

Group- and Electron-Transfer Reactions of Tetracarbonylferrate(2-)

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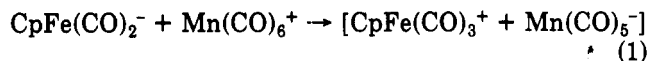
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Reactions of $\text{Fe}(\text{CO})_4^{2-}$ with metal carbonyl complexes lead to distinct mechanisms. Reaction with metal carbonyl cations gives a two-electron process that we interpret as a CO^{2+} transfer. Reaction with $\text{Mn}_2(\text{CO})_{10}$ occurs by a single-electron transfer producing $\text{Fe}_2(\text{CO})_8^{2-}$ and $\text{Mn}(\text{CO})_5^-$. Reaction with $\text{Mn}(\text{CO})_5\text{Br}$ also occurs by a single-electron transfer. Reaction with $\text{Re}(\text{CO})_5\text{Br}$ could be either SET or direct nucleophilic displacement. Kinetic studies are reported for several reactions.

The di-, tri-, and tetraanionic carbonyls form a fascinating group of complexes that illustrate metal complexes in their lowest oxidation states. Ellis and co-workers have managed to synthesize and, in some cases, structurally characterize complexes such as $\text{Cr}(\text{CO})_4^{4-}$, $\text{Mn}(\text{CO})_4^{3-}$, and $\text{V}(\text{CO})_5^{3-}$.¹ Although some of these complexes have been reported in the literature for a number of years, only a few reactions have been reported.

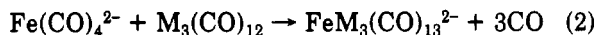
Because these polyanionic complexes strictly obey the 18-electron rule, they should be excellent candidates to expand the range of reactions that can, formally, be considered as CO^{2+} transfers. We have previously demonstrated such reactions in the two oxidation changes between metal carbonyl cations and anions.²



These reactions to the even-electron complexes occur more readily than the single-electron transfer to odd-electron complexes ($\text{CpFe}(\text{CO})_2^\bullet$ and $\text{Mn}(\text{CO})_6^\bullet$).²

Applications of $\text{Fe}(\text{CO})_4^{2-}$ to organic synthesis have been carefully explored.³ The reactivity of $\text{Fe}(\text{CO})_4^{2-}$ was dominated by oxidative addition reactions initiated by nucleophilic attack of $\text{Fe}(\text{CO})_4^{2-}$.³ $\text{Fe}(\text{CO})_4^{2-}$ is very nucleophilic and has been termed a "supernucleophile".^{3b} In all of these reactions with organic substrates, there was no evidence for a single-electron transfer from $\text{Fe}(\text{CO})_4^{2-}$.

Reactions of $\text{Fe}(\text{CO})_4^{2-}$ with $\text{M}_3(\text{CO})_{12}$ clusters have been reported as a route to heterocluster complexes, $\text{FeM}_3(\text{CO})_{13}^{2-}$ ($\text{M}_3 = \text{Ru}_3, \text{Os}_3, \text{Ru}_2\text{Os}, \text{RuOs}_2, \text{FeRu}_2, \text{Fe}_2\text{Ru}, \text{and Fe}_3$).⁴



In these reactions the nucleophilicity of $\text{Fe}(\text{CO})_4^{2-}$ was considered to be very important.⁴ Very recently the preparation of $\text{M}_2(\text{CO})_8^{2-}$ complexes has been reported (M_2

$= \text{Ru}_2, \text{Os}_2$, and FeRu) from reactions of $\text{M}(\text{CO})_4^{2-}$ with $\text{M}(\text{CO})_5$ (generated in situ).⁵

In this paper we describe the reactions of $\text{Fe}(\text{CO})_4^{2-}$ with a variety of metal carbonyl complexes. In these reactions $\text{Fe}(\text{CO})_4^{2-}$ demonstrates nucleophilic and electron-transfer capabilities. Because $\text{Fe}_2(\text{CO})_8^{2-}$ is an often observed product, we also describe its reactions.

Experimental Section

$\text{Mn}_2(\text{CO})_{10}$, $\text{Re}_2(\text{CO})_{10}$, $\text{Fe}(\text{CO})_5$, $\text{Cp}_2\text{Fe}_2(\text{CO})_4$, $\text{Ru}_3(\text{CO})_{12}$, $\text{Os}_3(\text{CO})_{12}$, and PPNCl ($\text{PPN} = \text{bis}(\text{triphenylphosphine})\text{nitrogen}(1+)$) were purchased from Strem Chemical Co. and used as received. $[\text{PPN}][\text{HFe}(\text{CO})_4]^-$,⁶ $\text{Mn}(\text{CO})_5\text{Br}$,⁷ and $\text{Re}(\text{CO})_5\text{Br}$ ⁸ were prepared by the literature procedures. The syntheses for the cations $\text{M}(\text{CO})_5\text{L}^+$ ($\text{M} = \text{Mn}, \text{Re}$; $\text{L} = \text{CO}, \text{PET}_3, \text{PPh}_3$) were previously described.² THF was purified by distillation from Na/benzophenone under N_2 and stored in an inert atmosphere glovebox until use. Acetonitrile was distilled from CaH_2 onto P_2O_5 and then to a fresh container under N_2 . Glassware was oven-dried and taken directly into the inert atmosphere glovebox. All compounds were identified by comparing the infrared spectra with authentic samples or literature values in the same solvent. Infrared spectra were recorded on a Beckman 4240 infrared spectrophotometer or on a Matteson Polaris FTIR.

Syntheses. Tetracarbonylferrate(2-), $\text{Na}_2\text{Fe}(\text{CO})_4$, was prepared by Na/Hg reduction of $\text{Fe}(\text{CO})_5$.^{3a,9} $\text{Fe}(\text{CO})_5$ (1.5 mL) was dried over CaH_2 and then vacuum distilled before being taken into an inert atmosphere glovebox. This $\text{Fe}(\text{CO})_5$ was slowly (10 min) added to 30 mL of THF over Na/Hg (1%, 40 g). White precipitate immediately formed; the red solution was stirred for an additional 15 min. The white precipitate was pipetted out, filtered, washed twice with THF, and dried under vacuum. The yield is ~70%. The carbonyl absorbance at 1756 (br) in CH_3CN is in reasonable agreement with literature reports.^{3a,7} Due to the presence of a small amount of moisture (or other proton source) 5% of the $\text{Na}_2\text{Fe}(\text{CO})_4$ was converted to $\text{HFe}(\text{CO})_4^-$ (2003 (w), 1913 (m), 1882 (s) cm^{-1})⁶ upon dissolving in CH_3CN . The remainder of the $\text{Fe}(\text{CO})_4^{2-}$ was stable for at least an hour. This hydride does not affect the reactions because it reacts much more slowly than $\text{Fe}(\text{CO})_4^{2-}$. While the yield of $\text{Na}_2\text{Fe}(\text{CO})_4$ is somewhat less by this procedure, the product purity (snow white powder) is quite good. The red polynuclear species are easily removed with THF.

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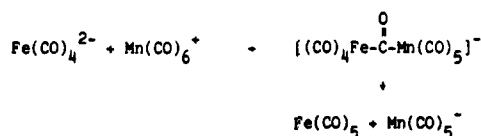
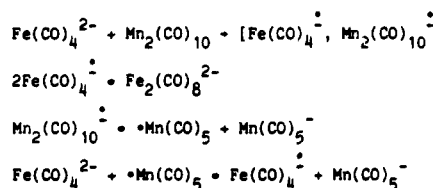
CO^{2+} TransferSingle Electron Transfer

Figure 1. Suggested schemes for reaction of $\text{Fe}(\text{CO})_4^{2-}$ with different metal carbonyl complexes.

Octacarbonyldiferrate(2-) was prepared by reaction of $\text{Fe}(\text{CO})_4^{2-}$ and $\text{Fe}(\text{CO})_5$.⁹ Equimolar $\text{Na}_2\text{Fe}(\text{CO})_4$ (1.0 g) and $\text{Fe}(\text{CO})_5$ (0.5 mL) were stirred in 20 mL of CH_3CN for 10 min. Then, 2.6 g of PPNCl in 15 mL of CH_3CN was added to the red solution and stirred for 20 min. The solution volume was reduced to 15 mL; addition of Et_2O resulted in the formation of dark red crystals of $[\text{PPN}]_2[\text{Fe}_2(\text{CO})_8]$. The product was recrystallized from $\text{CH}_3\text{CN}/\text{Et}_2\text{O}$ (70% yield). The infrared spectrum with absorbances at 1914 (m), 1862 (s), and 1830 (vw) cm^{-1} is in good agreement with a literature report.⁷ The PPN^+ salt has been previously reported as the di- CH_3CN solvate.¹⁰

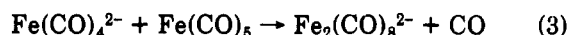
Reactions. For product determination equimolar amounts of both reactants were mixed in an Erlenmeyer flask and 10 mL of CH_3CN or THF was added. An infrared spectrum was taken immediately and the reaction was monitored every 30 min until completion. For some reactions the order of addition of reactants or the relative amounts of reactants were quite significant. The products were identified by comparing the infrared spectrum with authentic samples or literature values after separation.

Kinetics. Due to the limited solubility of $\text{Na}_2\text{Fe}(\text{CO})_4$ in THF, all kinetics were accomplished in CH_3CN at 27 °C. The reactions were run under pseudo-first-order conditions with the oxidant in excess. The kinetics were obtained on our infrared stopped-flow kinetic system¹¹ by following the decrease of the broad absorption at 1756 cm^{-1} due to $\text{Fe}(\text{CO})_4^{2-}$. Concentrations of $\text{Na}_2\text{Fe}(\text{CO})_4$ were in the range $(0.5\text{--}1.0) \times 10^{-3}$ M and oxidant concentrations were in the range 1×10^{-2} –0.5 M. Each solution was prepared in an inert atmosphere glovebox and sealed in a flask by a rubber septum. Each k_{obs} is the average of at least nine experiments; k values are the slope of plots of k_{obs} versus [oxidant]. Error limits on k_{obs} values are given as standard deviations, while error limits on second-order rate constants are 95% confidence limits.

Results and Discussion

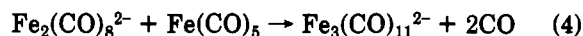
The dianions, $\text{Na}_2\text{Fe}(\text{CO})_4$ and $(\text{PPN})_2\text{Fe}_2(\text{CO})_8$, react with many metal carbonyl complexes to give a variety of products. Reactions of $\text{Fe}_2(\text{CO})_8^{2-}$ are invariably slower and frequently are responsible for products that appear late in reactions of $\text{Fe}(\text{CO})_4^{2-}$.

Reactions of $\text{Fe}(\text{CO})_4^{2-}$ and $\text{Fe}_2(\text{CO})_8^{2-}$ with $\text{Fe}(\text{CO})_5$. The synthesis of $\text{Fe}_2(\text{CO})_8^{2-}$ involves reaction of $\text{Fe}(\text{CO})_4^{2-}$ with $\text{Fe}(\text{CO})_5$.⁹



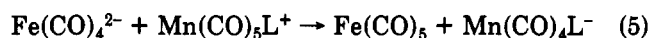
Since $\text{Fe}(\text{CO})_5$ is a frequently observed product in reactions of $\text{Fe}(\text{CO})_4^{2-}$, it is important to know the rate of reaction

3. The reaction is first order in each reactant with a second-order rate constant of $4.6 \pm 1.5 \text{ s}^{-1} \text{ M}^{-1}$. A recent electrochemical study of $\text{Fe}(\text{CO})_5$ is consistent with this value for the rate constant.¹² If an excess of $\text{Fe}(\text{CO})_5$ is used in reaction 3, further reaction with $\text{Fe}_2(\text{CO})_8^{2-}$ occurs.

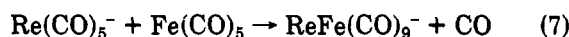
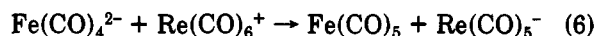


This reaction occurs over the course of several hours and is thus much slower than reaction 3. Similar sequences of reactions have been reported for $\text{Ru}_2(\text{CO})_8^{2-}$, which is converted to $\text{Ru}_3(\text{CO})_{11}^{2-}$ and $\text{Ru}_4(\text{CO})_{13}^{2-}$ sequentially.⁵ Reactions 3 and 4 show that $\text{Fe}_2(\text{CO})_8^{2-}$ and $\text{Fe}_3(\text{CO})_{11}^{2-}$ may be products for any reaction of $\text{Fe}(\text{CO})_4^{2-}$ that produces $\text{Fe}(\text{CO})_5$.

Reactions of $\text{Fe}(\text{CO})_4^{2-}$ and $\text{Fe}_2(\text{CO})_8^{2-}$ with Metal Carbonyl Cations. Reaction of $\text{Fe}(\text{CO})_4^{2-}$ with $\text{Mn}(\text{CO})_5\text{L}^+$ (L = CO, PPh_3 , PPh_2Me , PEt_3) results in $\text{Fe}(\text{CO})_5$ and $\text{Mn}(\text{CO})_4\text{L}^-$.

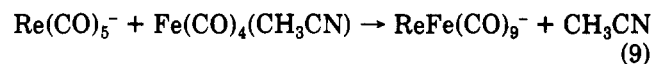
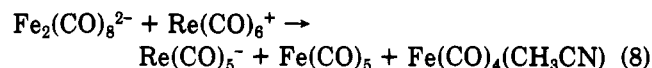


No other products are observed in reaction 5. The rate of reaction 5 is too rapid for examination on our stopped-flow system ($k_2 > 1000 \text{ s}^{-1} \text{ M}^{-1}$). The rapid rate of reaction 5 prohibits formation of $\text{Fe}_2(\text{CO})_8^{2-}$ or $\text{Fe}_3(\text{CO})_{11}^{2-}$ by consuming $\text{Fe}(\text{CO})_4^{2-}$. No further reaction is observed between $\text{Fe}(\text{CO})_5$ and $\text{Mn}(\text{CO})_4\text{L}^-$ under ambient conditions; refluxing¹³ or photochemical activation¹⁴ is reported to give $\text{MnFe}(\text{CO})_9^-$ and $\text{Fe}_2\text{Mn}(\text{CO})_{12}^-$. Reaction of $\text{Fe}(\text{CO})_4^{2-}$ with $\text{Re}(\text{CO})_6^+$ proceeded through a reaction similar to reaction 5, but the formed products react together to form $\text{ReFe}(\text{CO})_9^-$.



The $\text{ReFe}(\text{CO})_9^-$ (2096 (w), 1987 (vs), 1960 (s), 1943 (m, sh), 1876 (sh), and 1857 (m) cm^{-1}) decomposes slowly (2 weeks) to $\text{ReFe}_2(\text{CO})_{12}^-$ and $\text{Re}(\text{CO})_5^-$.¹⁵ Reaction 6 is too rapid to examine; reaction 7 occurs in a few hours.

Reaction of $\text{Fe}_2(\text{CO})_8^{2-}$ with $\text{Re}(\text{CO})_6^+$ immediately produces $\text{Re}(\text{CO})_5^-$, $\text{Fe}(\text{CO})_5$, and $\text{Fe}(\text{CO})_4(\text{CH}_3\text{CN})$. The acetonitrile complex was identified by comparison of its infrared spectrum (2063 (w) and 1953 (vs) cm^{-1}) to those of other $\text{Fe}(\text{CO})_4\text{L}$ complexes.¹⁶ This complex, $\text{Fe}(\text{CO})_4(\text{CH}_3\text{CN})$, is present when $\text{Fe}_2(\text{CO})_9$ is dissolved in CH_3CN . Within 30 min $\text{Re}(\text{CO})_5^-$ and $\text{Fe}(\text{CO})_4(\text{CH}_3\text{CN})$ react together to form $\text{ReFe}(\text{CO})_9^-$.¹⁵



If $\text{Re}(\text{CO})_6^+$ is in excess, $\text{Re}_2(\text{CO})_{10}$ is formed; this is consistent with the known rapid rate of reaction between $\text{Re}(\text{CO})_6^+$ and $\text{Re}(\text{CO})_5^-$.² The fact that $\text{Re}_2(\text{CO})_{10}$ is not formed when stoichiometric quantities are used indicates that reaction of $\text{Fe}_2(\text{CO})_8^{2-}$ with $\text{Re}(\text{CO})_6^+$ occurs very rapidly.

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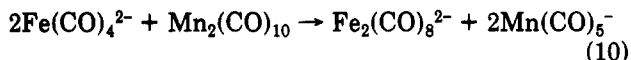
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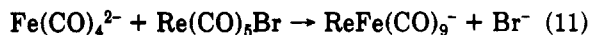
Reactions 5, 6 and 8 are consistent with transfer of a CO^{2+} from the cation to the dianion.¹⁷ For reaction of $\text{Fe}(\text{CO})_4^{2-}$ with $\text{Mn}(\text{CO})_5\text{L}^+$, reaction 5, no further reaction is observed and the products arise directly from a CO^{2+} transfer. In general, phosphine ligands prefer to bind to neutral metal centers instead of anions. Thus, thermodynamically, one would expect $\text{Fe}(\text{CO})_4\text{PPh}_3$ and $\text{Mn}(\text{CO})_5^-$ if total ligand scrambling occurred as expected for freely diffusing $\text{Mn}(\text{CO})_5\text{PPh}_3^+$ and $\text{Fe}(\text{CO})_4^{2-}$ as intermediates prior to the second electron transfer. That $\text{Mn}(\text{CO})_4\text{PPh}_3^-$ and $\text{Fe}(\text{CO})_5$ are the only products of the reaction of $\text{Fe}(\text{CO})_4^{2-}$ and $\text{Mn}(\text{CO})_5\text{PPh}_3^+$ is contrary to expectations for a free radical process. For the reactions involving $\text{Re}(\text{CO})_6^+$, $\text{Re}(\text{CO})_5^-$ can be observed early, before subsequent reactions with $\text{Fe}(\text{CO})_5$ or $\text{Fe}(\text{CO})_4(\text{CH}_3\text{CN})$ produce the heterobimetallic anion $\text{ReFe}(\text{CO})_9^-$. In reaction of $\text{Fe}_2(\text{CO})_8^{2-}$ with $\text{Re}(\text{CO})_6^+$, $\text{Fe}_2(\text{CO})_9$ is not observed, because $\text{Fe}_2(\text{CO})_9$ produces $\text{Fe}(\text{CO})_5$ and $\text{Fe}(\text{CO})_4(\text{CH}_3\text{CN})$ when dissolved in CH_3CN . Previously we demonstrated that CO^{2+} transfer occurs when the reactant anion is more nucleophilic than the product anion. The observed reactions show that $\text{Fe}(\text{CO})_4^{2-}$ and $\text{Fe}_2(\text{CO})_8^{2-}$ are more nucleophilic than $\text{Re}(\text{CO})_5^-$ and $\text{Mn}(\text{CO})_4\text{PEt}_3^-$. This is consistent with other reactions of $\text{Fe}(\text{CO})_4^{2-}$.³

Reactions of $\text{Fe}(\text{CO})_4^{2-}$ and $\text{Fe}_2(\text{CO})_8^{2-}$ with $\text{Mn}_2(\text{CO})_{10}$. Addition of an excess of $\text{Mn}_2(\text{CO})_{10}$ to $\text{Na}_2\text{Fe}(\text{CO})_4$ results in a very rapid change from yellow to brown. Immediate infrared analysis shows formation of $\text{Mn}(\text{CO})_5^-$, $\text{Fe}_2(\text{CO})_8^{2-}$, and traces of $\text{MnFe}(\text{CO})_9^-$ and $\text{Fe}(\text{CO})_5$.



The rate constant for disappearance of $\text{Fe}(\text{CO})_4^{2-}$ is $3300 \pm 600 \text{ s}^{-1} \text{ M}^{-1}$ in reaction 10. The $\text{Fe}_2(\text{CO})_8^{2-}$ could arise by dimerization of $\text{Fe}(\text{CO})_4^{2-}$ formed in a single-electron transfer or by reaction of $\text{Fe}(\text{CO})_4^{2-}$ with $\text{Fe}(\text{CO})_5$ formed from a CO^{2+} transfer. However, since the rate constant for reaction 3 is much less than that for reaction 10, a CO^{2+} transfer cannot be occurring and reaction 10 is likely a single-electron transfer. During the next 24 h $\text{Fe}_3(\text{CO})_{11}^{2-}$ was formed. Slowly adding $\text{Fe}(\text{CO})_4^{2-}$ to $\text{Mn}_2(\text{CO})_{10}$ gives $\text{MnFe}(\text{CO})_9^-$ and $\text{Mn}(\text{CO})_5^-$. These products are also consistent with a single-electron transfer producing $\text{Fe}(\text{CO})_4^{\cdot-}$ and $\text{Mn}_2(\text{CO})_{10}^{\cdot-}$. The $\text{Mn}_2(\text{CO})_{10}^{\cdot-}$ would dissociate to $\text{Mn}(\text{CO})_5^-$ and $\text{Mn}(\text{CO})_5^{\cdot}$ and the manganese and iron 17-electron complexes would couple to $\text{MnFe}(\text{CO})_9^-$. The slow addition of $\text{Fe}(\text{CO})_4^{2-}$ prohibits build up of $\text{Fe}(\text{CO})_4^{\cdot-}$, thus inhibiting formation of $\text{Fe}_2(\text{CO})_8^{2-}$. Reaction 5 shows that $\text{MnFe}(\text{CO})_9^-$ cannot be formed from $\text{Fe}(\text{CO})_5$ and $\text{Mn}(\text{CO})_5^-$.

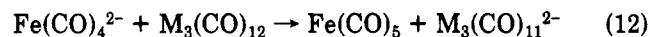
Reaction of $\text{Fe}(\text{CO})_4^{2-}$ and $\text{Fe}_2(\text{CO})_8^{2-}$ with $\text{M}(\text{CO})_5\text{Br}$, $\text{M} = \text{Mn}$ and Re . Reaction of $\text{Fe}(\text{CO})_4^{2-}$ with $\text{Re}(\text{CO})_5\text{Br}$ results in displacement of Br^- .



This reaction occurs with a second-order rate constant of $670 \pm 20 \text{ s}^{-1} \text{ M}^{-1}$. Reaction of $\text{Fe}(\text{CO})_4^{2-}$ with $\text{Mn}(\text{CO})_5\text{Br}$ does not produce such a clean reaction. In THF, where the solubility of $\text{Na}_2\text{Fe}(\text{CO})_4$ is limited, the bimetallic ion $\text{MnFe}(\text{CO})_9^-$ is formed in 70% yield. However, in CH_3CN , $\text{MnFe}(\text{CO})_9^-$, $\text{Mn}(\text{CO})_5^-$, and $\text{Fe}(\text{CO})_5$ are formed in nearly

equal amounts. This reaction occurs too rapidly for examination on our stopped-flow system. A route to $\text{Fe}(\text{CO})_5$ and $\text{Mn}(\text{CO})_5^-$ could involve CO^{2+} abstraction by $\text{Fe}(\text{CO})_4^{2-}$; however, this would lead to $\text{Mn}(\text{CO})_4^-$ or $\text{Mn}(\text{CO})_4\text{Br}^{2-}$. These do not appear to be likely intermediates. Another route lies in the reaction of $\text{Fe}_2(\text{CO})_8^{2-}$ with $\text{Mn}(\text{CO})_5\text{Br}$, which produces $\text{Fe}(\text{CO})_5$ and $\text{Mn}(\text{CO})_5^-$ as the major products in a rapid reaction. The mechanism of this reaction is unknown, but formation of $\text{Fe}_2(\text{CO})_8^{2-}$ in reaction of $\text{Fe}(\text{CO})_4^{2-}$ with $\text{Mn}(\text{CO})_5\text{Br}$ would provide a route to $\text{Fe}(\text{CO})_5$ and $\text{Mn}(\text{CO})_5^-$. The formation of $\text{Fe}_2(\text{CO})_8^{2-}$ would have to occur by single-electron transfer because reaction 3 occurs too slowly. In CH_3CN where the solubility of $\text{Na}_2\text{Fe}(\text{CO})_4$ is good, the buildup of $\text{Fe}(\text{CO})_4^{\cdot-}$ would lead to $\text{Fe}_2(\text{CO})_8^{2-}$ in addition to coupling of $\text{Fe}(\text{CO})_4^{\cdot-}$ and $\text{Mn}(\text{CO})_5^{\cdot}$ to give $\text{MnFe}(\text{CO})_9^-$. In THF where the solubility of $\text{Na}_2\text{Fe}(\text{CO})_4$ is limited, $\text{Fe}(\text{CO})_4^{\cdot-}$ would never be present in sufficient concentration for dimerization to be significant. Thus a single-electron transfer reaction to $\text{Fe}(\text{CO})_4^{\cdot-}$, $\text{Mn}(\text{CO})_5^{\cdot}$, and Br^- accounts for the product distributions in CH_3CN and THF. A single-electron transfer may also account for reaction 11 if the rate constant for coupling of $\text{Fe}(\text{CO})_4^{\cdot-}$ with $\text{Re}(\text{CO})_5^{\cdot}$ is substantially greater than that for coupling of two $\text{Fe}(\text{CO})_4^{\cdot-}$ or two $\text{Re}(\text{CO})_5^{\cdot}$. At this point there are no data to distinguish such a SET process from direct nucleophilic displacement for reaction 11.

Reaction of $\text{Fe}(\text{CO})_4^{2-}$ with $\text{M}_3(\text{CO})_{12}$, $\text{M} = \text{Ru}$ or Os . In CH_3CN , $\text{Fe}(\text{CO})_4^{2-}$ reacts cleanly with $\text{Ru}_3(\text{CO})_{12}$ or with $\text{Os}_3(\text{CO})_{12}$ to produce the $\text{M}_3(\text{CO})_{11}^{2-}$, $\text{M} = \text{Ru}$ or Os .



For $\text{M} = \text{Ru}$, further reactions of $\text{Fe}(\text{CO})_5$ with $\text{Ru}_3(\text{CO})_{11}^{2-}$ led to a complicated mixture, which was not further identified. Reaction 12 probably occurs by a CO^{2+} transfer process for such a clean reaction.

It is interesting that reactions of $\text{Fe}(\text{CO})_4^{2-}$ with trinuclear clusters previously reported⁴ (reaction 2) give different products than observed in this study (reaction 7). In our reactions resulting in $\text{Fe}(\text{CO})_5$ and $\text{M}_3(\text{CO})_{11}^{2-}$ the cluster is in excess. In the previous study the cluster was added to an excess of $\text{Fe}(\text{CO})_4^{2-}$ in refluxing THF.⁴ The formation of the mixed-cluster complex was attributed to nucleophilic attack of $\text{Fe}(\text{CO})_4^{2-}$ on the cluster.⁴ The ready formation of $\text{M}_3(\text{CO})_{11}^{2-}$ in our study may indicate a more complicated reaction sequence for formation of the $\text{FeM}_3(\text{CO})_{13}^{2-}$ cluster.

Conclusion

Most of the reactions previously reported for $\text{Fe}(\text{CO})_4^{2-}$ depend on the nucleophilicity.³⁻⁵ In this paper we have shown that a number of reactions with metal carbonyl complexes occur by single-electron transfer through $\text{Fe}(\text{CO})_4^{\cdot-}$. Reactions with $\text{Mn}_2(\text{CO})_{10}$, $\text{Mn}(\text{CO})_5\text{Br}$, and possibly $\text{Re}(\text{CO})_5\text{Br}$ are most readily interpreted in terms of a single-electron transfer. Reactions with cationic carbonyls and $\text{M}_3(\text{CO})_{12}$, $\text{M} = \text{Ru}$ and Os , occur by a nucleophilic abstraction of a CO^{2+} by $\text{Fe}(\text{CO})_4^{2-}$ to form $\text{Fe}(\text{CO})_5$. Reactions of $\text{Fe}_2(\text{CO})_8^{2-}$ appear to be very similar to those of $\text{Fe}(\text{CO})_4^{2-}$; indeed $\text{Fe}_2(\text{CO})_8^{2-}$ is a common intermediate in reactions of $\text{Fe}(\text{CO})_4^{2-}$ formed either from reaction of $\text{Fe}(\text{CO})_4^{2-}$ with $\text{Fe}(\text{CO})_5$ or by dimerization of $\text{Fe}(\text{CO})_4^{\cdot-}$.

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(17) The absence of $\text{MnFe}(\text{CO})_9^-$ and other bimetallic complexes makes any type of single-electron process unlikely. Either free radicals ($\text{Mn}(\text{CO})_5^{\cdot}$ and $\text{Fe}(\text{CO})_4^{\cdot-}$) or spin-trapped radicals ($\text{Mn}(\text{CO})_5^{\cdot+}$, $\text{Fe}(\text{CO})_4^{\cdot-}$) would be expected to produce coupling products ($\text{MnFe}(\text{CO})_9^-$, $\text{Mn}_2(\text{CO})_{10}$, or $\text{Fe}_2(\text{CO})_8^{2-}$).