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Interaction of iron carbonyls with Lewis bases

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The interaction of iron carbonyls $Fe_n(CO)_m$ (where $n = 1$, $m = 5$; $n = 2$, $m = 9$; $n = 3$, $m = 12$) with anionic Lewis bases (H^-, F^-, Cl^-, Br^-, I^-, CN^-, SCN^-, N_3^-, $MeSO_3^-$, $MeCO_2^-$, $CF_3CO_2^-$, S^{2-}, CO_3^{2-}, and SO_4^{2-}) passes through two-stage redox-disproportionation. The first stage is the formation of an iron carbonyl—base complex, $[Fe_n(CO)_{m-1}C(O)L]^-$, and the second is a single-electron reduction of this complex by another molecule of the initial iron carbonyl, giving rise to Fe(1) and Fe(−1) derivatives.

Key words: iron carbonyls, Lewis bases, interaction; iron carbonyl radical anions, single-electron redox-disproportionation.

In studies of the interaction of iron carbonyls $Fe(CO)_5$, $Fe_2(CO)_9$, and $Fe_3(CO)_{12}$ both with neutral (RSH and ROH (where R = Alk), DMF, DMSO, pyridine, *o*-phenanthroline) and with anionic (RSNa,[1,2] NaOR, $NaNR_2$,[1] $Na(CR_2NO_2)$ (where R = H, Alk) and $NaNO_2$[3]) Lewis bases we showed with the help of ESR spectroscopy that, irrespective of the base type, the reactions had a radical-chain mechanism with initial redox-disproportionation. At the first stage, the formation of an iron carbonyl—base complex took place. At the second stage, this complex reduced another molecule of the initial iron carbonyl. For instance, the following scheme can be written for a Lewis base in the anionic form, L:

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

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

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

It was also shown that radical iron carbonyl intermediates participate as catalysts in the catalytic cycle of reductive carbonylation of nitro compounds.[3]

In connection with the extensive use of iron carbonyl—Lewis base systems in different catalytic processes it became necessary to determine the applicability limits of radical-chain processes in the chemistry of iron carbonyls. Therefore, we extended the range of Lewis bases and also included the anions most commonly used as components of co-catalysts. These were single-charged (H^-, F^-, Cl^-, Br^-, I^-, CN^-, SCN^-, N_3^-, $MeCO_2^-$, $CF_3CO_2^-$, and $MeSO_3^-$) and double-charged anions (S^{2-}, CO_3^{2-}, and SO_4^{2-}), in the form of alkaline metal salts and of complex cations both in aprotic (THF, methyltetrahydrofuran, diethyl ether, monoglyme, dioxane, and dichloromethane) and in protic (methanol, ethanol, and 1 : 10 (v/v) THF—water mixture) solvents.

ESR investigation indicated that iron carbonyl radical anions, namely $Fe_2(CO)_8^{\cdot -}$ ($g = 2.0385$) (**1**), $Fe_3(CO)_{12}^{\cdot -}$ ($g = 2.0013$) (**2**), $Fe_3(CO)_{11}^{\cdot -}$($g = 2.0498$) (**3**) and $Fe_4(CO)_{13}^{\cdot -}$ ($g = 2.0135$) (**4**), arose in the course of the interaction of all the bases mentioned with iron carbonyls, $Fe_n(CO)_m$ (where $n = 1$, $m = 5$; $n = 2$, $m = 9$; $n = 3$, $m = 12$). The *g*-factor values given are those obtained for solutions in THF at −80 °C; they correlate well with literature data.[4] Mononuclear radical anion, $Fe(CO)_4^{\cdot -}$ (**5**) is detectable at the first stages of the reactions of $Fe(CO)_5$ with strong bases, such as NaOMe and NaOEt at −100 °C in THF ($g = 2.0486$).[5]

As a rule, radical anions **1**—**4** appear and can be detected with all combinations of the initial carbonyl and the base. The only differences concern the order of their appearance and consumption at various stages of the process. For instance, in reactions with $Fe(CO)_5$ radical anions appear in the following order: **5**, **1**, **2** and **3**, **4**. In reactions with $Fe_3(CO)_{12}$, **2** and **3** appear first, and **1** and **4** next.

The solubility of compounds is a factor exerting certain influence on their reactivity. Thus, with sodium salts, NaX (where X = F, Cl, Br, CN, SCN, $MeCO_2$, $MeSO_3$, and N_3) and Na_2Y (Y = S, SO_4, and CO_3), slightly soluble in ether-type solvents, the appearance of iron carbonyl radical anions is observed only at room temperature within 10—15 min after defrosting of tubes. With tetraalkylammonium halides, the solubility of which in THF is higher, radical anions are observed already at −80 °C at the very beginning of the reaction.

The shape and time variation of the ESR spectra, recorded in the course of the interaction of iron carbon-

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yls with all the above listed anions appeared to be the same as in the case of the earlier studied reactions with other N-, O-, and S-Lewis bases.[1—3] Therefore, we believe the earlier suggested two-stage mechanism of redox-initiation to have a general character, its versatility covering not only different bases but other carbonyls as well. Iron carbonyl radical anions **1—4** are produced during the interaction of $Fe_5C(CO)_{15}$ with sodium derivatives of the following anions as well: OH^-, OMe^-, OEt^-, SEt^-, NEt_2^-, Cl^-, and H^-. The formation of $Ru_3(CO)_{12}^{\cdot-}$ (g = 1.9803 at −80 °C, Ref. 6: g = 1.982) was observed in the interaction of $Ru_3(CO)_{12}$ with the same bases.

Experimental

"Chemically pure" salts of alkaline metals NaX (X = F, Cl, Br, I, CN, SCN, $MeCO_2$, $MeSO_3$, and N_3), Na_2Y (Y = S^{2-}, SO_4^{2-}, and CO_3^{2-}), KX (X = F, Cl, Br, I, CN, SCN, and $MeCO_2$), K_2Y (Y = SO_4^{2-} and CO_3^{2-}), LiX (X = F, Cl, and Br), and Li_2CO_3, as well as NaH and $(Ph_4P)Cl$ (Aldrich), were used without additional purification. Tetraalkylammonium salts $(NMe_4)X$, $(NEt_4)X$ (X = Cl and Br), and $(NBu^n{}_4)I$ of "pure" grade were dehydrated by distillation with benzene and by desiccating under reduced pressure in the presence of P_2O_5. (PPN)X (X = F, Cl, Br, I, CN, SCN, $MeCO_2$, and N_3) salts were prepared according to literature procedure[7]; $Ru_3(CO)_{12}$ was synthesized by the known procedure.[8] The synthesis of iron carbonyls and the preparation of samples were performed according to the known procedures.[1,3] The reactions were carried out in a tube placed into the resonator of an ESR-spectrometer, using equimolar ratios of reagents (0.01—0.1 mol L^{-1}). ESR spectra were recorded on an ERS-221 (ZWG, DDR) instrument in the X-range with high frequency modulation of 100 kHz.

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