Methyl Transfer Reactions to Tetracarbonylferrate(2−): Rate and Mechanistic Studies

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Summary: Reactions of $Na_2Fe(CO)_4$ with $MeMn(CO)_5$ and $MeMoCp(CO)_3$ result in transfer of the methyl group and formation of $MeFe(CO)_4^-$ and $Mn(CO)_5^-$ or $CpMo(CO)_3^-$, respectively. These reactions are first order in $[Fe(CO)_4^{2-}]$ and in the concentration of methyl complex. The reaction of $Na_2Fe(CO)_4$ with $MeRe(CO)_5$ is quite slow and produces a mixture of products. No reaction is observed between $Na_2Fe(CO)_4$ and $MeFeCp(CO)_2$.

There has been continuing interest in organic reactions that occur by electron transfer. In the last few years studies have been reported of (1) the relationship between S_N2 and single electron transfer reactions,[1] (2) homolysis and heterolysis of organic molecules,[2] (3) organic reactions that are purely electron transfer,[3] and (4) fundamental studies of proton transfer between organic molecules.[4] These studies show the ongoing interest in nucleophilic, electron-transfer, and proton-transfer reactivity in organic systems.[1-4]

Metal carbonyl anions have also shown 1e and 2e processes, similar to organic anions.[5] The similarities between 1e (single electron transfer) and 2e (nucleophile–electrophile) reactions and the differentiation between these mechanisms for metal carbonyl anions may be related to such considerations for organic reactions. Although the mechanism is unclear, $Co(CO)_4^-$ is reported to be a useful catalyst for the hydrolysis of propylene carbonate.[6] Kochi and colleagues have found that interactions of cationic complexes with metal carbonyl anions take three forms:[7] salts of $Co(CO)_4^-$, $V(CO)_6^-$, and $Mn(CO)_5^-$ with metallocenium and pyridinium cations were shown to be charge-transfer salts;[7a] reactions of $CpMo(CO)_3^-$ with $(dienyl)Fe(CO)_3^+$ were shown to be 1e processes for the η^5-cyclohexadienyl group, but 2e$^-$ for the η^5-hexadienyl complex.[7b] The metal carbonyl anions have also recently been involved in a number of proton-transfer and acidity studies. Kristjánsdöttir and Norton demonstrated that proton transfer between group 6 complexes, $HMCp(CO)_3$ and $CpM'(CO)_3^-$, follow Marcus' theory.[8] Several studies have expanded on the acidity of the metal carbonyl hydrides reported by Jordan and Norton.[9] The gas phase acidities of $HMn(CO)_5$, $H_2Fe(CO)_4$, and $HCo(CO)_4$ demonstrated that these species are strong acids in the gas phase.[10] Ryan, Tilset, and Parker have also examined the acidity and/or proton transfer reactions of transition metal hydride species.[11] Reactions of metal carbonyl anions with cations containing hydrocarbon fragments provided complexes with hydrocarbon bridges between metal centers.[12]

Electron exchange between ruthenocene, Cp_2Ru, and ruthenocene halides, Cp_2RuX^+, has been studied.[13] These reactions were interpreted as 2e transfer coupled to atom transfer but could be considered as X^+-transfer reactions. The halogen dependence, $X = I > Br > Cl$ is consistent with that observed for self-exchange between group 6 metals,[14] $CpM(CO)_3X/CpM(CO)_3^-$, and is consistent with expectations for X^+ transfer. Transfer of Br^+ to $Mn(CO)_5^-$ has been implicated in a ketene forming reaction.[15]

Alkyl transfer as the carbocation between two metals has been observed in our laboratories.[16]

$$CpFe(CO)_2^- + RM \rightarrow RFeCp(CO)_2 + M^- \qquad (1)$$

$$R = H, Me, Et, CH_2Ph;\ M = CpMo(CO)_3$$

$$R = Me, Ph, CH_2Ph,\ M = Mn(CO)_5$$

Kinetic studies show methyl transfer to be consistent with Marcus' relationships.[16] Transfer of Me^+ from a coordinated trimethyl phosphite ligand to metal carbonyl anions in a Michaels–Arbuzov type reaction has been reported.[17]

In this manuscript we examine the reactions of $Fe(CO)_4^{2-}$ with methyl complexes, $MeFeCp(CO)_2$, $MeRe(CO)_5$, $MeMn(CO)_5$, and $MeMoCp(CO)_3$. These reactions result in CH_3^+ transfer to $Fe(CO)_4^{2-}$ in some cases.

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Table I. Characterization Data for the Metal Carbonyl Anions and Alkyl Complexes

A. anionic compd	IR (cm^{-1})	^{1}H NMR (ppm)
$Na_2Fe(CO)_4$	1756 (br)^a	
$NaMn(CO)_5$	1896 (s), 1865 (s)^a	
$NaRe(CO)_5$	1915 (s), 1866 (s)^a	
$NaMoCp(CO)_3$	1896 (s), 1777 (vs)^a	
$NaFeCp(CO)_2$	1860 (s), 1843 (sh), 1784 (vs)^a	
$PPNFe(CO)_4Me$	1889 (m), 1871 (s)^a	0.13 (s)^c

B. alkyl compd	IR (cm^{-1})	^{1}H NMR (ppm)
$MeMn(CO)_5$	2110 (w), 2012 (s), 1991 (s)^b	−0.13 (s)^c
$MeFe(CO)_5$	2127 (w), 2041 (w), 2013 (s), 1983 (s)^b	−0.25 (s)^c
$MeMoCp(CO)_3$	2024 (s), 1941 (s)^b	0.33 (s), 5.40 (s)^c
$MeFeCp(CO)_2$	2014 (s), 1960 (s)^b	0.10 (s), 4.90 (s)^c

^{a} In CH_3CN. ^{b} In hexanes. ^{c} In acetone-d_6.

Table II. Rate Constants for the Reaction of $Na_2Fe(CO)_4$ with Alkyl Complexes

	k (M^{-1} s^{-1})		k (M^{-1} s^{-1})
$MeMn(CO)_5$	16 ± 3	$MeCpMo(CO)_3$	11 ± 2

Table III. Products of the Reactions between $Fe(CO)_4^{2-}$ and Alkyl Complexes

reacn	products
$MeMn(CO)_5$	$MeFe(CO)_4^-$, $Mn(CO)_5^-$
$MeMoCp(CO)_3$	$MeFe(CO)_4^-$, $CpMo(CO)_3^-$
$MeRe(CO)_5$	$MeFe(CO)_4^-$, $Re(CO)_5^-$, unidentified products
$MeFeCp(CO)_2$	no reacn

Experimental Section

The metal carbonyl dimers ($Mn_2(CO)_{10}$, $Re_2(CO)_{10}$, $Cp_2Fe_2(CO)_4$, $Cp_2Mo_2(CO)_6$, and $Fe(CO)_5$) were purchased from Strem Chemical and used as received. Solvents (THF, hexanes, CH_3CN, and acetone-d_6) were dried and degassed prior to use. All manipulations, unless otherwise indicated, were accomplished in an inert atmosphere glovebox under an argon atmosphere. Infrared spectra were recorded on a Mattson Polaris Fourier transform infrared spectrometer in 0.5-mm cells. NMR spectra were obtained using a Varian VXR-400 NMR spectrometer. The metal carbonyl anions[18] and metal carbonyl alkyl complexes[16] were prepared as previously described. Characterization data are given in Table I.

The dianion, $Na_2Fe(CO)_4$, was prepared by Na/Hg reduction of $Fe(CO)_5$ in THF.[19] $Fe(CO)_5$ (1.5 mL) was dried over CaH_2 for 2 h and vacuum distilled into a pressure tube. In a drybox, $Fe(CO)_5$ was added slowly to 30 mL of THF over excess Na(Hg), a white precipitate and a red solution formed immediately, and the mixture was stirred for 20 min. The precipitate was filtered, washed twice with THF and dried in vacuo. The yield is 58%. IR (CH_3CN): 1756 (br) cm^{-1}. A small amount of $HFe(CO)_4^-$ was usually found upon dissolution of $Fe(CO)_4^{2-}$ in CH_3CN.[19]

The methyliron anion, $MeFe(CO)_4^-$, was prepared by an adaptation of a previously reported procedure.[20] Reaction of $HFe(CO)_4PPN$[21] (1 g) in 10 mL of THF with 1 equiv of BuLi (10 M in hexane) added dropwise at −78 °C was accomplished in a Schlenk flask. The flask was removed from the −78 °C bath and stirred for 30 min. The reddish brown solid was collected and washed (3×) with THF and (1×) with hexanes and dried in vacuo. Addition of 10 mL of THF resulted in a suspension which was treated with predried and degassed methyl tosylate. The solution was filtered and the product crystallized from the filtrate by slow addition of Et_2O. The light yellow product was characterized by IR (1899 (m) and 1871 (s) cm^{-1} in THF) and ^{1}H NMR (0.13 (s) ppm in acetone-d_6).

The kinetic data were obtained on our infrared stopped-flow spectrometer with the data manipulated by the OLIS stopped-flow operating system.[22] All reactions were examined in CH_3CN solution under pseudo-first-order conditions with the alkyl complex in excess. The rate of disappearance of $Fe(CO)_4^{2-}$, initially present at a concentration of 0.001 M, was determined by following the absorbance at 1758 cm^{-1}. Rate constants were determined as the slope of plots of k_{obsd} versus [RM]. Error limits of k_{obsd} are standard deviations; error limits in k values are 95% confidence limits. The rate constants are presented in Table II.

Product determinations were accomplished in CH_3CN solution with a 1:1 ratio of $Fe(CO)_4^{2-}$ and alkyl complex and followed by infrared spectroscopy. Confirmation was obtained by removing the CH_3CN and washing with hexane to remove possible neutral species prior to redissolving to determine the anionic species.

Results

Products. Reaction of $Na_2Fe(CO)_4$ with $MeMn(CO)_5$ and $MeMoCp(CO)_3$ cleanly provided the methyl transfer products.

$$Fe(CO)_4^{2-} + MeMn(CO)_5 \rightarrow MeFe(CO)_4^- + Mn(CO)_5^- \quad (2)$$

$$Fe(CO)_4^{2-} + MeMoCp(CO)_3 \rightarrow MeFe(CO)_4^- + CpMo(CO)_3^- \quad (3)$$

These reactions were completed in seconds. In contrast, reaction of $Fe(CO)_4^{2-}$ with $MeRe(CO)_5$ was not completed after 18 h. In the first hour only $HFe(CO)_4^-$ was observed in addition to the reactants. After 18 h $Re(CO)_5^-$ and $CH_3Fe(CO)_4^-$ were observed with the reactants. No reaction was observed between $Na_2Fe(CO)_4$ and $MeFeCp(CO)_2$ after 18 h. No reaction was also observed between $[PPN][CH_3Fe(CO)_4]$ and $PPNCpFe(CO)_2$ with or without the presence of Na^+. The products are summarized in Table III.

Kinetics. Rate constants were determined for reactions 2 and 3 as the slope of plots of the pseudo-first-order rate constant versus the concentration of alkyl complex. The plot for $MeMoCp(CO)_3$ is shown in Figure 1. The rate law is

$$\text{rate} = k[Fe(CO)_4^{2-}][MeM]$$

typical for transfer processes. For these two reactions the kinetics are very well behaved. As frequently observed, the rate constant for reactions of the manganese complex (k = 16 ± 3 M^{-1} s^{-1}) and the molybdenum complex (k = 11 ± 2 M^{-1} s^{-1}) are very similar.

Discussion

The dianion, $Fe(CO)_4^{2-}$, has been termed a super nucleophile in its reactions with organic complexes.[19] Reaction of $Fe(CO)_4^{2-}$ with MeI is not clean,[20] preventing

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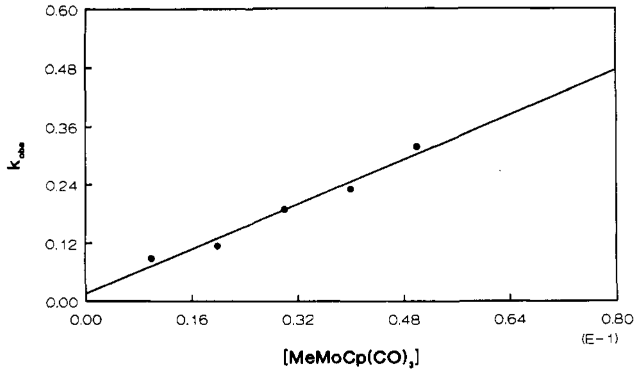

Figure 1. Plot of k_{obs} versus [MeMoCp(CO)$_3$] for the reaction with 1×10^{-3} M $Fe(CO)_4^-$ in 27 °C.

a direct measurement of its nucleophilicity for comparison to other anions. However, competition of $Fe(CO)_4^{2-}$ with other anions for a methyl group allows an assessment of the relative nucleophilicity. Reactions 2 and 3 can be considered as competitions of $Fe(CO)_4^{2-}$ with $Mn(CO)_5^-$ or $CpMo(CO)_3^-$ for CH_3^+. The methyl is transferred, forming $MeFe(CO)_4^-$ and the manganese and molybdenum anions. Thus, as expected, the $Fe(CO)_4^{2-}$ anion is more nucleophilic than $Mn(CO)_5^-$ or $CpMo(CO)_3^-$.[23] However, $Na_2Fe(CO)_4$ does not react with $MeFeCp(CO)_2$ and only partially reacts with $MeRe(CO)_5$, indicating $Fe(CO)_4^{2-}$ is less nucleophilic than might be expected. Very strong ion-pairing from the Na^+ may reduce the electron density on the iron center.[24] Attempts to prepare the PPN salt of $Fe(CO)_4^{2-}$ resulted in significant contamination by $HFe(CO)_4^-$. That $PPNFeCp(CO)_2$ does not react with [PPN][$MeFe(CO)_4^-$] indicates that $CpFe(CO)_2^-$ is not inherently more nucleophilic than $Fe(CO)_4^{2-}$. The failure of $Na_2Fe(CO)_4$ to react with $MeFeCp(CO)_2$ and the very slow reaction with $MeRe(CO)_5$ result from strong ion-pairing of the Na^+ ions which reduce the reactivity of the $Fe(CO)_4^{2-}$.

Reactions of $Na_2Fe(CO)_4$ with $MeMn(CO)_5$ and $MeMoCp(CO)_3$ appear to be very similar to the previously reported reactions with $CpFe(CO)_2^-$ where direct CH_3^+ transfer was suggested. The rate constant for reaction of $Na_2Fe(CO)_4$ with $MeMoCp(CO)_3$ in CH_3CN (11 ± 2 s^{-1} M^{-1}) is very similar to the rate constant for $NaCpFe(CO)_2$ with $MeMoCp(CO)_3$ in THF (16 s^{-1} M^{-1}). The absence of dimers, $Fe_2(CO)_8^{2-}$, $Mn_2(CO)_{10}$ and $Cp_2Mo_2(CO)_6$ makes single electron processes unlikely. We favor a direct transfer of CH_3^+ from $MeMn(CO)_5$ and $MeMoCp(CO)_3$ to $Fe(CO)_4^{2-}$ as the mechanism of these reactions.

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