Journal of Organometallic Chemistry, 383 (1990) 191–199
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
JOM 20335

Reactions of anionic transition metal carbonyl hydrides with electrophilic metal carbonyls: nucleophilic addition (hydride transfer) vs. electron transfer mechanisms

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(Received April 25th, 1989)

Abstract

The relative reactivity of anionic transition metal carbonyl hydrides towards hydride transfer to monomeric metal carbonyls is consistent with an ionic route, generating, in the best-matched cases of electrophilic carbonyls (highest f_{CO} or average $\nu(CO)$) and most nucleophilic hydrides (such as $HW(CO)_4P(OMe)_3{}^-$), metal formyls as sole product. With the metal carbonyl dimers $Co_2(CO)_8$, $[(\eta^5\text{-}C_5H_5)M(CO)_3]_2$ (M = Mo, W), and $Mn_2(CO)_{10}$ reductive cleavage to the respective anions occurs at rates which correlate with the nucleophilicity of the metal hydride, without observation of intermediate formyls. No reaction occurs with $Re_2(CO)_{10}$ or $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$.

Introduction

The reactions of octahedral group 6 anionic transition metal carbonyl hydrides, $HM(CO)_4L^-$ (M = Cr, W; L = PR_3, CO), as hydride-based nucleophiles towards alkyl halides have been well studied, eq. 1 [1]. Mechanistic studies demonstrated that the hydride transfer pathway was predominantly ionic, i.e., transfer as H^-, especially for unhindered reactive C–X sites. A radical chain mechanism, eq. 2, emerged for hindered sites or for those R–X sites for which radical intermediates are favored [2]. As might be expected, the hydride of weakest homolytic bond strength,

Nucleophilic displacement (S_N2):

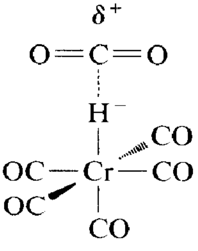
$$[M]{-}H^- + RX \longrightarrow \{[M]{-}H^-\cdots R^{\delta+}\cdots X^{\delta-}\} \longrightarrow RH + [M]{-}X^- \quad (1)$$

Radical chain (S_H2):

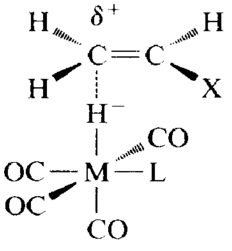
$$\left|\begin{array}{l}[\mathrm{M}]-\mathrm{H}^- + \mathrm{R}^\cdot \longrightarrow \mathrm{RH} + [\mathrm{M}]^{\cdot -}\\ [\mathrm{M}]^{\cdot -} + \mathrm{RX} \longrightarrow [\mathrm{M}]-\mathrm{X}^- + \mathrm{R}^\cdot\end{array}\right| \qquad (2)$$

$HCr(CO)_5^-$, displayed the greatest degree of radical chain character. Even so, with unhindered RX such as 1-hexenyl bromide, no more than 10% of the reaction path was of S_H2 character [2]. Consistent with this view, S_N2 reactivity (rates of reaction) increased with the electron-richness and polarizability of the M–H⁻ bond: $HFe(CO)_4^- \ll HCr(CO)_5^- < HW(CO)_5^- <$ *cis*-$HCr(CO)_4P(OEt)_3^- <$ *cis*-$HW(CO)_4$-$P(OEt)_3^-$ [3].

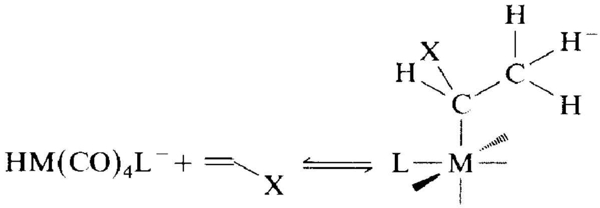
Nucleophile/electrophile adducts (**A** and **B**) are also proposed to precede the insertion of olefins, activated by electron-withdrawing groups (rate decreases as $X = C(O)Me > C(O)OMe > CN > C(O)NH_2 \gg Ph$ (no reaction)), eq. 3 [4], or carbon dioxide [5] into M–H⁻ bonds, eq. 4.



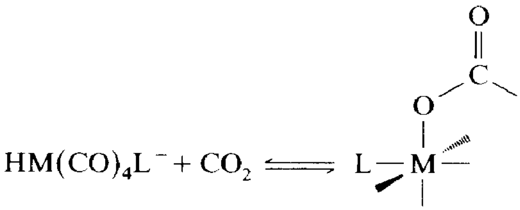
(**A**)



(**B**)



(3)

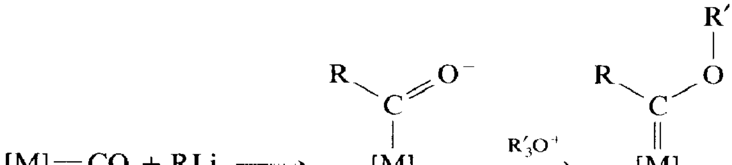


(4)

The adduct described by **B** has been calculated to be −6.8 kcal/mol lower in energy than its components [6].

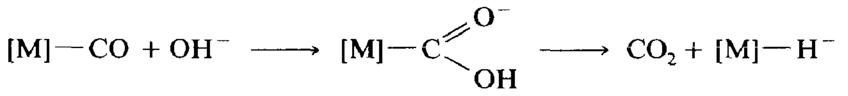
The addition of nucleophiles to metal-activated carbon monoxide has been established as a prominent reaction in metal carbonyl chemistry. As evidence of its significance the following examples are cited:

Carbene synthesis [7]:



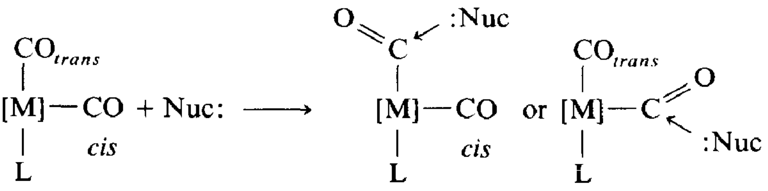
(5)

Intermediates in the water-gas shift reaction [8] and synthesis of metal hydrides [9]:



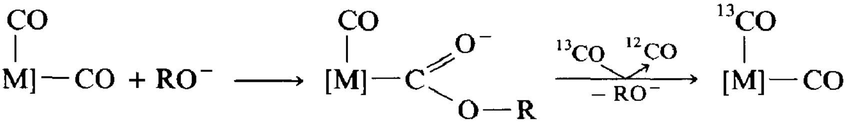
(6)

Delineation of charge distribution in asymmetric complexes [10]:



(7)

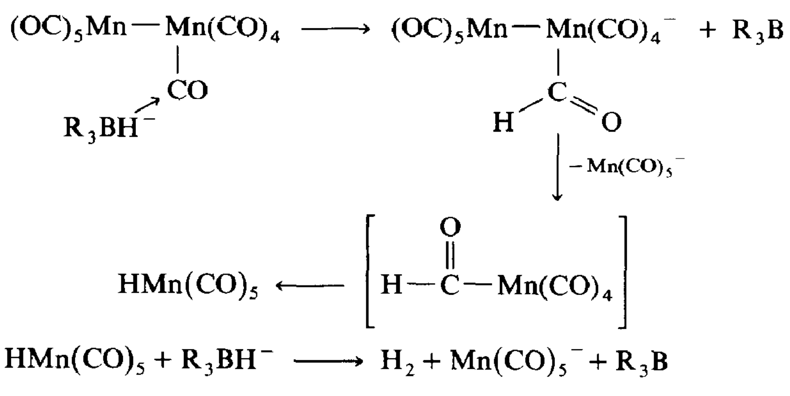
Promotion of ligand exchange for isotopic labelling [11]:



(8)

In addition to the above, the reductive cleavage of transition metal dimers via addition of a main group element source of H^- such as Li^+ $HBEt_3^-$ is also expected to occur via nucleophilic attack on a metal-bound CO. The proposed pathway for $Mn_2(CO)_{10}$ reduction to $Mn(CO)_5^-$ shown in Scheme 1 is based on the observation of a dimeric manganese formyl intermediate [12]. The formyl intermediate has precedence in monomeric metal carbonyl chemistry. Casey and Neumann discovered a variety of metal formyls, including $(OC)_4FeCHO^-$, resulting from reaction of $[Cat^+][HB(OR)_3]$ with $M(CO)_x$ [13].

Since the more reactive anionic group 6 transition metal carbonyl hydrides are similar to $Li^+HBR_3^-$ in their ability to reduce organic substrates [3], the hydride-transfer ability of anionic transition metal hydrides to metal bound CO and reactions with dimeric transition metal carbonyls were of interest and are reported herein.



Scheme 1

Experimental

A. Materials. Solvents were distilled under nitrogen from appropriate O_2 scavenging and drying agents: tetrahydrofuran, from Na°/benzophenone; hexane, from Na°/benzophenone/diglyme; methylene chloride, from P_2O_5. Common metal carbonyls and reagents were purchased from standard vendors and used as received without any further purification.

B. Instrumentation. Infrared spectra were recorded of THF solutions in sealed 0.1 mm CaF_2 cells, flushed with N_2, on an IBM FTIR/32 or a Perkin–Elmer 283B spectrophotometer calibrated below 2000 cm^{-1} on water vapor. Proton magnetic resonance spectra were measured on a Varian EM390 (90 MHz) spectrometer or a Varian XL-200 spectrometer (200 MHz). Anaerobic techniques including Schlenkware and an Ar-atmosphere glovebox were utilized throughout the experiments.

C. Preparations. Preparation of anionic hydrides and neutral metal carbonyls. The anionic hydrides [PPN][$HM(CO)_5$], (M = Cr, W) [14], [PPN][*cis*-$HM(CO)_4L$], (L = $P(OMe)_3$, $P(C_6H_5)_3$, M = Cr, W) [15], [PPN][$HFe(CO)_4$] [9], [PPN][$HFe(CO)_3$-$P(OMe)_3$] [16], [Cat][μ-$HM_2(CO)_{10}$] (Cat = PPN^+ or K^+, M = Cr, W) [17], the carbonyl cation of the salt [$CpFe(CO)_3$][$B(C_6H_5)_4$] [18], and the neutral carbonyl complexes $Fe(CO)_4P(C_2H_5)_3$ [19] and $[CpM(CO)_3]_2$ (M = Mo, W) [20,21] were prepared according to literature procedures.

D. Reactions. 1. Reactions of anionic metal hydrides with dimeric neutral metal carbonyls ($Cp_2Fe_2(CO)_4$, $Re_2(CO)_{10}$, $Fe_2(CO)_9$, $Cp_2W_2(CO)_6$, $Cp_2Mo_2(CO)_6$, $Mn_2(CO)_{10}$, and $Co_2(CO)_8$). In a typical reaction to be monitored by infrared, [PPN][$HCr(CO)_5$] (0.038 g, 0.052 mmol) was dissolved in 5 ml of THF in a 25 ml Schlenk tube. The metal carbonyl dimer (0.013 mmol) was dissolved in 5 ml of THF in 25 ml round bottom flask capped with a rubber septum. This latter solution was transferred via cannula to the [PPN][$HCr(CO)_5$] solution and magnetically stirred at 22°C. Samples were periodically withdrawn for infrared ν(CO) analysis. For ^1H NMR monitoring, [PPN][$HCr(CO)_5$] (0.073 g, 0.10 mmol) and metal carbonyl dimer (0.025 mmol) were loaded into a 5 mm NMR tube in the glovebox. The NMR tube was capped with a rubber septum, cooled to −23°C, and THF-d_8 solvent (ca. 0.5 ml) was transferred to the reaction via syringe. The reaction solution was kept at −23°C in a CCl_4/dry ice bath until spectra were measured.

2. Reaction of anionic metal hydrides with monomeric neutral metal carbonyls ($Fe(CO)_5$, $Fe(CO)_4P(C_2H_5)_3$, $M(CO)_6$ (M = Cr, W)). These were carried out as described for the dimeric complexes except a 1/1 stoichiometric ratio of $[HM(CO)_xL^-]/M'(CO)_yL'$ was used.

3. Reaction of [$CpFe(CO)_3$][$B(C_6H_5)_4$] with [PPN][$HW(CO)_4P(OMe)_3$]. A 0.10 g (0.1 mmol) sample of [PPN][$HW(CO)_4P(OMe)_3$] and a 0.055 g (0.10 mmol) sample of [$CpFe(CO)_3$][$B(C_6H_5)_4$] were loaded into a 5 mm NMR tube in the glovebox. The tube was cooled to −78°C and a 0.5 ml portion of cold acetone-d_6 was added. The tube was immediately placed in the NMR spectrometer and a spectrum was measured at −78°C. A resonance at +15.3 ppm was constant at −78°C and, on warming to −20°C, diminished in intensity with a concomitant appearance of a new resonance at −11.98 ppm. At room temperature, this resonance also disappeared. The dimeric species $[CpFe(CO)_2]_2$ was the sole iron-containing product as verified by IR.

Results and discussion

Carbonyl stretching force constants (or ν(CO) values used as approximations of f_{CO}) have been successfully used as indices to predict relative reactivities of the CO ligand in metal carbonyls. Larger CO stretching force constants correlate with a more positive carbon and therefore with nucleophilic attack at carbon [22,23]; lower values of f_{CO} correlate with addition of electrophiles to oxygen [24]. The metal carbonyls listed in Table 1 were selected to examine the appropriateness of this approach when metal hydrides are used as nucleophilic attack agents.

Whereas no reaction was observed upon mixing $HFe(CO)_4^-$ with $Cr(CO)_6$ or $W(CO)_6$ at 22° C, eq. 9, addition of $HM(CO)_5^-$ (M = Cr, W) to $Fe(CO)_5$ resulted in a variety of products derived from hydride transfer [25]. A ^1H NMR monitor of the reaction of $HW(CO)_5^-$ with $Fe(CO)_5$ initially found one new resonance at 14.54 ppm, characteristic of the iron formyl, $(OC)_4FeCHO^-$ [13,26]. On standing for 2 h at 22° C the formyl resonance diminished in relation to peaks at −8.7 ppm (assigned to $HFe(CO)_4^-$), −11.8 ($HFeW(CO)_9^-$) [25], and −12.6 ppm (μ-$HW_2(CO)_{10}^-$) [17]. With $HCr(CO)_5^-$ the distribution of products shown in eq. 10 was observed within 25 min whereas with *cis*-$HW(CO)_4P(OMe)_3^-$ hydride transfer was both rapid and complete, even at −20° C, resulting in $(OC)_4FeCHO^-$ and, subsequently, $HFe(CO)_4^-$, without production of any binuclear hydrides.

$$HFe(CO)_4^- + Cr(CO)_6 \longrightarrow \text{no reaction} \qquad (9)$$

$$HCr(CO)_5^- + Fe(CO)_5 \xrightarrow[22^\circ C]{THF} \underset{\substack{20\% \\ (\delta +14.54\ \text{ppm})}}{(OC)_4FeCHO^-} + \underset{\substack{40\% \\ (\delta -8.7\ \text{ppm})}}{HFe(CO)_4^-} + \qquad (10)$$

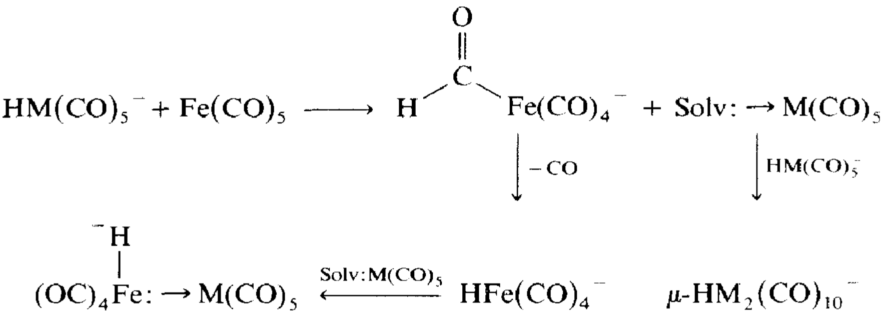
$$\underset{\substack{20\% \\ (\delta -14.66\ \text{ppm})}}{HFeCr(CO)_9^-} + \underset{\substack{20\% \\ (\delta -19.5\ \text{ppm})}}{\mu\text{-}HCr_2(CO)_{10}^-}$$

The presence of binuclear hydrides is explained by the known aggregation of $HFe(CO)_4^-$ or $HM(CO)_5^-$ with coordinatively-unsaturated $M(CO)_5^0$, as illustrated in Scheme 2. The absence of binuclear products for *cis*-$HW(CO)_4P(OMe)_3^-$ is consistent with both the great reactivity of that hydride as well as the reduced acceptor ability of 16-electron $[W(CO)_4P(OMe)_3]$ in the donor acceptor complex $(OC)_4HFe\!: \rightarrow W(CO)_4P(OMe)_3^-$ [25].

Table 1

Infrared spectral data of some metal carbonyls

Complex	Solvent	ν(CO) (cm^{-1})
$CpFe(CO)_3^+\ B(C_6H_5)_4^-$	(Acetone)	2120(vs), 2070(vs)
$Fe(CO)_5$	(DMF)	2020(s), 1995(s)
$Fe(CO)_4P(C_2H_5)_3$	(THF)	2044(m), 1966(m), 1931(s)
$Mn_2(CO)_{10}$	(THF)	2037(m), 2005(s), 1982(w)
$Co_2(CO)_8$	(THF)	2066(s), 2026(s), 1858(m)
$[CpFe(CO)_2]_2$	(THF)	1994(s), 1952(m), 1782(s)
$Re_2(CO)_{10}$	(Hexane)	2072(ms), 2016(s), 2005(m, sh), 1978(ms), 1960(vw), 1944(vw)

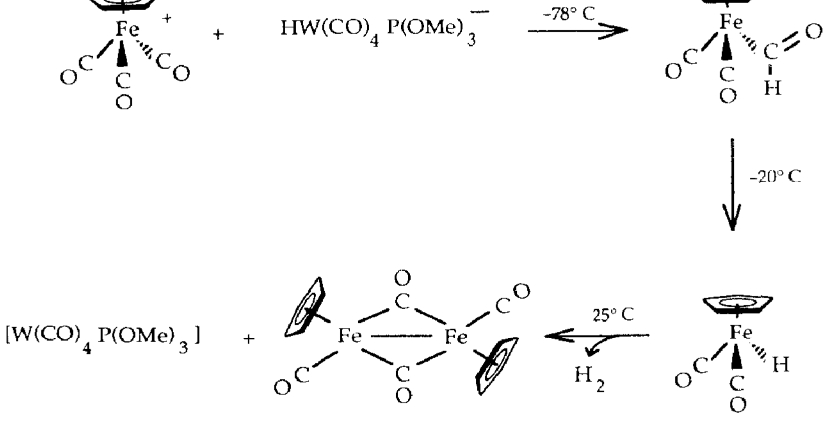


Scheme 2

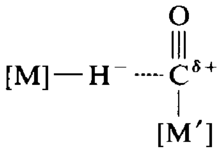
In contrast to the reactive nature of $Fe(CO)_5$ with anionic hydrides, the phosphine substituted $(CH_3CH_2)_3PFe(CO)_4$ was unreactive with $HCr(CO)_5^-$ as well as the better nucleophile *cis*-$HW(CO)_4P(OMe)_3^-$.

The importance of electrophilicity of the [M′]–CO in the hydride transfer reaction was further demonstrated by the extreme reactivity of $HW(CO)_4P(OMe)_3^-$ with $(\eta^5\text{-}C_5H_5)Fe(CO)_3^+$. Even at −78 °C there was immediate reaction with production of a species whose ^1H NMR resonance at +15.3 ppm suggested assignment to the formyl shown in Scheme 3. Upon raising the temperature to −20 °C, the formyl resonance disappeared with concomitant appearance of a peak at −12.0 ppm, assigned to $CpFe(CO)_2H$. Further warming to 25 °C resulted in loss of H_2 and production of the $[CpFe(CO)_2]_2$.

The above results, i.e., the order of reactivity of the anionic metal hydrides as measured by the extent to which formyl species are initially observed in reactions with metal carbonyls, $HFe(CO)_4^- < HCr(CO)_5^- < HW(CO)_5^- <$ *cis*-$HW(CO)_4P(OMe)_3^-$, are consistent with established nucleophilicities of anionic metal hydrides in reactions with RBr [3]. The dependence of reactivity on electrophilicity of the metal carbonyl acceptor further supports an ionic, hydride transfer via intermediacy of an electrophile/nucleophile adduct, **C**.



Scheme 3



$$[M]—H^{-}\cdots C^{\delta+}(\equiv O)—[M']$$

(C)

Alternate mechanisms involving radical chain routes can also account for the transfer of hydrides, Scheme 4. Radical mechanism 1 does not account for the formyl products observed in the above reactions, however it would account for an anomalous amount of $HFe(CO)_4^-$ produced early in the reaction of $HCr(CO)_5^-$ and $Fe(CO)_5$. That is, under the conditions described in eq. 10, $HFe(CO)_4^-$ is formed faster than the decomposition rate of isolated, moderately stable, $(OC)_4FeCHO^-$ [13,26]. Radical Mechanism 1 was earlier proposed to account for production of the metal hydrides $HFe(CO)_4^-$ and $HCr(CO)_5^-$ from reaction of $CpV(CO)_3H^-$ with $Fe(CO)_5$ and $Cr(CO)_6$, respectively [27]. No intermediate formyls were reported in those studies. Most importantly, the rate of hydride transfer or product formation, was enhanced on addition of catalytic amounts of $CpV(CO)_3^{2-}$, designed to increase the quantity of 19-electron radical initiators, $Fe(CO)_5^-$ or $Cr(CO)_6^{\cdot -}$ [27].

Radical mechanism 2 differs from Mechanism 1 in the localization of the odd electron on carbon rather than iron. In both mechanisms $HCr(CO)_5^-$ serves as a hydrogen atom source in chain propagation as well as a one-electron reducing agent

Radical mechanism 1 [27]

Initiation

$$HCr(CO)_5^- + Fe(CO)_5 \longrightarrow HCr(CO)_5^{\cdot} + Fe(CO)_5^{\cdot -}$$

Propagation

$$Fe(CO)_5^{\cdot -} \rightleftharpoons Fe(CO)_4^{\cdot -} + CO$$

$$Fe(CO)_4^{\cdot -} + HCr(CO)_5^- \longrightarrow HFe(CO)_4^- + Cr(CO)_5^{\cdot -}$$

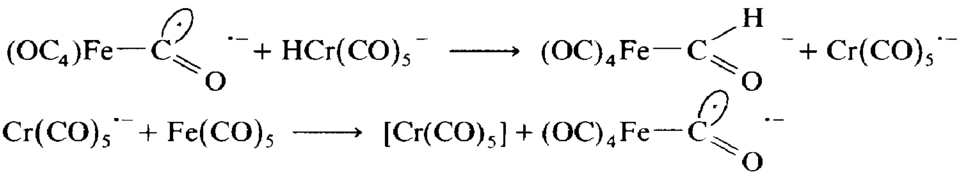
$$Fe(CO)_5 + Cr(CO)_5^{\cdot -} \longrightarrow Fe(CO)_5^{\cdot -} + [Cr(CO)_5]$$

Radical mechanism 2 [28]

Initiation

$$HCr(CO)_5^- + Fe(CO)_5 \longrightarrow HCr(CO)_5^{\cdot} + Fe(CO)_5^{\cdot -}$$

Propagation



$$(OC_4)Fe—C(=O)^{\cdot -} + HCr(CO)_5^- \longrightarrow (OC)_4Fe—C(H)(=O)^- + Cr(CO)_5^{\cdot -}$$

$$Cr(CO)_5^{\cdot -} + Fe(CO)_5 \longrightarrow [Cr(CO)_5] + (OC)_4Fe—C(=O)^{\cdot -}$$

Scheme 4

in the initiation step. Direct hydrogen-atom transfer to electrolytically generated $Cr(CO)_6^{\cdot -}$ has been demonstrated to produce $(OC)_5CrCHO^-$ using Bu_3SnH as hydrogen atom source [28]. Such an interpretation in the present work is, however, inconsistent with observations of the least amount of formyl product with the metal hydrides known to be the best hydrogen atom source, $HCr(CO)_5^-$ and $CpV(CO)_3H^-$. To the contrary, the greatest amount of formyl products were observed in reactions of the metal hydride expected to have the strongest homolytic bond strength, *cis*-$HW(CO)_4P(OMe)_3^-$. Importantly the latter hydride is, however, the best nucleophile [3].

Reaction of anionic metal hydrides with binuclear metal carbonyls. In comparison to the above results and in spite of the similarity of $\nu(CO)$ values for the monomeric and dimeric complexes listed in Table 1, there was no indication of formyl products in any reactions described by eq. 11.

$$L(OC)_xMH^- + M'_2(CO)_y \xrightarrow[H_2]{} M(CO)_{y/2}^- + [M(CO)_xL]^0 \qquad (11)$$

For $Co_2(CO)_8$, $Co(CO)_4^-$ was observed on time of mixing with $HCr(CO)_5^-$, $HW(CO)_5^-$, and *cis*-$HW(CO)_4P(OMe)_3^-$. Even the least reactive $HFe(CO)_4^-$ produced $Co(CO)_4^-$ and $HFe_3(CO)_{11}^-$ within 5 min of mixing with $Co_2(CO)_8$. The group 6 dimers, $[CpMo(CO)_3]_2$ and $[CpW(CO)_3]_2$ were similarly reductively cleaved with all hydrides studied, with reaction times of minutes to several hours, depending both on the stability of the dimer ($[CpW(CO)_3]_2$ less reactive than $[CpMo(CO)_3]_2$) and the reactivity of the hydride [3]. The very stable dimers $[CpFe(CO)_2]_2$ and $Re_2(CO)_{10}$ were resistant to reductive cleavage by even the most active group 6 hydrides, *cis*-$HCr(CO)_4P(OMe)_3^-$ or *cis*-$HW(CO)_4P(OMe)_3^-$ at room temperature. In view of the fact that the $\nu(CO)$ of the major CO vibrational mode is ~ 2000 cm^{-1} for these dimers, i.e., similar to that of $Fe(CO)_5$, the lack of hydride transfer in these cases is unexpected.

The reaction of $Mn_2(CO)_{10}$ with $HCr(CO)_5^-$ was sufficiently slow to monitor by $\nu(CO)$ IR and ^1H NMR spectroscopies at 22° C. In addition to the expected monomeric anion, $Mn(CO)_5^-$, the dimeric products resulting from trapping of the 16-electron $Cr(CO)_5^0$ by product $Mn(CO)_5^-$ or reactant $HCr(CO)_5^-$, i.e., $CrMn(CO)_{10}^-$ and μ-$HCr_2(CO)_{10}^-$, were also observed. The reaction of $Mn_2(CO)_{10}$ and PPN^+ *cis*-$HW(CO)_4P(OMe)_3^-$ in THF-d_8 was studied by ^1H NMR. Under conditions identical to those which permitted the observation of $(OC)_5Mn$-$Mn(CO)_4CHO^-$ using Li^+ $HBEt_3^-$ as hydride source, i.e., THF-d_8 solvent and -20 ° C [12], no reaction was observed for the transition metal hydride. Upon raising the temperature to 10° C, reaction commenced at a rate which allowed the accumulation of several spectra which showed the disappearance of the hydride of -4.4 ppm, however a resonance in the formyl region was never detected.

The above results are accounted for most reasonably by assuming either (1) the dimeric manganese formyl is less stable in the presence of the transition metal Lewis acid, $[W(CO)_4P(OMe)_3]$, than in the presence of the main group Lewis acid $[BEt_3]$; or (2) the formyl is never produced and the anionic metal hydride is acting solely as an electron-transfer reagent, directly reducing the Mn–Mn bond.

Comments. The most reasonable conclusion from the above is that the group 6 anionic transition metal carbonyl hydrides act as hydride-based nucleophiles towards metal-bound CO of monomeric metal carbonyls in a manner entirely consistent with their reactivity as nucleophiles in hydride/halide exchange reactions with 1°–RBr. Reductions of dimeric metal carbonyls to their respective monomeric anions also showed a dependence on anionic metal hydride consistent with the nucleophilicity of the latter, however no intermediate formyls were detected. Although this inability to detect the formyl cannot rule out its presence [30*] our preferred mechanism is that simple outer sphere electron transfer from the $HM(CO)_xL^-$ into the M′–M′ bond accounts for the reductive cleavages.

The complete lack of reactivity of even the most reactive hydrides with $[CpFe(CO)_2]_2$ and $Re_2(CO)_{10}$, despite the electrophilicities of their carbonyls as indicated by ν(CO), implies that not only are redox potentials not sufficiently matched for electron transfer, but also a nucleophilic attack, or hydride transfer to the carbonyl carbon pathway, is circumvented in these cases. To our knowledge there is no obvious explanation of this result.

Acknowledgement: The authors express appreciation to the National Science Foundation (Grant No. CHE 8603664) for financial support.

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