11}C(O)L]^{-} \longrightarrow \longrightarrow [Ru_3(CO)_{11}L]^{-} + [Ru_3\,(CO)_{11}C(O)L]^{\bullet}. \quad (60)$$

Taking into account reaction (57), in the overal process, a significant part of reactants is converted into the final product $[Ru_3(CO)_{11}L]^{-}$. The role of the single-electron transfer (58) in this process is reduced to the initial generation of the $[Ru_3(CO)_{11}C(O)L]^{\bullet}$ radical. Reactions (59) and (60) describe the formation of a possible product, $[Ru_3(CO)_{11}L]^{-}$. Other products, $[Ru_3(\mu_2\text{-}L)(CO)_{10}]^{-}$ (L = Cl, Br, I) and $[Ru_3(\mu_3\text{-}L)(CO)_9]^{-}$ (L = I),[248] are produced upon the subsequent transformation of the ligand L in the coordination sphere of the radical $[Ru_3(CO)_{11}L]^{\bullet}$ followed by reduction.

The more negative is the reduction potential of a metal carbonyl, the less important are the processes of its redox disproportionation induced by Lewis bases. For instance, for the $M(CO)_6$ (M = Cr, Mo, W),[214, 217] the formation of the carbonyl group adducts $[M(CO)_5C(O)L]^{-}$ and their transformation into $[M(CO)_5L]^{-}$ may be represented by reactions (57)–(60). In these reactions, thermodynamically the most unfavourable redox stage (58) is the first stage of the process initiation.

Whereas for metal carbonyls with the most negative reduction potentials the transformations of M^{+} complexes formed at the redox disproportionation step of process (58) are typical, in the case of complexes with higher reduction potentials, the transformations of the M(0) derivatives become more significant. The reaction of $Co_2(CO)_8$ with ligands L (L = $AsPh_3$, PBu_3, PPh_3, ^{13}CO) is an example of such transformation. The initiation of the reaction of the starting metal carbonyl by a base first produces the $[Co_2(CO)_8]^{-\bullet}$ radical anion [reactions (55) and (56)]; its further transformations proceed as follows:[231]

$$[Co_2(CO)_8]^{-\bullet} \longrightarrow [Co(CO)_4]^{-} + [Co(CO)_4]^{\bullet},$$

$$[Co(CO)_4]^{\bullet} + L \longrightarrow [Co(CO)_3L]^{\bullet} + CO,$$

$$[Co(CO)_3L]^{\bullet} + Co_2(CO)_8 \longrightarrow [Co(CO)_3L]^{+} + [Co_2(CO)_8]^{-\bullet},$$

$$[Co(CO)_3L]^{+} + L \longrightarrow [Co(CO)_3L_2]^{+},$$

$$[Co(CO)_4]^{\bullet} + [Co(CO)_3L]^{\bullet} \longrightarrow Co_2(CO)_7L,$$

$$[Co(CO)_3L]^{\bullet} + [Co(CO)_3L]^{\bullet} \longrightarrow Co_2(CO)_6L_2.$$

Substituted cobalt carbonyls $Co_2(CO)_7L$ (L = $AsPh_3$), $Co_2(CO)_6L_2$ (L = $AsPh_3$, PBu_3) and the ionic complex $[Co(CO)_3L_2][Co(CO)_4]$ (L = PBu_3, PPh_3) are the final products of the radical chain process. Similar radical chain substitution of CO by various basic ligands during photochemical disproportionation of $Mn_2(CO)_{10}$ has been described.[230]

Thus, the reactions of metal carbonyls with Lewis bases may be represented by a single scheme of redox disproportionation. This scheme includes the stage of activating complex formation (55) followed by single-electron transfer from a carbonyl complex activated by an electron donor to another metal carbonyl molecule. The radical and radical ion complexes formed at stage (56) may undergo two types of transformations: (i) further disproportionation yielding stable cationic metal complexes containing Lewis bases in the coordination sphere and (hydrido)carbonylmetallate anions; (ii) radical chain ETC processes, resulting in the formation of diamagnetic derivatives of metal carbonyl complexes with initial oxidation state of the metal M(0).

XI. Conclusion

Two types of redox reactions underlie catalytic carbonylation of various compounds by iron carbonyls. The first type is the redox disproportionation of iron carbonyl induced by Lewis bases (see Section III), while the second type is the oxidative addition of the Brønsted or Lewis acids to carbonylferrate and hydridocarbonylferrate anions (see Section IV). The reactions of both types include single-electron stages of redox initiation and subsequent radical chain transformations of iron carbonyl complexes. The resulting iron carbonyl radical anions are coordinatively unsaturated electron-deficient systems with labile coordination sphere, capable of the fast ligand and electron exchange. These particular properties allow one to suggest that ICRA are the catalytically active species in carbonylation processes (see Section VIII). It is very important to note that a catalytic cycle with radical anions as catalysts is based on the transformations which include consecutive formation of the odd-electron complexes (17e → 19e → 17e), the whole process having a radical chain character. This scheme uncontradictorily describes from a unified standpoint the two-electron redox processes of iron carbonyls and explains the formation of all known reaction products. Besides, this scheme is able to interpret the main chemical transformations of other metals carbonyls, to suggest new promising catalytic systems for carbonylation and to propose the optimal conditions for homogeneous catalysis (the heterogeneous catalysis is beyond the scope of the present review).

Mononuclear complexes and small clusters are effective homogeneuos catalysts of various processes with CO participation. It is advisable to use either carbonyl complexes of the Period 4 transition metals, which do not form big clusters, or to use complexes with bulky substituents, which prevents the clusterisation of the platinum-group metals, such as, for example, the Wilkinson catalyst $[RhCl(PPh_3)_3]$ or the complex $RhH(CO).(PPh_3)_3$. These platinum group metal-based catalysts may be effectively applied in the small-scale organic synthesis of expensive chemicals,[252] but they are not cost-effective in the large-scale industrial processes. Moreover, in the course of the process the ligands in the metal coordination sphere may be replaced by molecules of the main process participants (in our case, CO). This results in the change in the catalytic system properties. The metal carbonyl-based complexes are suitable catalysts as they contain the ligands taking part in the catalysis. In this respect, the commercially available carbonyl complexes of Group VIII metals, namely, Fe, Co and Ni, are the most promising as catalysts. The cobalt carbonyl complexes are industrially important and used in hydroformylation.[6, 12] Numerous studies of Fe and Ni carbonyl complexes have revealed their reduced catalytic activity in comparison with that of the platinum-group metal carbonyls in, for example, hydroformylation and water gas conversion[6, 17] and in the reductive carbonylation of nitro compounds.[253] A possible reason for such reduced activity may be the traditional approach towards the catalytic processes with participation of metal carbonyls, according to which they are carried out under the conditions similar to those of their synthesis (high pressure and temperature). Assuming that in the case of Fe and Ni, the metal carbonyl radical anions are the catalytically active species in carbonylation, it is possible to suggest that the optimal conditions for their catalytic activity will be controlled reduction potential of the medium and also relatively low temperature and a nearly

atmospheric CO pressure. This results in a new approach to catalytic carbonylation processes, namely, the idea to carry out the process under conditions favourable for chain propagation reactions rather than under the traditional conditions involving high pressures and temperatures. The traditional conditions increase the role of chain termination reactions and decrease the catalytic activity of metal carbonyl radical anions.

The reduction potential of the reaction medium is an important condition for the formation of Fe and Ni carbonyl complexes from their inorganic salts. For instance, the following compounds were obtained at room temperature and atmospheric CO pressure: $Na_2Fe(CO)_4$ from $FeCl_3$ and $[Na^+(C_{10}H_8)^{-\bullet}]$;[254] $[HFe(CO)_4]^-$ from $FeCl_3$ and $NaBH_4$ upon acetic acid treatment;[255] $Ni(CO)_4$ from $Ni(acac)_2$ (acac is acetylacetonate) upon reduction with Bu^i_2AlH, Bu^nLi or Pr^nMgBr;[256] $Ni(CO)_2$(bipy) (bipy is bipyridyl) upon electrochemical reduction of $[Ni(bipy)]^{2+}$ (Ref. 257). It should also be noted that the catalytic synthesis of ammonia from N_2 and H_2 (using the coal-supported $K_2Fe_2(CO)_8$–metallic sodium system[258] as a catalyst), quite similar to carbonylation, also proceeds in reductive media.

It is necessary to note the second important aspect of the catalytic processes, namely, that they follow a radical chain mechanism proceeding through the 17e → 19e → 17e complexes. Similar radical reaction schemes were discussed in the late 1970s,[259, 260] but this idea has not been generalised and was regarded as a specific case. The traditional approach, which describes the process in usual terms of the Tolman rule about 16-electron intermediates, has prevailed. However, the latest studies attest more and more often to the radical chain mechanism as the major one for such catalytic processes. For example, the electrochemical studies of very well known complexes, the Wilkinson catalyst and $RhH(CO)(PPh_3)_3$, have revealed that they easily form radical cations ($E_{1/2\,ox} = +0.035$ V, Ref. 261, and $E_{1/2\,ox} = -0.48$ V, Ref. 262, respectively). This means that, according to the Nernst equation, the radical cation concentration in a catalytic process may reach tens of percent even when the electrochemical potential of the reaction medium is close to neutral. The role of such active species must be taken into account.

Thus, the features of the radical chemistry of iron carbonyls discussed in the present review provide new opportunities in the search for effective catalysts for metal carbonyl-based carbonylation processes and in carrying out these processes as radical chain ones with odd-electron (17 and 19) intermediates and under the controlled electrochemical potential of the reaction media.

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