In the past year we have continued to progress in our basic studies of electron and group transfer reactions between organometallic complexes. In this summary we will highlight our research on: (1) group transfer reactions, (2) electron transfer to Co(o-phen)$_3^{3+}$ and metal carbonyl halides and (3) preliminary studies on reactions of metal carbonyl anions with propylene carbonate.

**Group transfer.** Substitution of phosphine ligands for CO on metal carbonyl anions and cations slows single-electron transfer processes without significantly affecting the CO$^{2+}$ transfer rate. Thus reactions such as:

$$\text{Mn(CO)}_3(PPh_3)_2^- + \text{Mn(CO)}_6^+ -> \text{Mn(CO)}_4(PPh_3)_2^+ + \text{Mn(CO)}_5^-$$

provide very clean examples of CO$^{2+}$ transfer. Reactions of Fe(CO)$_4^{2-}$ show the CO$^{2+}$ transfer expected for such a supernucophile, but for the first time also show a single-electron transfer process. Reactions of Fe(CO)$_4^{2-}$ with Mn(CO)$_6^+$, Re(CO)$_6^+$ and M$_3$(CO)$_{12}$ (M = Ru and Os), as shown below, occur by a CO$^{2+}$ transfer.

$$\text{Fe(CO)}_4^{2-} + \text{Re(CO)}_6^+ -> \text{Fe(CO)}_5^- + \text{Re(CO)}_5^-$$

$$\text{Fe(CO)}_4^{2-} + \text{Os}_3\text{(CO)}_{12} -> \text{Fe(CO)}_5^- + \text{Os}_3\text{(CO)}_{11}^{2-}$$
Reactions of Fe(CO)$_4^{2-}$ with Mn$_2$(CO)$_{10}$ and Mn(CO)$_5$Br provide kinetic evidence for single electron-transfer and dimerization of Fe(CO)$_4^{2-}$.

Our studies of reactions of metal carbonyl cations and anions have shown that metal carbonyl cations can catalyze CO exchange reactions on metal carbonyl anions. This result provides further evidence for a mechanism involving attack of the metal carbonyl anion on a carbon of the metal carbonyl cation in CO$^{2+}$ transfer reactions.

It is also possible to transfer H$^+$, Me$^+$ and Et$^+$ between metal carbonyl anions. A more nucleophilic anion abstracts the group from a less nucleophilic anion. The relative ease of group transfer, H$^+ \gg$ Me$^+ >$ Et$^+$, is consistent with nucleophilic attack for the transfer.

**Electron transfer.** Previously we examined reactions of metal carbonyl anions with Co(o-phen)$_3^{3+}$ and obtained rate data that were not consistent with inner sphere or outer sphere reactions. In the past year we have discovered that these inconsistent rate data arise from reaction of the anions with water in the crystals of [Co(o-phen)$_3$][ClO$_4$]$_3$. The anhydrous salts provide a reactivity that is consistent with outer sphere reactions as expected. Reaction with a pyridinium salt has also been used to define the outer sphere reactivity of the metal carbonyl anions. Reaction of metal carbonyl anions with Co(o-phen)$_2$Cl$_2^{+}$ also occurs by an outer sphere pathway.

Reaction of metal carbonyl anions with metal carbonyl halides is a common approach to formation of metal-metal bonds. We have begun to use kinetic data and product analysis to understand the formation of homobimetallic versus heterobimetallic products in such reactions. Initial data indicate a nucleophilic attack, possibly through a ring-slippage mechanism. We are currently preparing indenyl complexes to obtain further confirmation of this mechanism.
Propylene carbonate. We have only just begun examining reaction of the metal carbonyl anions with propylene carbonate. The products are not simple, but preliminary rate data indicate an outer sphere process.
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