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Hydride Participation in Electron Transfer Processes between Metal Carbonyl Anions and Cations

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Kinetic studies of selected metal carbonyl anions establish their reactivity as nucleophiles or for electron transfer. The iron species, $[HFe(CO)_3L]^-$ (L = CO, PPh_3), behave as metal-centered nucleophiles when reacted with $[M(CO)_6]^+$ (M = Mn, Re). Determination of the deuterium kinetic isotope ratio from kinetic studies of $[HFe(CO)_4]^-$ and $[DFe(CO)_4]^-$, $k_H/k_D = 2.8$, indicates primary isotope effects for reaction with $Mn(CO)_6{}^+$. Initial products from transfer of a CO and back transfer of two electrons are observed in some cases. For $Re(CO)_6{}^+$ exclusive formation of $HRe(CO)_5$ as a rhenium product strongly indicates a hydrogen transfer mechanism.

Introduction

Reactions between metal carbonyl anions and cations, which effect CO transfer, have been reported by Zhen and Atwood.[1] The transfer is a synchronous two-electron transfer and CO transfer in the opposite direction. For ionic species containing only carbonyls, phosphines, and phosphites, such a transfer process was observed when the reactant anion was a stronger nucleophile than the product anion.[1]

A potentially similar reaction was reported by Wang et al.[2]

$$[Mn(CO)_6]^+ + [HFe(CO)_4]^- \rightarrow HMn(CO)_5 + Fe(CO)_5 \tag{1}$$

The complexes $[Mn(CO)_6]^+$ and $[HFe(CO)_4]^-$ reacted in acetonitrile to form $HMn(CO)_5$, $Fe(CO)_5$ (major products), and $Mn_2(CO)_{10}$ (minor product). The anion, $[Mn(CO)_5]^-$, was observed early in the reaction. This reaction produced clean kinetics and followed the rate law

$$\text{rate} = k\,[HFe(CO)_4{}^-][Mn(CO)_6{}^+] \tag{2}$$

Hydride attack on an electrophilic carbonyl carbon by $[PPN][HFe(CO)_4]$ is unlikely. Such hydridic addition would yield the formyl, $Mn(CO)_5(CHO)$, as the initial manganese product. The initial formation of $[Mn(CO)_5]^-$ disfavors hydridic attack. Additionally, Darensbourg et al.[3] have shown $[HFe(CO)_4]^-$ to behave as a metal-centered nucleophile.

This article reports reactions of potential hydride donors, $HFe(CO)_3L^-$, with $M(CO)_6{}^+$ (L = CO, PPh_3; M = Mn, Re) to further define the mechanism for reactions that involve CO and H^- transfer.

Results

The nucleophilicity of $HFe(CO)_4{}^-$ was experimentally determined through reaction with CH_3I.

$$[HFe]^- + CH_3I \rightarrow CH_4 + Fe + I^- \tag{3}$$

$$(Fe = Fe(CO)_4,\ Fe(CO)_3PPh_3)$$

Reaction of $[PPN][HFe(CO)_4]$ and $[PPN][DFe(CO)_4]$ with CH_3I is first order in both the anion and CH_3I and proceeds at 25 °C in CH_3CN with rate constants of $(2.4 \pm 0.2) \times 10^{-2}$ and $(2.2 \pm 0.2) \times 10^{-2}$ $M^{-1}\,s^{-1}$, respectively ($k_H/k_D = 1.1 \pm 0.1$). Whitmire performed the same reaction[4] with the hydride, reporting an average second-order rate constant of $(1.7 \pm 0.1) \times 10^{-2}$ $M^{-1}\,s^{-1}$ at 25 °C. Our k_H/k_D value is similar to that reported by Darensbourg for reactions of $[HW(CO)_5]^-$ and $[DW(CO)_5]^-$ with 1-bromobutane, giving a k_H/k_D of 1.03.[5]

Kinetic analyses to determine the nucleophilicities of $[HFe(CO)_3PPh_3]^-$, $[HW(CO)_5]^-$, and $[HFe_3(CO)_{11}]^-$ were also performed. Previous reports[6] of nucleophilicity for metal−carbonyl anions can be expanded to give Table 1.

Kinetic data were obtained for reactions of both $[PPN][HFe(CO)_4]$ and $[PPN][DFe(CO)_4]$ with $[Mn(CO)_6][BF_4]$. Under pseudo-first-order conditions, k_{obs} values were obtained and subsequently plotted versus the concentrations of the excess species, $[Mn(CO)_6][BF_4]$. Average second-order rate constants for the hydride and deuteride reactions were 9 ± 1 and 3.3 ± 0.3 $M^{-1}s^{-1}$,

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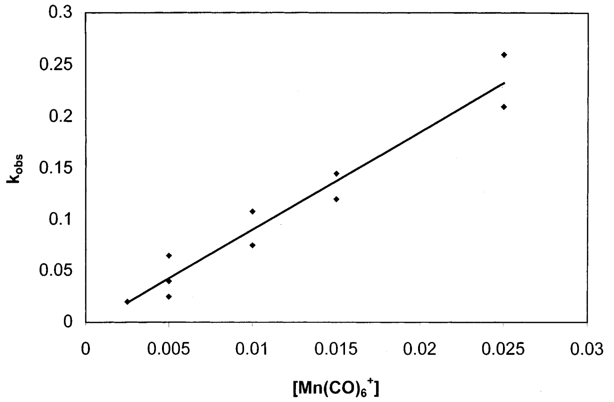


Figure 1. Second-order plot for the reaction of $[Mn(CO)_6][BF_4]$ with $[PPN][HFe(CO)_4]$.

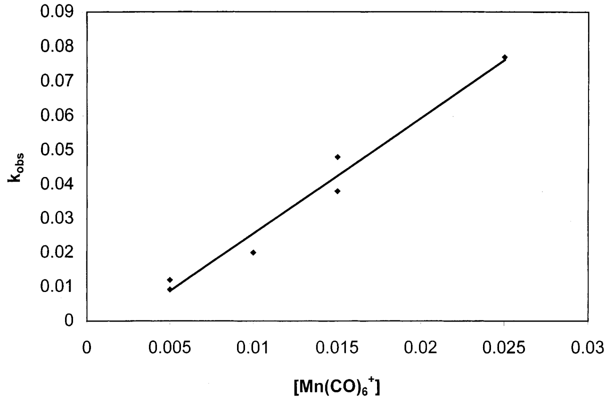


Figure 2. Second-order plot for the reaction of $[Mn(CO)_6][BF_4]$ with $[PPN][DFe(CO)_4]$.

respectively (Figures 1 and 2), indicating a significant deuterium isotope effect.

To determine whether the CO gain by the iron reagent is due to intermolecular CO transfer from the cation or from another iron complex, a ^{13}CO labeling study was performed. Figures 3 and 4 show the product spectra from reactions of ^{13}CO-enriched $[Mn(CO)_6][BF_4]$ and (unenriched) $[Mn(CO)_6][BF_4]$ with $[PPN][HFe(CO)_4]$. With all acquisition parameters equal, the ^{13}CO-enriched $[Mn(CO)_6][BF_4]$ reaction shows marked resonances for $HMn(CO)_5$ (δ 212.5, broad) and $Fe(CO)_5$ (δ 211.9) which were not observed in the unenriched control reaction.

Table 1. Order of Nucleophilicity from Reaction with MeI for Selected Metal–Carbonyl Anions[a]

Metal carbonyl anion	k_2 (M^{-1} s^{-1})	nucleophilicity (ln k_2)
$[CpFe(CO)_2]^-$	>400	
$[Re(CO)_5]^-$	74 ± 7	4.3
$[Mn(CO)_4PPh_3]^-$	7.8 ± 0.4	2.0
$[HFe(CO)_3PPh_3]^-$	**3.6 ± 0.2**	**1.3**
$[Mn(CO)_4P(OPh)_3]^-$	1.9 ± 0.1	0.64
$[Mn(CO)_5]^-$	1.5 ± 0.2	0.40
$[HW(CO)_5]^-$	**1.1 ± 0.1**	**0.09**
$[CpW(CO)_3]^-$	0.51 ± 0.009	−0.67
$[CpCr(CO)_3]^-$	0.058 ± 0.005	−2.8
$[HFe(CO)_4]^-$	**0.024 ± 0.002**	**−3.7**
$[DFe(CO)_4]^-$	**0.022 ± 0.002**	**−3.8**
$[Fe(CO)_3(NO)]^-$	0.013 ± 0.0013[7]	−4.3
$[Co(CO)_4]^-$	0.009 ± 0.001	−4.7
$[HFe_3(CO)_{11}]^-$	**no reaction**	

[a] New data are bolded.

The stronger nucleophile, $[Et_4N][HFe(CO)_3PPh_3]$, shows CO transfer products with both the manganese and rhenium ($[Re(CO)_6][BF_4]$) cations.

$$[Mn(CO)_6]^+ + [HFe(CO)_3PPh_3]^- \rightarrow HMn(CO)_5 + Fe(CO)_4PPh_3 \quad (4)$$

$$[Re(CO)_6]^+ + [HFe(CO)_3PPh_3]^- \rightarrow HRe(CO)_5 + Fe(CO)_4PPh_3 \quad (5)$$

A reaction of 0.005 M $[Mn(CO)_6][BF_4]$ with $[Et_4N][HFe(CO)_3PPh_3]$ (reaction 4) gave $Fe(CO)_4PPh_3$ (2050, 1974, 1939 cm^{-1}), $HMn(CO)_5$ (2012 cm^{-1}), and $[Mn(CO)_5]^-$ (1901, 1864 cm^{-1}) as major products. Over the course of 30 min, $[Mn(CO)_5]^-$ and unreacted $[Mn(CO)_6][BF_4]$ decreased by ~50% (from t = 3 min), as Fe-

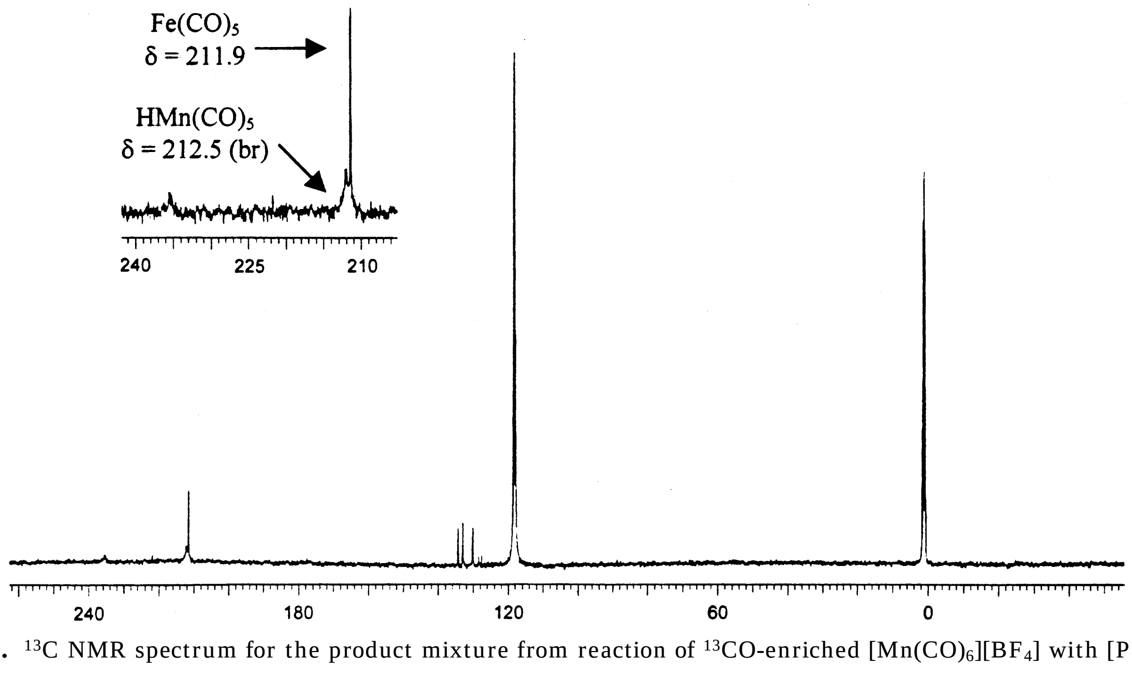


Figure 3. ^{13}C NMR spectrum for the product mixture from reaction of ^{13}CO-enriched $[Mn(CO)_6][BF_4]$ with $[PPN][HFe(CO)_4]$.

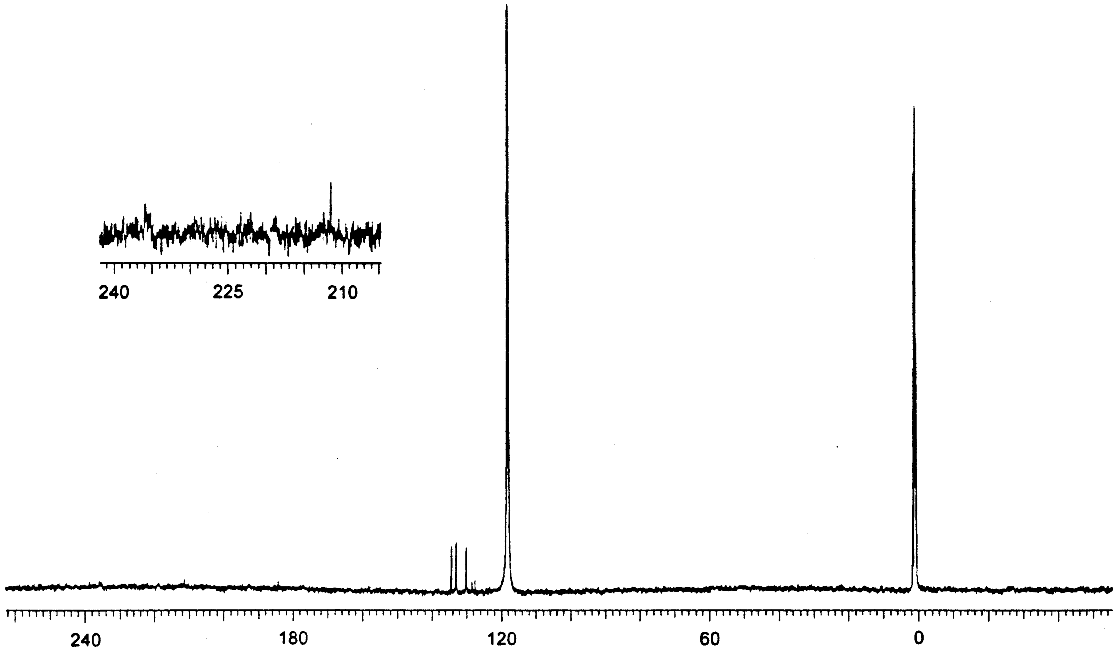


Figure 4. ^{13}C NMR spectrum for the reaction of unenriched $[Mn(CO)_6][BF_4]$ with $[PPN][HFe(CO)_4]$.

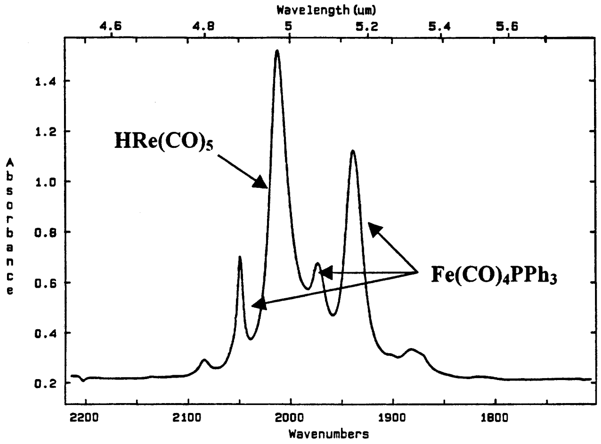


Figure 5. Infrared spectrum of the reaction mixture of $[Re(CO)_6][BF_4]$ with $[Et_4N][HFe(CO)_3PPh_3]$ after 5 min.

$(CO)_4PPh_3$ and $HMn(CO)_5$ increased by 15 and 35%, respectively. This suggests $[Mn(CO)_5]^-$ as the initial manganese product, which is then protonated to form $HMn(CO)_5$. A ^1H NMR spectrum of the reaction performed in CD_3CN showed a singlet at −7.9 ppm due to $HMn(CO)_5$.

The reaction of $[Re(CO)_6][BF_4]$ with $[Et_4N][HFe(CO)_3PPh_3]$ (reaction 5) showed clean conversion to $HRe(CO)_5$ (2012 cm^{-1}) and $Fe(CO)_4PPh_3$ (2050, 1973, 1939 cm^{-1}) as products (Figure 5). After 5 min, no $[Et_4N][HFe(CO)_3PPh_3]$ remained, with only a trace of the starting cation, $[Re(CO)_6][BF_4]$ (2085 cm^{-1}), present. A hexane extract of the product solution also showed both $Fe(CO)_4PPh_3$ (2051, 1979, 1946 cm^{-1}) and $HRe(CO)_5$ (2016 cm^{-1}). Analysis by ^1H NMR spectroscopy showed only an upfield singlet at δ −5.9, indicative of $HRe(CO)_5$.

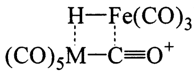
Like reactions with $[HFe(CO)_4]^-$, $[HFe(CO)_3PPh_3]^-$ does not yield an observable formyl product. Because reaction 4 initially forms some $[Mn(CO)_5]^-$, nucleophilic attack of the iron center on a cationic carbonyl with a CO transfer and back transfer of two electrons is the likely mechanism. For reaction 5 the products provide no mechanistic information. However, the absence of $Re(CO)_5^-$ does not preclude a nucleophilic attack on CO; $Re(CO)_5^-$ is known to react much more rapidly than $Mn(CO)_5^-$.[1,6] A radical mechanism is unlikely given the clean product formation and absence of $Re_2(CO)_{10}$.

Experiments using ^{13}CO-enriched $[Mn(CO)_6][BF_4]$ and $[Re(CO)_6][BF_4]$ showed ^{13}C NMR signal enhancement versus control experiments for the common product, $Fe(CO)_4PPh_3$. Reactions 4 and 5 proceeded too rapidly to obtain kinetic data using our infrared stopped-flow system.

Discussion

Our reactions of hydrido metal carbonyl anions with CH_3I indicate nucleophilicities consistent with trends regarding phosphine substitution. The second-order rate constant for the CH_3I reaction with $[Et_4N][HFe(CO)_3PPh_3]$ is 150 times that for $[PPN][HFe(CO)_4]$. In this case, the substitution of PPh_3 for CO has a larger effect than for $Mn(CO)_4L^-$. The studies on $Mn(CO)_4L^-$ showed the intermingling of steric effects (decreasing nucleophility) and electronic effects (increasing nucleophilicity). For $HFe(CO)_3PPh_3^-$ electronic effects must be more important.

The reactions of $[PPN][HFe(CO)_4]$ and $[PPN][DFe(CO)_4]$ with $[Mn(CO)_6][BF_4]$ give a deuterium kinetic isotope ratio of $k_H/k_D = 2.8$. This value indicates primary isotope effects[8] such that there is a greater role for the Fe−H bond in the transition state for these reactions than those with CH_3I. The larger kinetic isotope effect and the observation that reation 5 occurs even though $HFe(CO)_3(PPh_3)^-$ is considerably less nucleophilic than $Re(CO)_5^-$ both indicate that the hydride is directly involved in the mechanism for reactions of $HFe(CO)_3L^-$. Reaction 5 is clean, with only $HRe(CO)_5$ and $Fe(CO)_4PPh_3$ observed. Given the very rapid reaction of $Re(CO)_5^-$ with $Re(CO)_6^+$ to form $Re_2(CO)_{10}$,[1] it is unlikely that $Re(CO)_5^-$ is produced. Formation of $Re(CO)_5^-$ would not be expected on the basis of the relative nucleophilicities (Table 1). It is most likely that a transition state involving a four-center interaction forms. For M = Mn the observation of $Mn(CO)_5^-$



$$\begin{array}{ll} & \mathrm{H{-}Fe(CO)_3L^-} \\ \mathrm{(CO)_5M{-}C{\equiv}O^+} & \end{array}$$

suggests that the two-electron, CO transfer occurs in the transition state. For M = Mn, L = CO the significant deuterium isotope effect requires significant H−Fe bond breaking in the transition state. For M = Re it is most likely that hydrogen transfer occurs synchronously with the CO and electron transfer.

Darensbourg suggested such a transition state for reactions of $HW(CO)_5^-$ with alkyl bromides.[5] For reaction of $HFe(CO)_4^-$ with CH_3I the small deuterium isotope effect indicates relatively little H−Fe bond breaking in the transition state. However, an interaction with the hydride would force the *trans* PPh_3 away from the reaction site, providing a rationale for the reduced steric effects in reaction of CH_3I with $HFe(CO)_4^-$ and $HFe(CO)_3PPh_3^-$ compared to $Mn(CO)_5^-$ and $Mn(CO)_4PPh_3^-$. We have not considered radical mechanisms because of the clean product formation and the studies by Darensbourg[3] and Whitmire[4] that preclude radical mechanisms for similar reactions.

Conclusions

Reactions of $HFe(CO)_3L^-$ with $M(CO)_6^+$, L = CO, PPh_3 and M = Mn, Re, provide evidence that interaction of the hydride is important. For $Mn(CO)_6^+$ interaction of the hydride appears to diminish the steric hindrance for the synchronous CO and $2e^-$ transfer in opposite directions that produce $Mn(CO)_5^-$ as an initial product. For $Re(CO)_6^+$ direct transfer of the hydride is most likely to produce exclusively $HRe(CO)_5$ as rhenium product. Both reactions show that group transfer processes occur for reactions of these hydrido iron anions with metal carbonyl cations.

Experimental Section

A. Methods. All reactions were performed under an argon or nitrogen atmosphere. Solutions were prepared in dried, oxygen-free solvents. All reactions were performed in acetonitrile except the reaction of $[PPN][HW(CO)_5]$ with CH_3I, which was performed in THF.

B. Kinetic Analyses. Experiments were performed at 25 °C under pseudo-first-order conditions. Only for reactions of $HFe(CO)_4^-$ with $Mn(CO)_6^+$ were the reactions slow enough for kinetic analysis. Rate data were obtained from monitoring the decrease in infrared absorbances for anion species. Observed rate constants (k_{obs} (s^{-1})) were plotted versus the concentration of excess species to obtain the reported second-order rate constants, k ($M^{-1}\ s^{-1}$). The monitored absorbances for individual anions are $[PPN][HFe(CO)_4]$ (1882 cm^{-1}), $[PPN][DFe(CO)_4]$ (1882 cm^{-1}), $[Et_4N][HFe(CO)_3PPh_3]$ (1818 cm^{-1}), and $[PPN][HW(CO)_5]$ (1893 cm^{-1}).

Slower reactions were monitored using a Mattson FTIR spectrometer. Two solutions were combined (defining $t = 0$) in the glovebox, and a single aliquot was loaded into a NaCl cell. The cell was quickly removed from the glovebox, allowing the first absorbance measurement to be taken at approximately $t = 60$ s. These data were analyzed using Prism Plot and Microsoft Excel software.

Reactions with larger rate constants ($k_{obs} > 10^{-2}\ s^{-1}$) were analyzed using an infrared stopped-flow system. This system uses an Edinburgh CO/CO_2 laser as a monochromatic infrared source. Changes in infrared absorbance are monitored using an Infrared Associates model HCT 6-7 infrared detector in conjunction with OLIS software. Some reactions showed a minor induction period and/or mixing event, which was not considered as part of the change in absorbance used for kinetic analysis.

C. Reagents. $Mn_2(^{13}CO)_{10}$.[1b] To a Fischer−Porter pressure vessel was added 4.0 g of $Mn_2(CO)_{10}$ dissolved in 60 mL of benzene. The atmosphere was temporarily evacuated and then backfilled with ^{13}CO gas. An overpressure of 40 psig was established. The vessel was photolyzed for 24 h. The atmosphere was then evacuated and recharged with ^{13}CO, whereupon the solution was irradiated for an additional 48 h. Following this, the solvent was removed in vacuo and the yellow $Mn_2(CO)_{10}$ was analyzed by mass spectroscopy. By summing the weighted percents of $Mn_2(CO)_{10} = 389.9$ through $Mn_2(^{13}CO)_{10} = 399.9$, the degree of ^{13}C enrichment was determined to be 40%. ^{13}C NMR (δ, CD_3CN): 188.8 equatorial, 196.6 axial.

$Re_2(^{13}CO)_{10}$ was prepared in a manner identical to $Mn_2(^{13}CO)_{10}$. The degree of ^{13}C enrichment was not determined. ^{13}C NMR (δ, CD_3CN): 183.9, 192.8.

Anions. Metal carbonyl anion species were prepared according to published methods: $[PPN][HFe(CO)_4]$,[10] $[PPN][DFe(CO)_4]$ (this species was prepared in a manner identical to that for $[PPN][HFe(CO)_4]$ with the exception of using MeOD (CH_3OD) and NaOD instead of MeOH and NaOH; IR (cm^{-1}, CH_3CN) 2002 (w), 1906−1898 (sh), 1882 (s)), $[Et_4N][HFe(CO)_3PPh_3]$[3c], and $[PPN][HW(CO)_5]$.[11]

$[Mn(CO)_6][BF_4]$ was prepared according to a modified literature method of Beach and Gray.[12] To a 250 mL Schlenk flask fitted with a nitrogen gas feed were added 2.0 g of $[Na][Mn(CO)_5]$ and 30 mL of diethyl ether. While under nitrogen, 15 mL of ethyl chloroformate was added dropwise. The solution turned a pronounced orange. After stirring for 4 h, the mixture was filtered. The filtrate was combined with 30 mL of methylene chloride. To this solution was added liquid $BF_3\cdot$ etherate to immediately precipitate a white product. The product was separated by filtration and then thoroughly washed with both THF and ether. After drying, 1.11 g of white $[Mn(CO)_6][BF_4]$ was collected (39% yield). The compound is air-stable. IR (cm^{-1}, CH_3CN): 2096 (s).

$[Re(CO)_6][BF_4]$, **$[Mn(^{13}CO)_6][BF_4]$**, and **$[Re(^{13}CO)_6][BF_4]$** were made in a manner identical to that used for $[Mn(CO)_6][BF_4]$. ^{13}C-enriched cations were prepared from $Mn_2(^{13}CO)_{10}$ and $Re_2(^{13}CO)_{10}$. $[Re(CO)_6][BF_4]$: IR (cm^{-1}, CH_3CN) 2086 (s). $[Mn(^{13}CO)_6][BF_4]$: ^{13}C NMR (δ, CD_3CN) 201.0 (hextet, $J_{Mn-C} = 129$ Hz, ^{13}CO). $[Re(^{13}CO)_6][BF_4]$: ^{13}C NMR (δ, CD_3CN) 218.6.

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