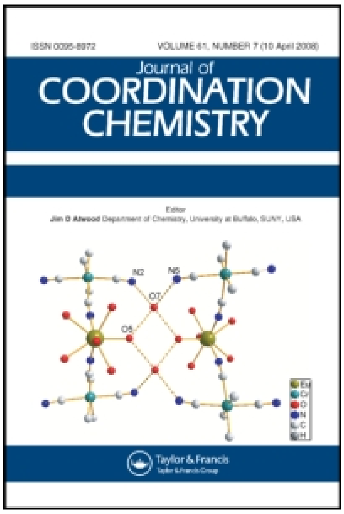

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POSSIBLE HYDRIDE AND METHIDE TRANSFER REACTIONS: REACTIONS OF $Fe(CO)_4R^-$ (R = H, CH_3) AND $W(CO)_5R^-$ (R = H, CH_3, Cl, Br, I) WITH METAL CARBONYL CATIONS

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Reactions of metal carbonyl cations ($M(CO)_6{}^+$, M = Mn, Re) with hydride-, methide- or halide-containing metal carbonyl anions ($Fe(CO)_4R^-$, R = H, Me; $W(CO)_5R^-$, R = H, Me, Cl, Br, I) produce products that indicate several mechanisms are operative. Reactions of the halo-tungsten complexes produce neutral, solvated tungsten complexes, $W(CO)_5(CH_3CN)$ and $W(CO)_4(CH_3CN)_2$ and $M(CO)_5X$ in a reaction that appears to be initiated by decomposition of $W(CO)_5X^-$. In contrast, the tungsten hydride and methide complexes react, predominantly, by transfer of the hydride or methide to a carbonyl of the cation at a much faster rate. The iron hydride and methide complexes react by iron-based nucleophilicity involving a two-electron process.

KEYWORDS: hydride, methide, metal carbonyl anion, metal carbonyl cation, electron transfer

INTRODUCTION

Atom transfer reactions form an important class of electron transfer reactions.[1] Usually such reactions are regarded as transfer of the atom separate from the electron transfer. However, in other cases it is more descriptive to consider transfer of the atom (or group) with its likely electron configuration. We have previously reported on transfers of H^+, $CH_3{}^+$, Br^+ and CO^{2+} between metal carbonyl anions.[2–4] In this paper we examine possible transfer of H^-, $CH_3{}^-$ and Br^- from $M(CO)_nX^-$ (M = Cr, Mo, W, n = 5, X = H, CH_3, Cl, Br, I; M = Fe, n = 4, X = H, CH_3) to metal carbonyl cations.

Hydride addition to metal carbonyl complexes is important in CO hydrogenation reactions; these reactions sometimes result in formyl complexes.[5,6] Studies have shown that these hydride additions occur through either hydride transfer reactions,[7] or by electron transfer reactions.[8]

$$CpW(CO)_3Me + LiBHEt_3 \xrightarrow{-70^\circ C} CpW(CO)_2C(O)HMe^- + Li^+ + BEt_3 \qquad (1)$$

$$Cp^*Mo(CO)_3L + \xrightarrow[20^\circ C]{LiAlH_4} CpMo(CO)L_2H + CpMo(CO)_2LH \qquad (2)$$

$$L = PMe_3 \text{ or } PMePh_2$$

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In reaction **1** a hydride is transferred, producing the formyl, while in reaction **2** the mechanism is suggested as an electron transfer with hydrogen atom extraction from LAH or solvent. Anionic hydride complexes and their reactions have been reviewed.[9]

The complexes $RFe(CO)_4^-$ have been very useful synthetic tools.[9–14] For R = H catalytic and stoichiometric reactions have been reported.[9–12] The complexes R = alkyl and acyl have proved to be very useful synthetic reagents for organic preparations.[13,14] Complexes R = CHO and R'S are also known.[15,16]

Anionic complexes, $RM(CO)_5^-$ and $RM(CO)_4L^-$ (R = H, CH_3, Cl, Br, I; L = a phosphine ligand) have also been prepared.[17–22] The hydride complexes have been reacted with alkyl halides,[17] acyl chlorides, CO_2[18] and metal carbonyls.[19] The methyl complexes have been reacted with CO_2 and a few other complexes.[20] The halide complexes have not been extensively studied.[22]

EXPERIMENTAL

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 and cations were prepared by literature procedures; the references and characterization data are shown in Table 1.

Reactions between metal carbonyl anions and cations were studied in CH_3CN at room temperature with equimolar solutions. The reactions were monitored by infrared spectra until no change was observed. The CH_3CN was removed by vacuum and the solids extracted with hexanes to characterize uncharged products.

Table 1 Preparation and characterization data for metal carbonyl anions and cations

Compound	Reference	Characterization
$Na_2[Fe(CO)_4]$	2b	IR(CH_3CN): 1756 cm^{-1}
$PPN[HFe(CO)_4]$	23	IR(CH_3CN): 2002(w), 1913(m), 1882(s) cm^{-1}
$PPN[CH_3Fe(CO)_4]$	2b, 24	IR(CH_3CN): 1994(w), 1874(vs) cm^{-1}; ^1H NMR(d^6-acetone): 0.13 ppm
$PPN[HW(CO)_5]$	25	IR(THF): 2029(w), 1888(s), 1856(m) cm^{-1}; ^1H NMR(CD_3CN): −4.2 ppm
$NEt_4[CH_3W(CO)_5]$	26	IR(THF): 2031(w), 1884(s), 1836(m) cm^{-1}; ^1H NMR(CD_3CN): −0.84(s,3H), 1.19(tt, 12 H), 3.14(q,8H)
$NEt_4[W(CO)_5Cl]$	22b	IR(CH_3CN): 1920(s), 1848(m) cm^{-1}
$NEt_4[Cr(CO)_5Cl]$	22b	IR(CH_3CN): 1926(s), 1854(m) cm^{-1}
$[Re(CO)_6]BF_4$	27	IR(CH_3CN): 2085 cm^{-1}
$[Mn(CO)_6]BF_4$	27	IR(CH_3CN): 2096 cm^{-1}
$[CpFe(CO)_3]BF_4$	39	IR(CH_3CN): 2124(m), 2077(s) cm^{-1}

The residue was redissolved in CH_3CN for characterization. Where appropriate NMR spectra were examined.

Kinetic studies of a few reactions were examined by infrared stopped-flow techniques.[28] These were accomplished by following anion absorptions with the cation in excess in CH_3CN solution. Rate constants were obtained from plots of k_{obs} *vs.* $[M^+]$. Error limits in k_{obs} are standard deviations; error limits in k are 95% confidence limits.

RESULTS AND DISCUSSION

Reactions of $M(CO)_5X^-$ with Metal Carbonyl Cations

The reactions of a metal carbonyl halo anion with a metal carbonyl cation produces four products as shown below for reaction of $W(CO)_5Cl^-$ with $Re(CO)_6{}^+$ in CH_3CN.

$$W(CO)_5Cl^- + Re(CO)_6{}^+ \xrightarrow{CH_3CN} W(CO)_5(CH_3CN) + W(CO)_4(CH_3CN)_2 + Re(CO)_5Cl + Re_2(CO)_{10} \qquad (3)$$

These products were formed over a couple of days at room temperature. Similar products were formed for the molybdenum anion or for $Mn(CO)_6{}^+$ and $CpFe(CO)_3{}^+$ as the cations. Reaction products and infrared spectra are shown in Table 2. To further define the nature of reaction **3**, we examined the

Table 2 Reaction products and infrared spectra for reaction of $M(CO)_5X^-$ with metal carbonyl cations

Reactants	Products	Absorptions
$Re(CO)_6{}^+$ + $W(CO)_5Cl^-$	$W(CO)_5(CH_3CN)$	1939
	$W(CO)_4(CH_3CN)_2$	1898(s), 1840(m)
	$Re(CO)_5Cl$	2045(s), 1968(m)
	$Re_2(CO)_{10}$	2071(m), 2012(s), 1968(m)
$Mn(CO)_6{}^+$ + $W(CO)_5Cl^-$	$W(CO)_5(CH_3CN)$	1939
	$W(CO)_4(CH_3CN)_2$	1898(s), 1840(m)
	$Mn(CO)_5Cl$	2052(s), 2010(m)
	$Mn_2(CO)_{10}$	2046(s), 2012(vs), 1981(m)
$CpFe(CO)_3{}^+$ + $W(CO)_5Cl^-$	$W(CO)_5(CH_3CN)$	1939
	$W(CO)_4(CH_3CN)_2$	1898(s), 1840(m)
	$CpFe(CO)_2Cl$	2076(w), 2051(s), 2003(s)
	$Cp_2Fe_2(CO)_4$	1991(s), 1952(w), 1775(s)
$Re(CO)_6{}^+$ + $Cr(CO)_5Cl^-$	$Cr(CO)_5(CH_3CN)$	1944
	$Cr(CO)_4(CH_3CN)_2$	1904(s), 1844(m)
	$Re(CO)_5Cl$	2045(s), 1968(m)
	$Re_2(CO)_{10}$ - trace	
$Mn(CO)_6{}^+$ + $Cr(CO)_5Cl^-$	$Cr(CO)_5(CH_3CN)$	1944
	$Cr(CO)_4(CH_3CN)_2$	1904(s), 1844(m)
	$Mn(CO)_5Cl$	2052(s), 2010(m)
	$Mn_2(CO)_{10}$	2046(s), 2012(vs), 1981(m)
$CpFe(CO)_3{}^+$ + $Cr(CO)_5Cl^-$	$Cr(CO)_5(CH_3CN)$	1944
	$Cr(CO)_4(CH_3CN)_2$	1904(s), 1844(m)
	$CpFe(CO)_2Cl$	2051(s), 2003(m)
	$Cp_2Fe_2(CO)_4$	late in reaction

reaction of $W(CO)_5Cl^-$ with CH_3CN which produces $W(CO)_5(CH_3CN)$ and $W(CO)_4(CH_3CN)_2$[29]

$$W(CO)_5Cl^- \xrightarrow{CH_3CN} W(CO)_5(CH_3CN) + W(CO)_4(CH_3CN)_2{}^+Cl^- \qquad (4)$$

$$Re(CO)_6{}^+ + Cl^- \longrightarrow Re(CO)_5Cl + CO \qquad (5)$$

and the reaction of $Re(CO)_6{}^+$ with $[Et_4N^+][Cl^-]$ which produces $Re(CO)_5Cl$.[31] Both of these reactions occur as readily as reaction **3**. It thus seems likely that $W(CO)_5Cl^-$ decomposes to $W(CO)_5(CH_3CN)$ and reaction of the free Cl^- with $Re(CO)_6{}^+$ gives $Re(CO)_5Cl$. The only product not easily ascribed to this scheme is $Re_2(CO)_{10}$ which must arise from an electron transfer. In these reactions there is no evidence to support transfer of X^- between the metal centers.

Reaction of $HW(CO)_5{}^-$ with $M(CO)_6{}^+$, M = Mn and Re

A number of products are observed in the reaction of $Mn(CO)_6{}^+$ with $HW(CO)_5{}^-$. The final products are $MnW(CO)_{10}{}^-$ (see Table 3 for infrared spectra),[31–33] $W(CO)_5(CH_3CN)$, $W(CO)_6$ and $Mn_2(CO)_{10}$ (minor). Early in the reaction $Mn(CO)_5{}^-$ was observed and the low temperature ^1H NMR spectrum (−30°C) showed $HMn(CO)_5$ to be formed.

$$\begin{aligned} Mn(CO)_6{}^+ + HW(CO)_5{}^- \longrightarrow\ & HMn(CO)_5 + W(CO)_5(CH_3CN) + CO \\ & + \\ & W(CO)_6 + Mn(CO)_5{}^- \\ & + \\ & MnW(CO)_{10}{}^- + Mn_2(CO)_{10} \qquad (6) \end{aligned}$$

At −40°C the resonance for $W(CO)_5H^-$ (−4.5 ppm) was not present; trace resonances were observed at 14 ppm (unassigned) and at −7.9 ppm ($HMn(CO)_5$). The major new resonance at low temperature and persisting to room temperature was observed between 3.9–4.2 ppm. After two hours at room temperature this resonance disappeared and the resonance for $HMn(CO)_5$ increased. The resonance at ~4.0 ppm is likely a fast exchange limit spectrum for the exchange between $HW(CO)_5{}^-$ and a carbonyl of $Mn(CO)_6{}^+$. The freezing point of CH_3CN (−45°C) prevented proper analysis. Very similar observations pertain to the reaction of $HW(CO)_5{}^-$ with $Re(CO)_6{}^+$. The primary products at room temperature are $W(CO)_5(CH_3CN)$ and $ReW(CO)_{10}{}^-$,[33] with similar observations by low temperature ^1H NMR spectroscopy.

Reaction of $CH_3W(CO)_5{}^-$ with $Mn(CO)_6{}^+$

Reaction of the methyl complex, $CH_3W(CO)_5{}^-$ with $Mn(CO)_6{}^+$ is much cleaner than similar reactions of the hydride; $CH_3C(O)Mn(CO)_5$, $W(CO)_5(CH_3CN)$ and $WMn(CO)_{10}{}^-$ are the products from IR studies. Low temperature ^1H NMR experiments showed $CH_3C(O)Mn(CO)_5$[34] and CH_4 formed in equal amounts from −30°C to room temperature as the resonance for $CH_3W(CO)_5{}^-$ decreased. Methane (0.188 ppm in CD_3CN) was identified by comparison to an authentic sample in CD_3CN. This reaction was slower than the similar reaction between $HW(CO)_5^-$ with $Mn(CO)_6^+$, but occurred readily at 0°C.

Reactions of $HFe(CO)_4^-$ *with* $M(CO)_6^+$, $M = Mn, Re$

Reaction of $HFe(CO)_4^-$ with $Mn(CO)_6^+$ in CH_3CN at room temperature produces $HMn(CO)_5$[35] and $Fe(CO)_5$. $Mn(CO)_5^-$ was observed early in the reaction and a small amount of $Mn_2(CO)_{10}$ was observed. Reaction of $HFe(CO)_4^-$ with $Mn(CO)_6^+$ under an atmosphere of ^{13}CO gave enrichment in $Fe(CO)_5$ and $HMn(CO)_5$ but only a very small amount in $Mn(CO)_5^-$. Low temperature NMR spectra showed that as $HFe(CO)_4^-$ decreased in quantity $HMn(CO)_5$ increased. $HFe(CO)_4^-$ does not react significantly with $Re(CO)_6^+$.

Reaction of $HFe(CO)_4^-$ with $Mn(CO)_6^+$ provided good kinetic data fitting a rate law.

$$\text{rate} = k\,[HFe(CO)_4^-][Mn(CO)_6^+]$$

A plot of k_{obs} *vs.* $[Mn(CO)_6^+]$ is shown in Figure 1, giving $k = 23 \pm 3\ s^{-1}M^{-1}$.

Reaction of $CH_3Fe(CO)_4^-$ *with* $Mn(CO)_6^+$

Reaction of $CH_3Fe(CO)_4^-$ with $Mn(CO)_6^+$ was quite different than reaction of $HFe(CO)_4^-$. Reaction of a 1.5:1 ($CH_3Fe(CO)_4^-$: $Mn(CO)_6^+$) ratio produced $FeMn(CO)_9^-$ with a trace of $Mn_2(CO)_{10}$ and $Fe(CO)_5$.[36] Methane was evolved. A 1:1 ratio produced somewhat more $Mn_2(CO)_{10}$. Low temperature ^1H NMR did not show any product resonances, as expected for the products observed by IR.

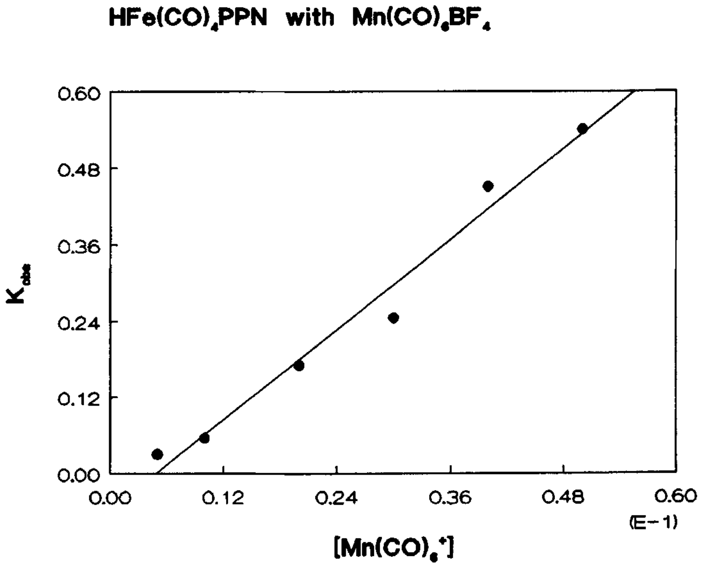

Figure 1 Pseudo first-order plot of k_{obs} *vs.* $[Mn(CO)_6^+]$ for reaction of $HFe(CO)_4^-$ with $Mn(CO)_6^+$ in CH_3CN at room temperature. The second-order rate constant is obtained as the slope.

Mechanism of Reactions of $RW(CO)_5^-$ and $RFe(CO)_4^-$ with $M(CO)_6^+$, M = Mn, Re

For these reactions three distinct mechanisms are possible: (a) A transfer of R^- to the cation, probably at a carbon of the carbonyl would lead to the acetonitrile-coordinated species, $W(CO)_5(CH_3CN)$ or $Fe(CO)_4(CH_3Cn)$ and $RC(O)M(CO)_5$ or $RM(CO)_5$ as initial products. (2) A single electron transfer producing odd-electron complexes, $M(CO)_5\cdot$ or $RFe(CO)_4\cdot$ would probably lead to $M_2(CO)_{10}$, RH (from hydrogen atom abstraction by $R\cdot$) and other products from radical reactions. (3) Transfer of CO^{2+} is possible producing $M(CO)_5^-$ and $W(CO)_6$ (or $Fe(CO)_5$) with R^+, initially, and $RM(CO)_5$ later in the reaction.

Evidence for each mechanistic type is present in some of the observed reactions. Previous studies of reactions of $HFe(CO)_3L^-$ and $HW(CO)_4L^-$ with alkyl halides showed that the tungsten complex displayed hydride-based nucleophilicity while the iron complex displayed metal-based nucleophilicity.[9,12e,17,21] Both hydride transfer and electron transfer were observed in reactions with metal carbonyl complexes.[19] The three possibilities are shown in Figure 2 for reaction between $HW(CO)_5^-$ and $Mn(CO)_6^+$. From Marcetta Darenbourg's studies,[9,12e,17,21] reactions of $HW(CO)_5^-$ would be expected to proceed by hydride transfer or electron transfer while reactions of $HFe(CO)_4^-$ would be more likely to show nucleophilic-based CO^{2+} transfer.

Most of the observed products shown in Table 3 could be accommodated by any of the schemes in Figure 2. The most diagnostic product is the heterobimetallic anion, $MnW(CO)_{10}^-$ for example. This species has been prepared by two related reactions.[32,33]

$$NaMn(CO)_5 + W(CO)_6 \xrightarrow{\Delta} NaMnW(CO)_{10} + CO \qquad (7)$$

$$NaMn(CO)_5 + W(CO)_5(THF) \longrightarrow NaMnW(CO)_{10} + THF \qquad (8)$$

Reactions 8 occurs readily at room temperature and is the likely source of $MnW(CO)_{10}^-$; however, this requires the presence of $Mn(CO)_5^-$. The manganese anion can arise from: (1) reduction or disproportionation of $Mn_2(CO)_{10}$, (2) deprotonation of $HMn(CO)_5$, (3) disproportionation of $Mn(CO)_5$ and (4) two electron reduction of $Mn(CO)_6^+$ (CO^{2+} transfer). The reaction conditions are not sufficiently severe for reduction or disproportionation of $Mn_2(CO)_{10}$ or for deprotonation of $HMn(CO)_5$. In two cases $Mn(CO)_5^-$ is identified as an intermediate, but does not persist, consistent with the conditions not being sufficiently forcing for $Mn(CO)_5^-$ formation from $Mn_2(CO)_{10}$ or $HMn(CO)_5$. Disproportionation of radicals is commonly observed,[37] but for $Mn(CO)_5\cdot$ requires temperatures sufficient for CO dissociation to compete with radical recombination. This seems to be well above room temperature for $Mn(CO)_5\cdot$.[38] Thus the most likely source for

Table 3 Reaction products for $RM(CO)_n^-$ with $Mn(CO)_6^+$ (R = H or Me, M = W, n = 5; R = H or Me, M = Fe, n = 4)

Reactants	Products
$HW(CO)_5^- + Mn(CO)_6^+$	$HMn(CO)_5 + W(CO)_5(CH_3CN) + W(CO)_6 + Mn(CO)_5^- + MnW(CO)_{10}^- + Mn_2(CO)_{10}$
$CH_3W(CO)_5^- + Mn(CO)_6^+$	$CH_3C(O)Mn(CO)_5 + W(CO)_5(CH_3CN) + MnW(CO)_{10}^-$
$HFe(CO)_4^- + Mn(CO)_6^+$	$Mn(CO)_5^- + Fe(CO)_5 + HMn(CO)_5$
$CH_3Fe(CO)_4^- + Mn(CO)_6^+$	$FeMn(CO)_9^- + Fe(CO)_5 + Mn_2(CO)_{10}$

Hydride Transfer

$$HW(CO)_5^- + Mn(CO)_6^+ \xrightarrow{CH_3CN} W(CO)_5(CH_3CN) + HC(O)Mn(CO)_5$$

$$HC(O)Mn(CO)_5 \xrightarrow{-CO} HMn(CO)_5 \xrightarrow{-H_2} Mn_2(CO)_{10}$$

Single Electron Transfer

$$HW(CO)_5^- + Mn(CO)_6^+ \longrightarrow HW(CO)_5\cdot + Mn(CO)_6\cdot$$

$$Mn(CO)_6\cdot \xrightarrow{-CO} Mn(CO)_5.$$

$$2\ Mn(CO)_5. \longrightarrow Mn_2(CO)_{10}$$

$$Mn(CO)_5\cdot + HW(CO)_5\cdot \longrightarrow HMnW(CO)_{10}$$

CO^{2+} Transfer or Two-Electron Transfer

$$HW(CO)_5^- + Mn((CO)_6^+ \longrightarrow HW(CO)_6^+ + Mn(CO)_5^-.$$

$$HW(CO)_6^+ \longrightarrow H^+ + W(CO)_6$$

$$Mn(CO)_5^- + H^+ \longrightarrow HMn(CO)_5$$

$$Mn(CO)_5^- + Mn(CO)_6^+ \longrightarrow Mn_2(CO)_{10} + CO$$

Figure 2 Possible mechanisms and expected products for reaction of $HW(CO)_5^-$ with $Mn(CO)_6^+$

$Mn(CO)_5^-$ is two-electron reduction of $Mn(CO)_6^+$.[4] In previous reductions of $Mn(CO)_6^+$ to $Mn(CO)_5^-$ we had demonstrated that a single-event, two-electron reduction occurred. The systems currently under investigation were not amendable to such detailed studies and a single-event, two-electron transfer cannot be distinguished from two, one-electron transfers. Formation of the heterobimetallic anion (except for $ReFe(CO)_9^-$) also requires the presence of the acetonitrile complexes $W(CO)_5(CH_3CN)$ or $Fe(CO)_4(CH_3CN)$ since reactions of the binary carbonyls with $Mn(CO)_5^-$ are slow.[4b,32] In the reaction of $HFe(CO)_4^-$ with $Mn(CO)_6^+$ where $Fe(CO)_5$ is formed, the $Mn(CO)_5^-$ is a final product ($Fe(CO)_5$ doesn't react with $Mn(CO)_5^-$).

The formation of the heterobimetallic anion (or $Mn(CO)_5^-$) is an indication that each reaction of $RM(CO)_n^-$ with $M'(CO)_6^+$ proceeds with some component of the two-electron transfer mechanism. However, other mechanisms may also be operative. For example it is quite likely that CH_3^- transfer is responsible for formation of $CH_3C(O)Mn(CO)_6$ from reaction of $CH_3W(CO)_5^-$ with $Mn(CO)_6^+$. Failure to form the acetylmanganese complex from a similar reaction with $CH_3Fe(CO)_4^-$ is consistent with Darenbough's suggestion that the tungsten methyl carries more negative charge.[21b] Methane formation most likely arises from $CH_3\cdot$ abstracting a hydrogen atom from the solvent.

Most of these reactions had complications that did not allow kinetic analysis. The one reaction, $HFe(CO)_4^- + Mn(CO)_6^+$, that provided good kinetic data had the typical rate law with a first-order dependence on both reactants. This reaction gives similar products to the reaction of $Fe(CO)_4^{2-}$ with $Mn(CO)_6^+$,[4b] but at a much slower rate (at least 50 × slower). If $HFe(CO)_4^-$ reacts with $Mn(CO)_6^+$ by a CO^{2+} transfer, it would be the first example of CO^{2+} transfer that was sufficiently slow for kinetic analysis. Although good kinetic analysis wasn't possible, the reactions of the tungsten complexes, $W(CO)_5X^-$, show a rate dependence on the X group, X = H>Me >halide, indicating the order of X group based nucleophilicity.

CONCLUSION

For the reactions reported in this manuscript, different mechanisms pertain. In general, however, the results agree with Darensbourg's conclusion that $HW(CO)_5^-$ shows hydride-based nucleophilicity while $HFe(CO)_4^-$ shows metal-based nucleophilicity.

Reactions of the halo anions ($W(CO)_5Cl^-$, $W(CO)_5Br^-$ and $W(CO)_5I^-$) do not require reaction between the anion and cation and are best interpreted as decomposition of $W(CO)_5X^-$ (see reactions **4** and **5**). The cleanest reaction, $HFe(CO)_4^-$ with $Mn(CO)_6^+$ appears to proceed through only a $2e^-$ process, showing the iron-based nucleophilicity. For the tungsten hydride an initial exchange of hydride from tungsten to the carbon of a carbonyl on $Mn(CO)_6^+$ is followed by a mixture of all three mechanisms leading to the array of products shown in reaction **6**. For the methyl complexes a component of single electron transfer for both $CH_3Fe(CO)_4^-$ and $CH_3W(CO)_5^-$ is accompanied by CH_3^- transfer for the tungsten complex and the two-electron process for the iron complex. Thus the methyl complexes also show that the iron complex shows metal based nucleophilicity while the tungsten complex shows methyl-based nucleophilicity.

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