1624 *Organometallics* 1982, *1*, 1624-1628

Interaction of Metal Carbonyl Hydrides with Lewis Acids†

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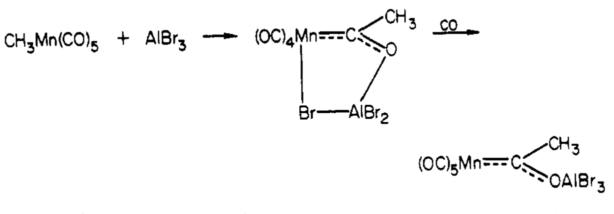
Received June 8, 1982

Recent studies on Lewis acid promoted CO migratory insertion to produce metal acyls prompted a comprehensive study of the interaction of metal carbonyl hydrides with molecular Lewis acids. Stable metal formyl formation was not achieved in this study, but insight was obtained into reactions that may compete with migratory insertion in metal carbonyl hydrides. The reactivity of metal carbonyl hydrides with strong Lewis acids is dominated by the basic character of the hydride ligand. Variable-temperature multinuclear NMR characterization of the low-temperature complex $Mn(CO)_5$-H-BCl_3 is presented. The susceptibility to electrophilic metal hydrogen bond cleavage increases with decreasing acidity of the hydride. Steric factors are also important as evidenced by the observation that $H_3Re_3(CO)_{12}$ is much more resistant to electrophilic attack than is $HRe(CO)_5$. Also discussed are reactions of Lewis acids with $HCo(CO)_4$, [PPN][$HFe(CO)_4$], [$Ir(CO)_2(PPh_3)_2H_2$][BPh_4], $HMn(CO)_4PPh_3$, $CpMo(CO)_3H$, and $CpMo(CO)_2(PPh_3)H$.

Introduction

Although the alkyl migration reaction to coordinated carbon monoxide in transition-metal complexes is well-known,[1] the analogous hydride migration reaction is apparently much less favorable thermodynamically and perhaps kinetically. Indeed, direct synthesis of a metal formyl complex from a metal hydride has only been reported on a synthetic scale in two instances: addition of CO to Rh(OEP)H[2,3] and low-temperature reaction of CO with $(Me_5C_5)_2Th(OR)H$.[4] Only in the latter case is a hydride migration mechanism believed to be operative. The great interest in elucidating and controlling the formation of metal formyl species from metal carbonyl hydrides stems from the frequent invocation of formyl formation in the mechanisms for CO reduction by homogeneous catalysts.[5]

Our recent discovery of the molecular Lewis acid promotion[6] of CO insertion showed that both kinetic and thermodynamic barriers to alkyl migration are reduced in the presence of molecular Lewis acids. The rate of CO insertion is increased[7] by more than 10^8 through interaction of $AlBr_3$ with the carbonyl oxygen, and the inserted product is stabilized by formation of a metal acetyl–Lewis acid complex, eq 1.[8]



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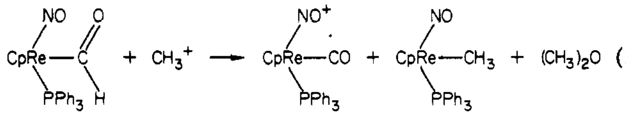
We have examined the reactions of Lewis acids with a variety of transition-metal carbonyl hydrides to explore the possibility of promoting hydride migration to produce stable metal formyl complexes. The compound $(C_5Me_5)_2Th(OR)CHO$ is stabilized by η^2 coordination of the formyl oxygen to the oxophilic thorium metal center.[4] Electrophiles may also induce further reaction in a metal formyl complex. Disproportionation has been observed by Gladysz and co-workers[9] when CpRe(NO)(PPh_3)(CHO) is treated with electrophiles such as CH_3^+ or H^+ (eq 2).



(2)

Similarly, protonation of the unstable formyl $Os_3(CO)_{11}CHO^-$ leads to the methylidene-bridged cluster $Os_3(CO)_{11}CH_2$ and $Os_3(CO)_{12}$.[10] The diborane reduction of metal formyls to methyl complexes[11] may involve electrophilic attack on the formyl oxygen prior to hydride transfer, as proposed for the analogous reduction of metal acetyl complexes.[12]

Previous work on the interaction of metal hydrides with molecular Lewis acids has concentrated on the early transition-metal hydrides. A metal-centered adduct is obtained in the reaction of Cp_2WH_2 with $AlMe_3$[13] or BF_3 (1),[14,15] whereas hydride-bridged adducts have been synthesized from highly hydridic early transition-metal hydrides and aluminum alkyls (2). The protonic $CpW(CO)_3H$ complex reacts with $AlMe_3$, to evolve methane and form Al–O bonds with the carbonyl ligands, eq 3.[17]

Results and Discussion

$HMn(CO)_5$. Addition of excess BCl_3 to a hexane solution of $HMn(CO)_5$ at room temperature does not affect the IR spectra of the hydride nor of BCl_3. Similarly, the solution is unchanged when exposed to 2 atm of CO. How-

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[3] Abbreviations: OEP, octaethylporphyrin; PPN^+, $[(Ph_3P)_2N]^+$; Ph, phenyl; Tf, $CF_3SO_3^-$.

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† Dedicated to the memory of Professor Rowland Pettit.

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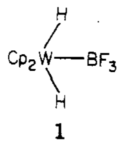

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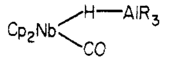

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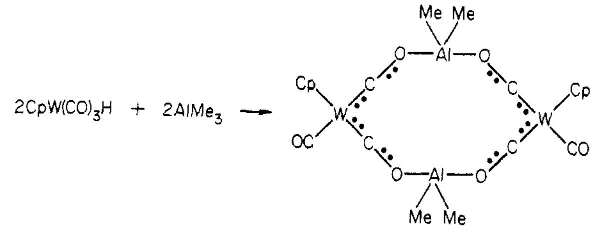

(3)

ever, upon cooling to -80 °C, a yellow color develops and a bright yellow precipitate is formed. The solid redissolves, and the color change is reversible when the solution is warmed to room temperature, suggesting a reversible $HMn(CO)_5$–BCl_3 interaction, eq 4. The nature of this reaction was further characterized by variable-temperature multinuclear NMR spectroscopy.

$$HMn(CO)_2 + BCl_3 \rightleftharpoons Cl_3B\text{-}H\text{-}Mn(CO)_5 \quad (4)$$

The chemical shift of the hydride proton in 0.058 M $HMn(CO)_5$ in CD_2Cl_2/CF_2Cl_2 linearly shifts slightly to higher field as the temperature is reduced from +12 to -96 °C. The shift relative to the solvent peak in CD_2Cl_2 is -0.20 ppm (18.2 Hz). When the ^1H NMR spectra of 0.054 M $HMn(CO)_5$ and 0.31 M BCl_3 in CD_2Cl_2/CF_2Cl_2 is recorded, a much more dramatic shift is observed. At 25 °C the chemical shift corresponds to that observed for free $HMn(CO)_5$ (δ -7.75). However, on cooling to -100 °C, the resonance shifts by 2.12 ppm to higher field. The change in chemical shift for this sample as a function of temperature, corrected for small shifts observed in free $HMn(CO)_5$ is depicted in Figure 1. The resonance remains a sharp singlet until -100 °C at which point it broadens, probably owing to the formation of the yellow solid. No new peaks are detected in the formyl region of the spectrum, even under 8.2 atm of CO. Similar changes are observed in the ^{11}B NMR spectroscopy of a sample of 0.030 M in both $HMn(CO)_5$ and BCl_3 in CD_2Cl_2 solution. The BCl_3 resonance shifts upfield by 4.97 ppm over the temperature range +20 to -85 °C (Figure 1). Although only a single peak is resolved, the resonance is broadened at low temperatures ($\nu_{1/2}$ = 23 Hz at 20 °C; $\nu_{1/2}$ = 68 Hz at -80 °C). These results suggest that a hydride-bridged adduct is formed at low temperatures. The hydride resonances in alkyl aluminum bridged hydride adducts of niobium, such as **2**, are shifted to higher field by 5–8 ppm.[15] Since only one resonance is observed in the ^1H NMR, the adduct must be exchanging rapidly with free BCl_3 on the NMR time scale.

Variable-temperature ^{13}C NMR of ^{13}CO-enriched $HMn(CO)_5$ and BCl_3 provides further support for this formulation. At -50 °C, peaks at 210.2 and 203.3 ppm of relative intensity 3:1 are observed. The former is the resonance for $HMn(CO)_5$; the axial and equatorial CO ligands have nearly the same chemical shift and are not resolved except at very low temperatures because of quadrupole pole broadening by manganese.[18] Upon warming to -30 °C, the relative intensity is 10:1. The intensity of the new peak at 203.3 ppm increases relative to the $HMn(CO)_5$ peak when the temperature is lowered until at -80 °C they are approximately equal. In $^{13}C\{H\}$ spectra, the intensity of the 203.3 ppm peak is reduced by a factor of 2 relative to that of $HMn(CO)_5$, suggesting that the nuclear Overhauser enhancement of the ^{13}C signal is stronger in $HMn(CO)_5$ than in the adduct. No new low-field resonances (200–400 ppm), characteristic of the electrophile O bonded to a carbonyl ligand, are observed. The new peak at 203.3 ppm is similar to that seen for the equatorial carbonyls in $Mn(CO)_5Tf$ (Tf = $CF_3SO_3^-$) at 202.4 ppm.[19] The ^{13}C signal for axial CO in $Mn(CO)_5Tf$ appears at 209.6 ppm, and a similar peak for $HMn(CO)_5{\cdot}BCl_3$ would be obscured by the $HMn(CO)_5$ resonance. Alternatively, the two expected ^{13}C signals for the adduct could be accidently degenerate as seen for $Mn(CO)_5I$.[18] Thus, the NMR evidence is consistent with the reversible formation of a hydride-bridged adduct. A metal-centered adduct is unlikely on steric grounds in this octahedral complex.

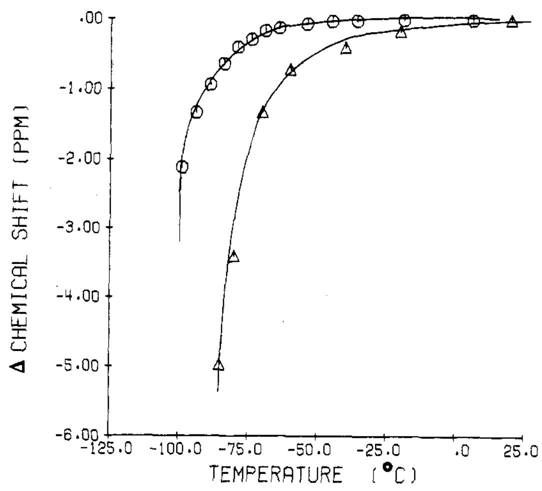

Figure 1. Change in chemical shift as a function of temperature for the $HMn(CO)_5$–BCl_3 system: ^1H chemical shift for 0.054 M $HMn(CO_5$ and 0.31 M BCl_3 in CD_2Cl_2/CF_2Cl_2 solution (○); ^{11}B chemical shift for 0.030 M $HMn(CO)_5$ and 0.030 M BCl_3 in CD_2Cl_2 (Δ).

In contrast to BCl_3, $AlBr_3$ reacts irreversibly with $HMn(CO)_5$ to afford $Mn(CO)_5AlBr_4$[20] as the metal carbonyl product when excess $AlBr_3$ is employed. The low-temperature ^1H NMR spectrum of an equimolar mixture of $AlBr_3$ and $HMn(CO)_5$ in toluene-d_8 shows a broad resonance at -11.1 ppm ($\nu_{1/2}$ = 40 Hz) at -84 °C. The resonance sharpens and shifts downfield on warming (-9.79 ppm at -54 °C; -8.11 ppm at -35 °C). These changes are irreversible, and a yellow-orange solid forms in the sample tube. Parallel IR studies show this to be a mixture of $Mn(CO)_5Br$, $Mn(CO)_5AlBr_4$, and a small amount of $Mn_2(CO)_{10}$. A transient peak at 2113 cm^{-1} is observed when the reaction is monitored by IR spectroscopy. This may be the A_1 mode of the presumed intermediate Br_3-Al-H-$Mn(CO)_5$. This latter species must be very labile since both $Mn(CO)_5AlBr_4$ and $Mn(CO)_5Br$ are also detected by IR immediately after mixing. Hydrogen gas evolution (0.4 mol/$HMn(CO)_5$) also is observed in this reaction, and no transient infrared bands characteristic of Al–H species (1800–1950 cm^{-1}) are observed. In summary, aluminum bromide also appears to react initially at the hydride ligand to form a transient hydride-bridged complex, which rearranges to the products shown in eq 5.

$$HMn(CO)_5 + AlBr_3 \rightarrow [Br_3Al\text{-}H\text{-}Mn(CO)_5] \rightarrow Mn(CO)_5Br + [Mn(CO)_5][AlBr_4] + 0.5H_2 \quad (5)$$

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These results suggest that the hydride ligand is the most basic site in $HMn(CO)_5$. Hydride basicity in $HMn(CO)_5$ has previously been observed only in neat CF_3SO_3H[19] (eq 6).

$$HMn(CO)_5 + CF_3SO_3H \rightarrow Mn(CO)_5(O_3SCF_3) + H_2 \quad (6)$$

$HMn(CO)_4PPh_3$. Phosphine substitution would be expected to increase the basicity of the terminal carbonyl oxygen,[15] as well as reduce the acidity[21] of $HMn(CO)_4PPh_3$ compared to $HMn(CO)_5$. Thus, the reactions of Lewis acids with this phosphine-substituted manganese carbonyl hydride were investigated. The reaction of $HMn(CO)_4PPh_3$ with BCl_3 or $AlBr_3$ leads to hydride cleavage and the formation of the chloro and bromo derivatives,[22] respectively, as the major metal carbonyl products. Neither adduct formation (as determined by low-temperature ^1H NMR spectroscopy) nor hydride cleavage takes place with the weaker electrophiles BF_3 or $AlMe_3$.

The trend in reactivity between $HMn(CO)_5$ and $HMn(CO)_4PPh_3$ demonstrates that phosphine substitution enhances the basicity and reactivity of the hydride more than that of the carbonyl ligands. As described in the next section similar trends are observed in the reactivity of $CpMo(CO)_3H$ and $CpMo(CO)_2(PPh_3)H$.

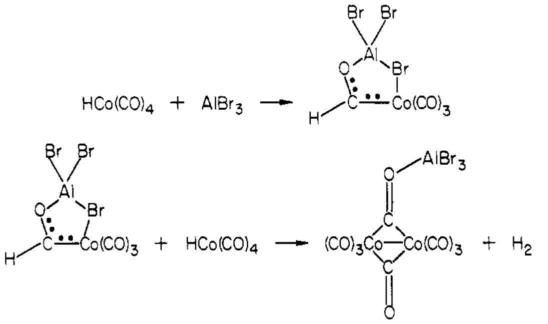
$CpMo(CO)_3H$. Low-temperature NMR studies do not show any interaction between BCl_3 and $CpMo(CO)_3H$. With an organometallic Lewis acid $[CpMo(CO)_3]^+$, Beck and Schloter[23] have synthesized a hydride-bridged dimer from $CpMo(CO)_3H$, eq 7. Phosphine substitution promotes metal hydride bond cleavage as illustrated by the reaction of $CpMo(CO)_2(PPh_3)H$ with BCl_3 to afford the corresponding chloride complex.[24] No low-temperature interactions are detected between BF_3 or $AlMe_3$ and $CpMo(CO)_2(PPh_3)H$ although the reported cis–trans isomerization takes place.[24]

$$[CpMo(CO)_3]^+ + CpMo(CO)_3H \rightarrow [Cp(CO)_3Mo\text{–}H\text{–}MoCp(CO)_3]^+ \quad (7)$$

$HRe(CO)_5$. Metal hydride basicity increases on moving down a column in the periodic table,[15,25] so the reactions of $HRe(CO)_5$ were investigated to compare with the reactivity of $HMn(CO)_5$. Interaction of $HRe(CO)_5$ with Lewis acids also results in metal hydride bond cleavage and formation of pentacarbonyl halide species. Even at −80 °C, reaction of BCl_3 and $HRe(CO)_5$ lead to formation of $Re(CO)_5Cl$[26] and $HBCl_2$[27] as identified by comparison of IR spectra with published data. Similarly, excess $AlBr_3$ reacts with $HRe(CO)_5$ to give $Re(CO)_5AlBr_4$.[20] The milder Lewis acids BF_3 and $AlMe_3$ do not perturb the IR spectra of $HRe(CO)_5$ at room temperature. However, after several hours the intensity of the hydride absorbance decreases, but no metal carbonyl products were evident in solution. Dimethylaluminum hydride has been reported to react with $HRe(CO)_5$ affording $HRe_3(CO)_{11}$ in 25% yield.[17]

$H_3Re_3(CO)_{12}$. The reactions of this trinuclear carbonyl hydride with Lewis acids were investigated because the reported steric inhibition of proton exchange[28] indicates that electrophilic attack at the carbonyl oxygen sites might be favored. In contrast to $HRe(CO)_5$, the triangular cluster $H_3Re_3(CO)_{12}$, in which the hydrides bridge the metal–metal bonds, does not react readily with electrophiles. No changes in the ^1H or ^{11}B NMR are observed at low temperature in the presence of BCl_3. Likewise, $AlBr_3$ reacts only very slowly with this complex; the cluster remains intact after 5 h of stirring with excess $AlBr_3$ at room temperature. After 3 days, $Re_2(CO)_{10}$ and $Re(CO)_5AlBr_4$[20] are observed by IR in the solution along with unreacted starting material. Thus, no stable carbonyl oxygen adducts nor stabilized formyl compounds were formed.

$HCo(CO)_4$. Since Lewis acids appear to react readily with "basic" metal hydrides, we chose to examine interactions between electrophiles and the strong acid $HCo(CO)_4$.[21] Addition of excess BCl_3 to a hexane solution of $HCo(CO)_4$ results in scavenging of trace quantities of $Co_2(CO)_8$ presumably to form $Co_2(CO)_8{\cdot}BCl_3$,[29] but no interaction is observed with the hydride. Solutions of $HCo(CO)_4$ and BCl_3 are much more stable to thermal decomposition than similar solutions in the absence of BCl_3, owing to the scavenging of $Co_2(CO)_8$ which is thought to promote a free radical decomposition pathway.[30] Low-temperature ^1H and ^{11}B NMR studies did not reveal any interaction between the hydride and BCl_3. In addition, no new resonances (δ −20 to +25) were observed in ^1H NMR spectra recorded under 5.8 atm of CO in the presence of BCl_3. In contrast, $AlBr_3$ reacts rapidly with gas evolution at −80 °C to yield $Co_2(CO)_8{\cdot}AlBr_3$ identified by IR spectroscopy.[29] Unfortunately, no intermediates could be detected in this transformation. The $AlBr_3$ adduct of $Co_2(CO)_8$ is much more stable[29] than is the BCl_3 analogue, and this may be the driving force for this reaction. The mechanism of dimer formation may be a radical process or possibly involve an insertion to produce a formyl intermediate, which would be expected to exhibit hydride donor ability.[31] This could react with the acidic $HCo(CO)_4$ to form the observed product, eq 8.



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Subsitution of $HCo(CO)_4$ by PPh_3[32] was carried out in the presence of BF_3 in an attempt to trap a formyl intermediate which may be formed in the substitution process.[33] Although substitution is much slower[32] than in the absence of BF_3 ($BF_3{\cdot}PPh_3$ is only slightly soluble in tolu-

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ene), the expected reaction product $HCo(CO)_3PPh_3$ formed cleanly and no intermediates were detected by ^1H NMR spectroscopy. Similar results were obtained for carbon monoxide substitution by $AsPh_3 \cdot BF_3$.

$[PPN][HFe(CO)_4]$. In order to investigate the effect of charge on the reactivity of metal hydrides with Lewis acids, $[HFe(CO)_4]^-$, which is isoelectric with $HCo(CO)_4$, was studied. Infrared studies by Darensbourg et al.[34] of $[PPN][HFe(CO)_4]$ in the presence of $NaBPh_4$ show that the Na^+ cation interacts specifically with a terminal carbonyl oxygen. For this reason it is of interest to examine the interaction of a molecular Lewis acid with this hydride.

Addition of excess BF_3 to a THF solution of $[HFe(CO)_4]^-$ does not perturb the IR spectrum of the hydride. However reaction at room temperature with 2 equiv of BF_3 over several hours proceeds according to eq 9. Infrared and

$$3[HFe(CO)_4]^- + BF_3 \xrightarrow{THF} [HFe_3(CO)_{11}]^- + CO + H_2 \qquad (9)$$

NMR spectra show that $[HFe_3(CO)_{11}]^-$[35] is the only metal carbonyl product formed. One equivalent of $[PPN][BF_4]$ per $[PPN][HFe(CO)_4]$ can be isolated from the reaction mixture; the remainder of the boron-containing products is unknown. A transient intermediate characterized by a B–H stretch of 2337 cm^{-1} is observed by IR spectroscopy.[36]

If the reaction is conducted under 2 atm of CO, $Fe(CO)_5$ is the only metal carbonyl product obtained, eq 10. The

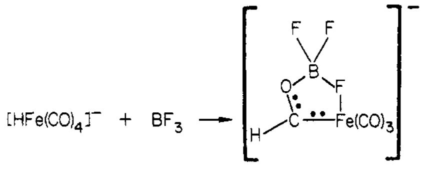
$$[HFe(CO)_4]^- + BF_3 \xrightarrow[THF]{CO} Fe(CO)_5 + [BF_3H]^- \qquad (10)$$

$$[HFe(CO)_4]^- + BF_3 \rightarrow [Fe(CO)_4] + [BF_3H]^- \qquad (11)$$

$$[Fe(CO)_4] + CO \rightarrow Fe(CO)_5 \qquad (12)$$

product of eq 9, $[HFe_3(CO)_{11}]^-$, is stable under the reaction conditions and does not form $Fe(CO)_5$ under 2 atm of CO for 12 h. Further reaction of $[HFe_3(CO)_{11}]^-$ with electrophiles in less basic solvents such as methylene chloride occurs at the bridging carbonyl oxygen.[37] The formation of $[BF_3H]^-$ suggests that hydride abstraction by BF_3 from $[HFe(CO)_4]^-$ takes place to form the coordinatively unsaturated $Fe(CO)_4$ intermediate, eq 11. This highly reactive species could be trapped by CO (eq 12) or react further to form the cluster product. Reactions of $[HCr(CO)_5]^-$ with transition-metal and main-group Lewis acids also appear to involve initial interaction at the hydride ligand.[38]

Although hydride attack appears likely, it is difficult to rule out a formyl mechanism (eq 13). The formyl intermediate could act as a hydride donor to BF_3 to afford $[BF_3H]^-$ and $[Fe(CO)_4]$. Note that $[Fe(CO)_4(CHO)]^-$[39] is known to be a strong hydride donor[31] and that it reacts rapidly with BF_3 according to eq 14.[40]



(13)

$$[Fe(CO)_4CHO]^- + BF_3 \rightarrow Fe(CO)_5 + [BF_3H]^- \qquad (14)$$

$[Ir(CO)_2(PPh_3)_2H_2][BPh_4]$. Since both neutral and anionic hydrides react readily with molecular Lewis acids, the reactions of this cationic hydride were briefly investigated. No interaction was observed with BCl_3, even at −90 °C by low-temperature ^1H NMR spectroscopy. Similarly, the hydride does not react with 1 equiv of $AlBr_3$ at room temperature; additional $AlBr_3$ leads to decomposition to uncharacterized products. The positive charge on this complex results in rather acidic hydrides that do not interact with BCl_3. Also, attack at the carbonyl oxygen is not observed, presumably due to the low basicity (e.g., high CO stretching frequency) of the carbonyl oxygen.[15]

Summary

The reaction chemistry of metal carbonyl hydrides with strong Lewis acids is dominated by the behavior of the hydride ligand as a Lewis base. The hydride ligand appears to be the more basic site relative to the carbonyl oxygen in the simple transition-metal carbonyl hydrides studied. Although hydride basicity is well documented for the early transition-metal hydrides, it is a surprising result for relatively acidic hydrides such as $HMn(CO)_5$ ($pK_a \sim 7$).[21] The basicity of the hydride ligand increases with the decreasing pK_a of the hydride[15,21] in the series $HCo(CO)_4 < HMn(CO)_5 < HMn(CO)_4PPh_3 < HRe(CO)_5$, which is the order of increasing M–H cleavage by Lewis acids. Similarly, the negatively charged hydride $[HFe(CO)_4]^-$ is more basic than the neutral isoelectronic $HCo(CO)_4$ and more reactive toward Lewis acids. Steric considerations are also important as illustrated by the stability of $H_3Re_3(CO)_{12}$ and $[HFe_3(CO)_{11}]^-$ in the presence of electrophiles that readily react with the mononuclear analogues $HRe(CO)_5$ and $[HFe(CO)_4]^-$. Stable metal formyl complexes were not observed as a reaction product with any of the carbonyl hydrides studied. Promotion of hydride migration of CO would require electrophilic attack at a carbonyl oxygen. However, electrophilic attack at the hydride ligand is prevalent, often resulting in metal–hydride bond cleavage. The propensity of metal formyls to act at hydride donors could result in the destruction of any transient metal formyl intermediates by reaction with the Lewis acid or with the parent hydride.

Experimental Section

All manipulations were carried out under an atmosphere of prepurified nitrogen by using standard Schlenk techniques, a N_2-filled glovebox, or a high vacuum line. Greaseless Teflon in glass valves and O-ring sealed glassware were used in reactions involving Lewis acids. Toluene, hexane, and THF were distilled from sodium benzophenone ketyl under N_2. Methylene chloride was dried with P_2O_5. Solvents were degassed by free–pump–thaw cycles prior to use. Following an initial sublimation from Al powder, $AlBr_3$ was resublimed prior to use. BF_3 was trap-to-trap distilled until its vapor pressure agreed with the literature value.[41] BCl_3 was distilled under high vacuum, and HCl was removed by pumping at −78 °C. $AlMe_3$ was vacuum distilled. Volatile Lewis acids were measured and transferred on the high vacuum line.

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Metal carbonyl hydrides $HMn(CO)_5$,[42] $HMn(CO)_4PPh_3$,[43] $HCo(CO)_4$,[44] $[PPN][HFe(CO)_4]$,[34] $CpMo(CO)_3H$,[42] $CpMo(CO)_2(PPh_3)H$,[45] and $[Ir(CO)_2(PPh_3)_2H_2][BPh_4]$[46] were prepared by literature methods and judged pure by IR and NMR spectroscopy. $HRe(CO)_5$[47] was prepared by a modification of the literature procedure by using 100% H_3PO_4 as the proton source, and the hydride was dried with 4A molecular sieves. $H_3Re_3(CO)_{12}$[48] was a gift from M. A. Drezdzon. The solid hydrides were stored in the glovebox, while the volatile hydrides were stored at −78 °C under vacuum.

NMR samples were prepared by loading solids in the glovebox, followed by addition of volatile components and solvent on the high vacuum line. NMR tubes were sealed off under vacuum at −196 °C. Samples were warmed to ca. −80 °C and mixed immediately prior to inserting the sample into the precooled probe. A specially designed thick-walled NMR tube that could be sealed off with a 2-mm Teflon valve was used to record spectra under 5–10 atm of CO. Satisfactory ^1H spectra were obtained without spinning the sample tube. Reactions of metal carbonyl hydrides with Lewis acids were studied by IR spectroscopy at room temperature in 0.1-mm path length CaF_2-windowed cells by using a Nicolet 7199 FT-IR or Perkin-Elmer 399 spectrometer. Variable-temperature ^1H (89.55 MHz), ^{11}B (28.69 MHz), and ^{13}C (22.49 MHz) NMR were recorded on a JEOL FX-90Q spectrometer. Temperatures are believed to be accurate to ±1 °C. The details of the investigations on $HMn(CO)_5$ are given below; reactions of the other hydrides were studied in a similar manner.

$HMn(CO)_5 + BCl_3$. Low-temperature spectra were recorded in 50% by weight CF_2Cl_2 in CD_2Cl_2. Chemical shifts were referenced to the solvent peak of CH_2Cl_2 (δ 5.32). The chemical shift of the hydride in a solution 0.054 M $HMn(CO)_5$ and 0.31 M BCl_3 as a function of temperature relative to a 0.058 M $HMn(CO)_5$ sample in the same solvent is given in Figure 1. A yellow solid formed in the NMR tube below ca. −95 °C.

The ^{11}B chemical shift referenced to external BCl_3 for a CD_2Cl_2 solution 0.030 M in both BCl_3 and $HMn(CO)_5$ is also recorded in Figure 1.

$HMn(^{13}CO)_5 + BCl_3$. A sample of $HMn(CO)_5$ was enriched by approximately 15% by stirring overnight with ^{13}CO gas. Spectra were recorded on a sample 0.092 M in $HMn(^{13}CO)_5$ and 0.25 M BCl_3 in CD_2Cl_2. Chemical shifts were referenced to the solvent peak of CD_2Cl_2 and converted to Me_4Si reference by the formula $\delta = \delta(CD_2Cl_2) + 53.8$. Signal-to-noise was enhanced when broad-band proton decoupling was employed. A yellow precipitate formed in this sample below −80 °C.

$HMn(CO)_5 + AlBr_3$. A toluene-d_8 solution of 0.068 M $HMn(CO)_5$ at 0.065 M $AlBr_3$ was warmed to −84 °C, and ^1H spectra were recorded as a function of temperature. At −84 °C, a broad peak at −11.1 ppm ($\nu_{1/2}$ = 40 Hz) is observed. On warming the sample, the resonance narrows and irreversibly shifts downfield to −8.11 ppm at −35 °C. The yellow-orange solid in the tube is identified by IR as a mixture of $AlBr_4Mn(CO)_5$[20] and $BrMn(CO)_5$.

$HMn(CO)_5 + AlBr_3$. $AlBr_3$ (0.12 mmol) at $HMn(CO)_5$ (0.08 mmol) were mixed in 10 mL of toluene. An IR spectrum taken immediately after mixing shows peaks assigned to unreacted $HMn(CO)_5$ (2117 (vw), 2012 (vs) cm^{-1}), $AlBr_4Mn(CO)_5$[20] (2153 (w), 2104 (vw), 2071 (vs), 2031 (s) cm^{-1}), and $BrMn(CO)_5$ (2136 (vw), 2050 (s), 2002 (m) cm^{-1}) and a new band at 2124 cm^{-1}. Other new ν_{CO} bands at lower frequency are obscured by the above metal carbonyls. After 1 h of stirring at room temperature, the remaining hydride reacts and the $BrMn(CO)_5$ concentration increases at the expense of $AlBr_4Mn(CO)_5$. The band at 2124 cm^{-1} decreases in intensity over the course of 2 h. On standing overnight, some $Mn_2(CO)_{10}$ is found in the solution.

Note Added in Proof. Recent work has shown that $H_2Fe(CO)_4$ is an intermediate in the reaction of $[HFe(CO)_4]^-$ and BF_3 (eq 9). In addition, the rate of thermal decomposition of $H_2Fe(CO)_4$ is reduced by at least an order of magnitude in the presence of BCl_3.

Acknowledgment. This work was supported by the National Science Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society. T.G.R. is the recipient of an NSF predoctoral fellowship.

Registry No. $HMn(CO)_5$, 16972-33-1; $HMn(CO)_4PPh_3$, 39796-96-8; $CpMo(CO)_3H$, 12176-06-6; $HRe(CO)_5$, 16457-30-0; $H_3Re_3(CO)_{12}$, 12146-47-3; $HCo(CO)_4$, 16842-03-8; $[PPN][HFe(CO)_4]$, 56791-54-9; $[Ir(CO)_2(PPh_3)_2H_2][BPh_4]$, 82903-52-4; $CpMo(CO)_2(PPh_3)H$, 33519-69-6; BCl_3, 10294-34-5; $AlBr_3$, 7727-15-3; $Mn(CO)_5AlBr_4$, 35803-93-1; $Mn(CO)_5Br$, 14516-54-2; $Mn_2(CO)_{10}$, 10170-69-1; BF_3, 7637-07-2; $AlMe_3$, 75-24-1; $Re(CO)_5Cl$, 14099-01-5; BCl_2H, 10325-39-0; $Re(CO)_5AlBr_4$, 82903-53-5; $Re_2(CO)_{10}$, 14285-68-8; $Co_2(CO)_8 \cdot AlBr_3$, 40964-38-3; $HCo(CO)_3PPh_3$, 19537-79-2; $[HFe_3(CO)_{11}]^-$, 55188-22-2; $HMn(^{13}CO)_5$, 82903-54-6.

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