Activation of Coordinated Carbon Monoxide toward Alkyl and Aryl Migration (CO Insertion) by Molecular Lewis Acids and X-ray Structure of the Reactive Intermediate $\overline{\text{Mn(C(OAlBr}}\text{Br}_2)\text{CH}_3)(\text{CO})_4$

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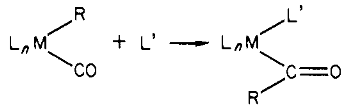
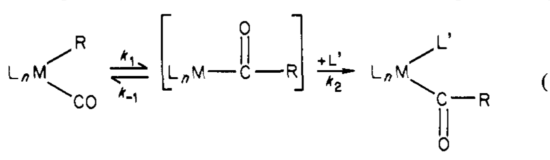
Abstract: In the absence of carbon monoxide, the strong Lewis acid $AlBr_3$ induces a rapid alkyl migration in the compounds $L_nM(R)(CO) = Mn(CH_3)(CO)_5$, $Mn(CH_2C_6H_5)(CO)_5$, $(\eta^5\text{-}C_5H_5)Fe(CH_3)(CO)_2$, and $(\eta^5\text{-}C_5H_5)Mo(CH_3)(CO)_3$ to produce acyl complexes in which Al is coordinated to the acyl oxygen, $L_n\overline{M(C(OAlBr}Br_2)R)$. In the X-ray structure of $\overline{Mn(C(O\text{-}AlBr}Br_2)CH_3)(CO)_4$ a Br atom from the $AlBr_3$ fills the sixth coordination site of the metal, thereby creating the five-membered ring $\overline{Mn\text{–}C\text{–}O\text{–}Al\text{–}Br}$ [$a = 6.835$ (2) Å, $b = 16.374$ (6) Å, $c = 12.278$ (4) Å, $\beta = 94.18$ (2)°, monoclinic space group $P2_1/c$]. Analogous acetyl complexes are formed also by the reaction of $Mn(CH_3)(CO)_5$ with $AlCl_3$ and BF_3. Each of these cyclic adducts reacts with 1 equiv of CO at subatmospheric pressures to produce the corresponding simple adduct $L_nM(C(OMX_3)R)(CO)$ in which the incoming CO ligand has replaced the Lewis acid halogen ligand in the coordination sphere of the metal. These reactions occur more rapidly and under much milder conditions than do the reactions between the parent alkyl complexes, $L_nM(R)(CO)$ and CO. Lewis acid promoted CO insertion into a metal–aryl bond was observed with $W(C_6H_5)(CO)_5^-$ in the presence of $Al(C_6H_5)_3$. In addition to the rate enhancement of CO insertion, the Lewis acid can also exert a strong stabilizing effect on unstable acetyl compounds. Thus a stable complex $(\eta^5\text{-}C_5H_5)Mo(C(OAlBr_3)CH_3)(CO)_3$ is readily formed in the presence of CO and $AlBr_3$. By contrast, the simple acetyl $(\eta^5\text{-}C_5H_5)Mo(C(O)CH_3)(CO)_3$ is unstable with respect to CO evolution.

Introduction

The formal insertion of coordinated carbon monoxide into a metal–alkyl bond to produce a metal–acyl complex (eq 1) has been the subject of numerous kinetic, mechanistic, and synthetic studies.[2,3] Interest in this topic stems both from its fundamental importance as a class of reactions and from its relevance to the synthesis of oxygenated hydrocarbons catalyzed by transition-metal surfaces or transition-metal complexes.[4–7] Kinetic data for the reactions of several metal–alkyl complexes with a variety of ligands are consistent with a mechanism involving a reversible alkyl migration to form a coordinatively unsaturated acyl intermediate, which subsequently reacts with incoming ligand (eq 2).[3] Application of the steady-state approximation yields an expression for the reaction rate (eq 3) which is consistent with the observed kinetic behavior.



(1)



(2)

$$\text{rate} = \frac{k_1k_2[L'][L_nM(R)(CO)]}{k_{-1} + k_2[L']} \tag{3}$$

Equation 3 indicates that stabilization of the transition state for the formation of the acyl intermediate should increase k_1 and thus increase the overall rate of reaction. In a reaction which proceeds by a quite different mechanism, Severson and Wojcicki found that the addition of Lewis acid dramatically increases the rate of SO_2 insertion into a metal–alkyl bond.[8] Collman and co-workers demonstrated that the small, nonpolarizable cations Li^+ and Na^+, which form tight ion pairs with the anion, cause reaction 4 to occur at a rate which is about 10^3 times faster than the rate observed when M^+ is the bulky, polarizable ion $((C_6H_5)_3P)_2N^+$.[9]

$$M^+[RFe(CO)_4]^- + (C_6H_5)_3P \xrightarrow[25\ °C]{THF} M^+[RC(O)Fe(CO)_3(P(C_6H_5)_3)]^- \tag{4}$$

$$M^+ = Li^+, Na^+, \text{or } ((C_6H_5)_3P)_2N^+$$

Lithium ion promotion also has been observed for the addition of cyclopentene oxide to $(\eta^5\text{-}C_5H_5)Fe(CO)_2^-$ and nucleophilic attack of $Mn(CO)_5^-$.[10] Lewis and Johnson have reported several cases in which the addition of $AlCl_3$ or $AlBr_3$ to a tricarbonyliron–arene or –diene complex resulted in the formation of a cyclic ketone arising from the formal addition of CO to the arene or diene ligand.[11] Demitras and Muetterties noted that $Ir_4(CO)_{12}$ supports the synthesis of aromatic

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hydrocarbons from synthesis gas (H_2/CO = 3:1) at an appreciable rate only in a highly acidic medium such as molten NaCl–$2AlCl_3$.[12]

It appeared to us that the role of molecular acids in the promotion of CO insertion deserved attention, and we therefore undertook a systematic investigation of simple CO insertion reactions in the presence of molecular Lewis acids. In this work we have discovered great acceleration of CO insertion, an interesting cyclic intermediate, and Lewis acid stabilization of an otherwise unstable metal acetyl. Some of these findings have been reported in a communication.[13]

Experimental Section

Materials. The carbonyls $Mn(CH_3)(CO)_5$,[14a] $(\eta^5\text{-}C_5H_5)Fe(CH_3)(CO)_2$,[14b] $(\eta^5\text{-}C_5H_5)Mo(CH_3)(CO)_3$,[14c] $Mn(C_6H_5CH_2)(CO)_5$,[15] $[NEt_4][W(C_6H_5)(CO)_5]$,[16] and $[NEt_4][W(C(O)C_6H_5)(CO)_5]$[17] were prepared by modifications of literature procedures and were purified by sublimation or recrystallization. The identity and purity of these compounds were verified by IR and NMR analysis. Aluminum bromide (Alfa) was sublimed twice in vacuo at 60 °C ($AlBr_3$ was ground with Al powder for the first sublimation). Aluminum chloride was sublimed in vacuo at 120 °C from Al powder and NaCl. Boron trichloride and BBr_3, which had been previously purified by fractionation, were cooled to −83 and −23 °C, respectively, and exposed to vacuum for several minutes in order to remove any HX. Boron trifluoride (Linde) was purified by fractionation. The BX_3 vapor pressures agreed with the literature values.[18] Trimethylaluminum (Texas Alkyls), $Al(i\text{-}C_4H_9)_3$ (Texas Alkyls), and $Al(C_6H_5)_3$ (ROC/RIC) were used as received. Carbon monoxide (Matheson CP grade) was used as received. Dichloromethane was distilled under nitrogen from P_2O_5; diethyl ether, toluene, and hexane were distilled under nitrogen from sodium benzophenone ketyl immediately before use.

General Procedures. Since Lewis acids and their adducts are very sensitive to oxygen and water, air and moisture were rigorously excluded during their manipulation by means of a nitrogen-filled glovebox or a Schlenk line. Gases were handled in a preparative high-vacuum line, and liquids were transferred in a vacuum line or by syringe. Solid products were separated from the reaction mixture by filtration, rinsed with a minimum volume of toluene and then with hexane, and dried in vacuo.

Kinetic experiments were carried out in a simple, grease-free tensimeter[18] with the solution of the alkyl compound thermostated at 20.0 ± 0.1 °C and solutions of the aryl compound at 17.9 ± 0.1 °C. Carbon monoxide, which was saturated with solvent vapor, was admitted to the tensimeter, the solution was stirred vigorously, and carbon monoxide pressure was monitored as a function of time. Toluene was employed as solvent for all kinetic runs, except for those on $W(C_6H_5)(CO)_5^-$ where methylene chloride was used. The initial rate of reaction was calculated for the first 10% of reaction for the alkyl compounds and between ca. 10–30% reaction for the aryl compound. Experimental error in the rates is ca. ±10%.

Spectra. Infrared spectra of solutions were recorded on a Nicolet 7199 FT-IR spectrophotometer using a cell with Irtran-2 windows and a 0.025-mm path length or on a Perkin-Elmer 399 spectrophotometer using matched 0.1-mm path length cells with Irtran-2 or CaF_2 windows. Solvent bands were eliminated from the Nicolet spectra by digital subtraction of a solvent spectrum. NMR spectra were recorded on a Hitachi Perkin-Elmer R-20B or a Varian T-60 instrument.

Elemental Analyses. All elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

Carbon Monoxide Insertion Reactions in the Absence of Lewis Acid. A 0.0974 M solution of $Mn(CH_3)(CO)_5$ (0.948 mmol) in toluene was stirred under CO at an initial pressure of 377 torr. When the reaction to produce $Mn(C(O)CH_3)(CO)_5$ was stopped after 25 h, it had gone to 10% completion, which is significantly less than the extent of reaction at equilibrium. Under similar conditions no CO uptake was detected for $Mn(CH_2C_6H_5)(CO)_5$ or $(\eta^5\text{-}C_5H_5)Fe(CH_3)(CO)_2$. A 0.069 M solution of $[NEt_4][W(C_6H_5)(CO)_5]$ in CH_2Cl_2 was stirred under CO at an initial pressure of 312 torr (extrapolated value). After 7 days the reaction producing $[NEt_4][W(C(O)C_6H_5)(CO)_5]$ was 18% complete.

Carbon Monoxide Insertion Reactions in the Presence of Lewis Acid. A. $Mn(CH_3)(CO)_5$ + $AlBr_3$. Equimolar amounts of $Mn(CH_3)(CO)_5$ and $AlBr_3$ react rapidly in solution or in the solid state to produce the $AlBr_3$-coordinated acetyl complex $Mn(C(OAlBrBr_2)CH_3)(CO)_4$ (I). Stable yellow-orange crystals of I were isolated from toluene solution. Anal. Calcd for $Mn(C(OAlBrBr_2)CH_3)(CO)_4$: C, 15.11; H, 0.63; Br, 50.29. Found: C, 14.33; H, 0.75; Br, 49.50.

In a typical kinetic experiment 379 torr of carbon monoxide and a 0.297 M solution of I were employed. The reaction was followed by CO uptake and was stopped at 89% completion (based on I). The product, $Mn(C(OAlBr_3)CH_3)(CO)_5$ (II), precipitated from the reaction mixture and was isolated in a 63% yield (based on I) as a pale yellow powder. Anal. Calcd for $Mn(C(OAlBr_3)CH_3)(CO)_5$: C, 16.66; H, 0.60; Br, 47.49. Found: C, 16.17; H, 0.78; Br, 47.49.

B. $Mn(CH_3)(CO)_5$ + $AlCl_3$. The addition of $AlCl_3$ to an equimolar amount of $Mn(CH_3)(CO)_5$ results in a rapid and complete reaction to produce the Lewis acid coordinated acetyl compound $Mn(C(OAlClCl_2)CH_3)(CO)_4$ (III), which was isolated as orange crystals from toluene solution. Anal. Calcd for $Mn(C(OAlClCl_2)CH_3)(CO)_4$: C, 20.99; H, 0.88; Mn, 16.00; Al, 7.86; Cl, 30.98. Found: C, 20.72; H, 0.96; Mn, 16.30; Al, 8.08, Cl, 31.06.

Carbon monoxide was added to 9.6 mL of a 0.100 M solution of III to produce an initial pressure of 382 torr. The reaction was terminated at 91% completion (based on III). The product, IV, precipitated from the reaction mixture and was isolated in 67% yield (based on III) as a cream-colored powder. Anal. Calcd for $Mn(C(OAlCl_3)CH_3)(CO)_5$: C, 22.64; H, 0.81; Mn, 14.79; Al, 7.27; Cl, 28.64. Found: C, 20.90; H, 1.22; Mn, 15.12; Al, 8.74; Cl, 30.50.

C. $Mn(CH_3)(CO)_5$ + BF_3. $Mn(CH_3)(CO)_5$ reacts rapidly and reversibly with BF_3 to produce the yellow BF_3-coordinated acetyl compound $Mn(C(OBFF_2)CH_3)(CO)_4$ (V), which was identified on the basis of its IR and NMR spectra. Compound V could not be isolated as a solid because it rapidly establishes an equilibrium with $Mn(CH_3)(CO)_5$ and BF_3. This was the only reaction of a Lewis acid with an alkyl metal carbonyl in which we obtained clear-cut evidence for an equilibrium.

Carbon monoxide at an inital pressure of 382 torr was introduced into a tensimeter containing an equilibrium mixture of BF_3 (54.8 torr) and $Mn(CH_3)(CO)_5$ (0.18 mmol) and $Mn(C(OBFF_2)CH_3)(CO)_4$ (0.73 mmol) in 9.10 mL toluene. The reaction was observed to go to 87% completion (based on total Mn), and the product, VI, which precipitated from the reaction mixture, was isolated in 75% yield (based on total Mn) as a very pale yellow powder. Anal. Calcd for $Mn(C(OBF_3)CH_3)(CO)_5$: C, 27.47; H, 0.99; Mn, 17.97; B, 3.54; F, 18.64. Found: C, 26.65; H, 1.04; Mn, 19.31; B, 3.84; F, 20.00.

D. $Mn(CH_3)(CO)_5$ + BCl_3 or BBr_3. The exposure of $Mn(CH_3)(CO)_5$ to BCl_3 or BBr_3 for ca. 10 min under conditions similar to those employed with BF_3 gave $MnCl(CO)_5$ or $MnBr(CO)_5$ as the primary metal carbonyl product.

E. $Mn(CH_3)(CO)_5$ + $Al(CH_3)_3$. A solution 0.13 M in $Mn(CH_3)(CO)_5$ and 0.21 M in $Al(CH_3)_3$ immediately acquired a light brown color, but the IR spectrum indicated that no reaction occurred.

F. $Mn(CH_3)(CO)_5$ + $Al(i\text{-}C_4H_9)_3$. A toluene solution 0.12 M in $Mn(CH_3)(CO)_5$ and 0.27 M in $Al(i\text{-}C_4H_9)_3$ turned light brown, and, judging from the IR spectrum, a reaction had occurred. This solution was vigorously stirred under CO at a pressure of ca. 400 torr for 14 h. The IR spectrum of the resulting red-brown solution indicated further reaction, but the products could not be identified.

G. $Mn(C_6H_5CH_2)(CO)_5$ + $AlBr_3$. The addition of $AlBr_3$ to an equimolar amount of $Mn(C_6H_5CH_2)(CO)_5$ results in a rapid CO insertion reaction to produce $Mn(C(OAlBrBr_2)CH_2C_6H_5)(CO)_4$ (VII), which was identified by its IR and NMR spectra. Attempts to isolate VII as a solid from a toluene solution were unsuccessful; removal of toluene under reduced pressure left an orange-red oil.

Carbon monoxide was added to 8.80 mL of a 0.0998 M solution of VII to produce an initial pressure of 384 torr. The reaction was terminated at 90% completion (based on VII). The product, VIII, precipitated from the reaction mixture and was isolated in 63% yield (based on VII) as a very pale yellow powder. Anal. Calcd for $Mn(C(OAlBr_3)CH_2C_6H_5)(CO)_5$: C, 26.88; H, 1.22; Mn, 9.46; Al, 4.64; Br, 41.27. Found: C, 26.77; H, 1.36; Mn, 9.62; Al, 4.87; Br, 41.53.

H. $(\eta^5\text{-}C_5H_5)Fe(CH_3)(CO)_2$ + $AlBr_3$. Aluminum bromide reacts very rapidly with $(\eta^5\text{-}C_5H_5)Fe(CH_3)(CO)_2$ to produce a brown compound identified as $(\eta^5\text{-}C_5H_5)Fe(C(OAlBrBr_2)CH_3)(CO)$ (IX) by its IR and

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NMR spectra. Extensive decomposition occurred when the reactants were mixed in the solid state, but IX was produced cleanly when a toluene solution of $AlBr_3$ was added slowly to a stirred solution of $(\eta^5\text{-}C_5H_5)Fe(CH_3)(CO)_2$ cooled to 0 °C. Attempts to isolate IX from toluene solution were unsuccessful; removal of the toluene under reduced pressure left a gummy, dark brown solid which would not completely redissolve.

Carbon monoxide, ca. 400 torr, was added to 10.9 mL of a 0.100 M solution of IX, and the reaction was terminated at 81% completion (based on IX). Some decomposition was indicated by the presence of a small amount of unidentified beige precipitate, which was removed by filtration. Attempts to isolate the product $(\eta^5\text{-}C_5H_5)Fe(C(OAlBr_3)CH_3)(CO)_2$ (X) from the light red-brown reaction mixture were unsuccessful; removal of toluene under reduced pressure left a brown-red oil. Since X could not be isolated, it was hydrolyzed to give the simple acyl complex $(\eta^5\text{-}C_5H_5)Fe(C(O)CH_3)(CO)_2$. The oil was redissolved in toluene and the solution cooled to 0 °C and hydrolyzed. The toluene was removed under reduced pressure, and the remaining $(\eta^5\text{-}C_5H_5)Fe(C(O)CH_3)(CO)_2$ was purified by sublimation. The resulting $(\eta^5\text{-}C_5H_5)Fe(C(O)CH_3)(CO)_2$ (0.12 g, 50% yield) was identified spectroscopically and by C, H, and Fe analysis.

In a CO-uptake experiment performed with less than a stoichiometric amount of $AlBr_3$, equal volumes of 0.077 M $AlBr_3$ and 0.22 M $(\eta^5\text{-}C_5H_5)Fe(CH_3)(CO)_2$ were mixed, and an initial CO pressure of 379 torr was established. The reaction was 72% complete (based on $AlBr_3$ and 24% complete based on $(\eta^5\text{-}C_5H_5)Fe(CH_3)(CO)_2$ after 1.5 days. No further CO uptake occurred in 3 days. The IR and NMR spectra of the reaction mixture (after 5 days) indicated that $(\eta^5\text{-}C_5H_5)Fe(CH_3)(CO)_2$ and $(\eta^5\text{-}C_5H_5)Fe(C(OAlBr_3)CH_3)(CO)_2$ were present in a ratio of ca. 7:3. No IX was detected in the reaction mixture.

I. $(\eta^5\text{-}C_5H_5)Mo(CH_3)(CO)_3 + AlBr_3$. Aluminum bromide reacts very rapidly with $(\eta^5\text{-}C_5H_5)Mo(CH_3)(CO)_3$ to produce a thermally unstable red compound identified by IR and NMR as $(\eta^5\text{-}C_5H_5)Mo(C(OAlBrBr_2)CH_3)(CO)_2$ (XI). Extensive decomposition occurred when the reactants were mixed in the solid state, but XI was produced cleanly when a toluene solution of $AlBr_3$ was added dropwise to a toluene solution of $(\eta^5\text{-}C_5H_5)Mo(CH_3)(CO)_3$ cooled to 0 °C. Compound XI could not be isolated as a solid.

In order to obtain a clean product, we developed the following procedure for the reaction between XI and CO. A solution of 1.03 mmol of $(\eta^5\text{-}C_5H_5)Mo(CH_3)(CO)_3$ in 4.0 mL of toluene was cooled in an ice bath and bubbled with CO as a solution of 1.02 mmol of $AlBr_3$ in 1.5 mL of toluene was added dropwise over a period of 20 min. The product was induced to precipitate by removing the homogeneous, light red-orange reaction mixture from the ice bath for several minutes and then returning it to the bath. After 1.5 h of stirring under an atmosphere of CO, the mustard yellow precipitate was collected by filtration, rinsed with 2 mL of cold toluene, and dried in vacuo. The product, $(\eta^5\text{-}C_5H_5)Mo(C(OAlBr_3)CH_3)(CO)_3$ (XII), was isolated in 51% yield (based on $AlBr_3$). Anal. Calcd for $(\eta^5\text{-}C_5H_5)Mo(C(OAlBr_3)CH_3)(CO)_3$: C, 21.65; H, 1.45; Mo, 11.53; Al, 4.86; Br, 43.21. Found: C, 21.49; H, 1.63; Mo, 13.37; Al, 4.85; Br, 43.46. Exposure to light and further rinsing with toluene caused XII to darken in color.

The reaction between XI and CO also was carried out in the tensimeter in order to determine the rate. To a solution 0.10 M in XI was added CO to a pressure of 385 torr. The reaction proceeded to 95% completion (based on XI), but the presence of dark brown precipitate indicated that some decomposition had occurred.

J. $[NEt_4][W(C_6H_5)(CO)_5] + Al(C_6H_5)_3$. Triphenylaluminum and $[NEt_4][W(C_6H_5)(CO)_5]$ (XIII) do not appear to react in the solid state. A solution which was 0.065 M in $Al(C_6H_5)_3$ and 0.071 M in XIII was initially gold-colored but darkened in several minutes to red-brown. Carbon monoxide was added to an initial pressure of 287 torr (extrapolated value), and the reaction was terminated in 42 h at which point it was 90% complete. The product $[NEt_4][W(C(OAlPh_3)C_6H_5)(CO)_5]$ (XIV) was identified by IR and by dimethylamine displacement to produce the benzoyl complex free of Lewis acid, $[NEt_4][W(C(O)C_6H_5)(CO)_5]$ (XV).

Determination of the Equilibrium Constant for the Reaction of $Mn(CH_3)(CO)_5$ with BF_3. The equilibrium constant at 20 °C was determined by adding 0.949 mmol of BF_3 gas saturated with toluene vapor to a tensimeter containing a vigorously stirred solution of 0.910 mmol of $Mn(CH_3)(CO)_5$ in 9.10 mL of toluene, which was thermostated at 20.0 °C. Equilibrium was established within 25 min at a BF_3 pressure of 54.8 torr. This pressure corresponds to conversion of 81% of the $Mn(CH_3)(CO_5)$ to $Mn(C(OBFF_2)CH_3)(CO)_4$.

X-ray Diffraction Data for $Mn(C(OAlBrBr_2)CH_3)(CO)_4$. The crystal selected for study was sealed in a 0.2-mm capillary and was measured at room temperature on a Syntex P2$_1$ diffractometer. (Crystals of the compound were observed to undergo a phase change between room temperature and −120 °C). Cell dimensions (Table I) were determined by least-squares fit of the angles measured for 12 independent reflections during alignment procedures. Data were corrected for background, for Lorentz and polarization effects, and for absorption.

Table I. Data for the X-ray Diffraction Study of $C_6H_3AlBr_3MnO_5$

(A) Crystal Data

cryst system: monoclinic	$\beta = 94.18\ (2)^\circ$
space group: $P2_1/c\,[C_{2h}{}^5$; No. 14]	$V = 1370.4\ (3)\ Å^3$
	$T = 23$ °C
$a = 6.835\ (2)$ Å	$Z = 4$
$b = 16.374\ (6)$ Å	mol wt 476.74
$c = 12.278\ (4)$ Å	ρ(calcd) = 2.310 g cm^{-3}

(B) Intensity Data

radiation: Mo Kα ($\lambda = 0.71070$ Å)
monochromator: oriented graphite
reflns measd: $+h, +k, +l$
max 2θ: 50.1°
min 2θ: 2.5°
scan type: θ–2θ
scan speed: between 1.0 and 29.3° min^{-1} depending on intensity of 2 s prescan
reflns collected: 2743 independent, 1717 observed ($I > 3\sigma(I)$)
std reflns: 3 measured every 97 reflns; no significant decay
abs coeff: $\mu = 48.3$ cm^{-1} (transmission factors: 0.538 min, 0.616 max)

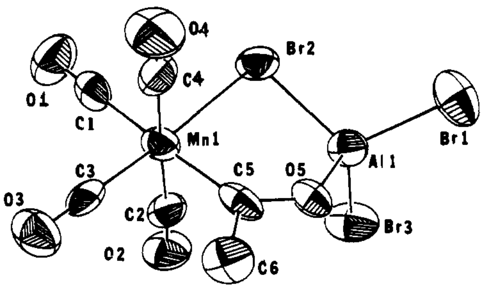
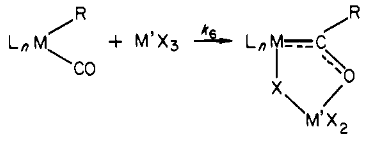


Figure 1. Structure of $Mn(C(OAlBrBr_2)CH_3)(CO)_4$. C_6 is a methyl carbon.

The structure was solved by using heavy-atom procedures and refined by full-matrix least-squares methods (function minimized: $\sum w(|F_0| - |F_c|)^2$, $w = 1/\sigma(F_0)^2$) to a final $R_1 = (\sum||F_0| - |F_c||/\sum|F_0|) = 0.075$ and $R_2 = (\sum w||F_0| - |F_c||^2/\sum w|F_0|^2)^{1/2} = 0.066$. The XRAY76 system was used for all calculations.[19] Atomic scattering factors were taken from Cromer and Mann[20] and those for Mn, Al, and Br were corrected for the real and imaginary parts of anomalous dispersion.[21]

Results and Discussion

Reaction of Lewis Acids with Metal Alkyl Carbonyls. In contrast with typical CO insertion reactions which require the addition of an external ligand (eq 1), it was found that strong Lewis acids such as $AlBr_3$ induce a very rapid CO insertion reaction in alkylmetal–carbonyl complexes in the absence of added CO (eq 5). As will be described in detail, the Lewis acid serves



$$L_nM(R)(CO) + M'X_3 \xrightarrow{k_5} L_nM{=}C(R){-}O{\cdot}M'X_2{-}X \qquad (5)$$

three functions: it increases the rate of alkyl migration, it stabilizes the acyl group, and it provides an electron-rich atom which acts as a ligand to fill the vacant coordination site left by the creation of the acyl group.

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(19) J. M. Stewart, "The XRAY System-Version of 1976", Technical Report TR-446, Computer Science Center, University of Maryland, College Park, Maryland, 1976.

(20) D. T. Cromer and J. B. Mann, *Acta Crystallogr., Sect. A*, **24**, 321–324 (1968).

(21) "International Tables for X-Ray Crystallography", Vol. IV, Kynoch Press, Birmingham, England, 1974.

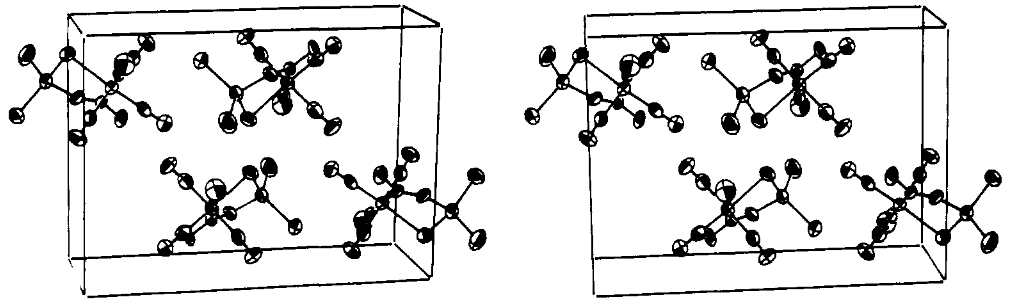

Figure 2. Stereoscopic view of the packing in $\mathrm{Mn(C(OAlBrBr_2)CH_3)(CO_4)}$.

Table II. Positional Parameters for $\mathrm{C_6H_3AlBr_3MnO_5}$

atom	*x* (σ(*x*))	*y* (σ(*y*))	*z* (σ(*z*))
Mn(1)	0.5469 (5)	0.3955 (2)	0.2472 (2)
Al(1)	0.8547 (10)	0.5691 (4)	0.2513 (5)
Br(1)	0.1381 (4)	0.6132 (2)	0.3293 (2)
Br(2)	0.6476 (4)	0.5160 (1)	0.3743 (2)
Br(3)	0.6994 (5)	0.6589 (1)	0.1336 (2)
C(1)	0.3232 (29)	0.3846 (12)	0.3243 (17)
C(2)	0.4116 (34)	0.4640 (11)	0.1456 (15)
C(3)	0.4783 (36)	0.3083 (12)	0.1643 (15)
C(4)	0.6920 (32)	0.3269 (13)	0.3432 (15)
C(5)	0.7841 (32)	0.4091 (10)	0.1693 (14)
C(6)	0.8710 (32)	0.3488 (10)	0.0878 (13)
O(1)	0.1838 (23)	0.3798 (11)	0.3691 (13)
O(2)	0.3225 (24)	0.5019 (9)	0.0811 (11)
O(3)	0.4288 (28)	0.2530 (8)	0.1132 (11)
O(4)	0.7874 (28)	0.2828 (9)	0.3996 (12)
O(5)	0.8874 (19)	0.4762 (7)	0.1753 (9)

The existence of the five-membered ring in $\mathrm{Mn(C(OAlBrBr_2)CH_3)(CO)_4}$, which was inferred from spectroscopic and chemical properties, is confirmed by the structural data (Figure 1). The five-membered ring is not planar. Al(1) and O(5) deviate by 0.80 and 0.33 Å, respectively, from the plane: Mn(1), Br(2), C(5), C(1), and C(3) (standard deviation 0.02). Coordination about manganese is not notably distorted from octahedral geometry (right angles 87.5 (6)–92.4 (6)°). The manganese-bromine distance is 2.579 (9) Å as compared to 2.526 (5) Å in $\mathrm{[BrMn(CO)_4]_2}$.[22] Both structures show Mn–C trans to Mn–Br to be shorter (1.76 (2) Å in $\mathrm{[BrMn(CO)_4]_2}$ and 1.79 (2) Å in this work) than those trans to other bonds (1.87 (2) Å in $\mathrm{[BrMn(CO)_4]_2}$ and 1.86 (2)–1.87 (2) Å in this work). Other distances and angles appear normal. There are no short contact distances between molecules in the cell (Figure 2).

The C(5)O(5) distance, 1.30 (2) Å, in the aluminum-coordinated acetyl ligand is longer than that in simple η^1-acetyls, which range from 1.19 to 1.21 Å,[23] and it is even longer than the CO distance, 1.25 Å, in $\mathrm{Al[Mn(CO)_4(C(O)CH_3)_2]_3}$ where all six of the acetyl groups are coordinated to the $\mathrm{Al^{3+}}$ ion.[24] This considerable lengthening of the CO by coordination to $\mathrm{AlBr_3}$ parallels the great decrease seen for ν(CO) in the present work and in a previous study of simple acetyl complexes of Lewis acids.[25] It is probable that this effect is much smaller in $\mathrm{Al[Mn(CO)_4(C(O)CH_3)_2]_3}$ because of the existence of weaker and longer (1.87 vs. 1.81 Å in the present work) Al–O interactions to the six-coordinate aluminum ion in that compound.[24]

Simple bonding considerations lead to the expectation that an increase in CO bond length, which indicates a decrease in CO bond order, would be accompanied by higher MnC(5) bond order and shortening of this bond length. This, however, is not observed; thus the MnC(5) distance observed here, 1.95 (2) Å, is in the range (1.90–1.47 Å) of other M–C bonds for single acyls of first-row transition metals.[23] Our Mn–C distance is longer than that in the diacetyl compound $\mathrm{Al[Mn(CO)_4(C(O)CH_3)_2]_3}$ (1.82 (1) Å) where conjugation between the acetyl ligands has been postulated.[24]

Table III. Bond Distances (Å) and Angles (Deg) for $\mathrm{C_6H_3AlBr_3MnO_5}$

Bond Distances			
Mn(1)–C(1)	1.86 (2)	Mn(1)–C(3)	1.79 (2)
Mn(1)–C(2)	1.87 (2)	Mn(1)–C(4)	1.86 (2)
Mn(1)–C(5)	1.95 (2)	Mn(1)–Br(2)	2.580 (4)
O(1)–C(1)	1.14 (3)	O(3)–C(3)	1.14 (2)
O(2)–C(2)	1.15 (2)	O(4)–C(4)	1.17 (2)
C(5)–C(6)	1.55 (2)	O(5)–Al(1)	1.81 (1)
C(5)–O(5)	1.30 (2)		
Al(1)–Br(1)	2.219 (7)	Al(1)–Br(3)	2.270 (6)
Al(1)–Br(2)	2.313 (7)		
Bond Angles			
C(1)–Mn(1)–C(2)	90.6 (9)	C(2)–Mn(1)–Br(2)	92.4 (6)
C(1)–Mn(1)–C(3)	91.3 (10)	C(3)–Mn(1)–C(4)	89.2 (9)
C(1)–Mn(1)–C(4)	92.3 (9)	C(3)–Mn(1)–C(5)	90.4 (9)
C(1)–Mn(1)–C(5)	178.3 (8)	C(3)–Mn(1)–Br(2)	117.2 (6)
C(1)–Mn(1)–Br(2)	87.5 (6)	C(4)–Mn(1)–C(5)	87.5 (9)
C(2)–Mn(1)–C(3)	90.2 (9)	C(4)–Mn(1)–Br(2)	88.4 (6)
C(2)–Mn(1)–C(4)	177.0 (10)	C(5)–Mn(1)–Br(2)	90.8 (5)
C(2)–Mn(1)–C(5)	89.6 (9)		
Mn(1)–C(1)–O(1)	177.7 (18)	Mn(1)–C(3)–O(3)	177.7 (22)
Mn(1)–C(2)–O(2)	175.9 (17)	Mn(1)–C(4)–O(4)	177.0 (18)
Mn(1)–Br(2)–Al(1)	92.3 (2)	Br(1)–Al(1)–Br(3)	114.6 (3)
Br(2)–Al(1)–O(5)	97.3 (5)	Al(1)–O(5)–C(5)	130.5 (12)
Br(2)–Al(1)–Br(1)	113.4 (2)	O(5)–C(5)–Mn(1)	122.3 (13)
Br(2)–Al(1)–Br(3)	112.3 (3)	O(5)–C(5)–C(6)	109.8 (16)
O(5)–Al(1)–Br(1)	111.1 (5)	C(6)–C(5)–Mn(1)	127.7 (13)
O(5)–Al(1)–Br(3)	106.6 (4)		

Fractional coordinates for the atom positions are given in Table II, and bond distances and bond angles may be found in Table III.

On the basis of analogy with $\mathrm{Mn(C(OAlBrBr_2)CH_3)(CO)_4}$ and on the basis of spectroscopic data, the other products, $\mathrm{Mn(C(OAlClCl_2)CH_3)(CO)_4}$, $\mathrm{Mn(C(OBFF_2)CH_3)(CO)_4}$, $\mathrm{Mn(C(OAlBrBr_2)CH_2C_6H_5)(CO)_4}$, $\mathrm{(\eta^5\text{-}C_5H_5)Fe(C(OAlBrBr_2)CH_3)(CO)}$, and $\mathrm{(\eta^5\text{-}C_5H_5)Mo(C(OAlBrBr_2)CH_3)(CO)_2}$ are proposed to have similar ring structures. Each Lewis acid complex has a methyl or methylene ^{1}H NMR resonance in the acyl region and an infrared band corresponding to the Lewis acid coordinated acyl group in the region from 1350 to 1490 cm^{-1} (Tables IV and V). The positions of the acyl bands and the small shifts to higher frequency of the terminal bands have been well documented in our laboratory for more conventional Lewis acid adducts of metal-acyl complexes.[25]

The rates of reaction between the strong Lewis acids and alkylmetal-carbonyl complexes are very rapid. Attempts to measure these reaction rates by NMR methods were frustrated by the

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[23] C. P. Casey and C. A. Bunnell, *J. Chem. Soc., Chem. Commun.*, 737 (1974); F. A. Cotton, B. A. Frenz, and A. Shaver, *Inorg. Chim. Acta*, **7**, 161 (1973); M. R. Churchill and S. W. Y. Chang, *Inorg. Chem.*, **14**, 1680 (1975); M. R. Churchill, B. G. DeBoer, and J. J. Hackbarth, *ibid.*, **13**, 2098 (1974); M. R. Churchill and J. P. Fennessey, *ibid.*, **7**, 953 (1968).

[24] C. M. Lukehart, G. P. Torrence, and J. V. Zeile, *J. Am. Chem. Soc.*, **97**, 6903 (1975).

[25] R. E. Stimson and D. F. Shriver, *Inorg. Chem.*, in press.

Table IV. CO Stretching Frequencies for Metal–Alkyl and -Acyl Compounds and Their Lewis Acid Adducts

	compd	$\nu(CO)_{terminal}$, cm^{-1}				$\nu(CO)_{acyl}$, cm^{-1}	
	$\mathrm{Mn(CH_3)(CO)_5}{}^{a}$	2110 (w)		2010 (vs)	1987 (m)		
	$\mathrm{Mn(C(O)CH_3)(CO)_5}{}^{a,c}$	2115 (m)	2045 (w)	2008 (vs)		1653 (m)	
I	$\overline{\mathrm{Mn(C(OAlBr}}\mathrm{Br_2)CH_3)(CO)_4}{}^{a}$	2106 (m)		2024 (vs)	1976 (m)	1450 (m)	1381 (vw)
II	$\mathrm{Mn(C(OAlBr_3)CH_3)(CO)_5}{}^{b}$	2141 (w)	2085 (vw)	2047 (vw)	2014 (sh)	1483 (w, br)	
III	$\overline{\mathrm{Mn(C(OAlCl}}\mathrm{Cl_2)CH_3)(CO)_4}{}^{a}$	2015 (m)		2024 (vs)	1973 (s)	1435 (w, br)	1380 (w, br)
IV	$\mathrm{Mn(C(OAlCl_3)CH_3)(CO)_5}{}^{b}$	2135 (m)	2080 (w)	2044 (vs)	2008 (m)	1484 (m)	
V	$\overline{\mathrm{Mn(C(OBF}}\mathrm{F_2)CH_3)(CO)_4}{}^{a}$	2112 (m)	2045 (sh)	2026 (vs)	1970 (s)	1452 (m, br)	
VI	$\mathrm{Mn(C(OBF_3)CH_3)(CO)_5}{}^{h}$	2136 (m)	2080 (sh)	2044 (vs)	2013 (sh)	1509 (m)	
	$\mathrm{Mn(CH_2C_6H_5)(CO)_5}{}^{a}$	2106 (m)	2038 (sh)	2008 (vs)	1984 (sh)		
	$\mathrm{Mn(C(O)CH_2C_6H_5)(CO)_5}{}^{b,c}$	2118 (m)	2055 (w)	2015 (vs)	1988 (sh)	1635 (m)	
VII	$\overline{\mathrm{Mn(C(OAlBr}}\mathrm{Br_2)CH_2C_6H_5)(CO)_4}{}^{a}$	2102 (s)	2035 (sh)	2025 (vs)	1968 (vs)	1415 (s)	
VIII	$\mathrm{Mn(C(OAlBr_3)CH_2C_6H_5)(CO)_5}{}^{b}$	2135 (m)	2082 (w)	2046 (vs)	2014 (sh)	1472 (m)	
	$(\eta^5\text{-}C_5H_5)\mathrm{Fe(CH_3)(CO)_2}{}^{a}$		2007 (s)	1951 (s)			
	$(\eta^5\text{-}C_5H_5)\mathrm{Fe(C(O)CH_3)(CO)_2}{}^{a,c}$		2017 (s)	1958 (s)		1661 (m)	
IX	$(\eta^5\text{-}C_5H_5)\overline{\mathrm{Fe(C(OAlBr}}\mathrm{Br_2)CH_3)(CO)}{}^{a}$		1986 (s)			1368 (m)	
X	$(\eta^5\text{-}C_5H_5)\mathrm{Fe(C(OAlBr_3)CH_3)(CO)_2}{}^{a}$		2055 (s)	2007 (s)		1460 (m)	
	$(\eta^5\text{-}C_5H_5)\mathrm{Mo(CH_3)(CO)_3}{}^{a}$		2019 (s)	1930 (vs)			
	$(\eta^5\text{-}C_5H_5)\mathrm{Mo(C(O)CH_3)(CO)_3}{}^{a,c}$	2017 (s)	1940 (sh)	1923 (vs)		1661 (m)	
XI	$(\eta^5\text{-}C_5H_5)\overline{\mathrm{Mo(C(OAlBr}}\mathrm{Br_2)CH_3)(CO)_2}{}^{a}$		2004 (s)	1915 (s)		1363 (m)	
XII	$(\eta^5\text{-}C_5H_5)\mathrm{Mo(C(OAlBr_3)CH_3)(CO)_3}{}^{a}$	2052 (s)	1986 (sh)	1963 (vs)		1457 (m)	
XIII	$\mathrm{[NEt_4][W(C_6H_5)(CO)_5]}{}^{b}$	2035 (m)	1935 (s, sh)	1890 (vs)	1840 (s)		
XIV	$\mathrm{[NEt_4][W(C(OAlPh_3)C_6H_5)(CO)_5]}{}^{b}$	2055 (m)	1967 (m)	1925–1905 (vs)	1850 (s, sh)	1395 (w)	
XV	$\mathrm{[NEt_4][W(C(O)C_6H_5)(CO)_5]}{}^{b}$	2040 (m)	1945 (m, sh)	1898 (vs)	1865 (s)	1515 (w)	

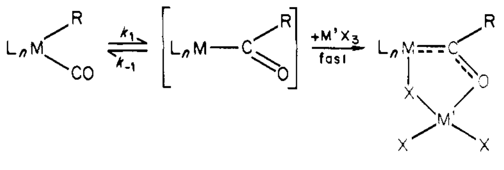
[a] Toluene solution. [b] CH_2Cl_2 solution. [c] These samples were obtained by hydrolyzing the Lewis acid adducts; observed spectra agree with literature values.

Table V. ^{1}H NMR Resonances for Metal–Alkyl and -Acyl Compounds and Their Lewis Acid Adducts[c]

	compd	$\delta(CH_3)$	$\delta(CH_2)$	$\delta(C_6H_5)$	$\delta(C_5H_5)$
	$\mathrm{Mn(CH_3)(CO)_5}{}^{a}$	−0.21 (s)			
	$\mathrm{Mn(C(O)CH_3)(CO)_5}{}^{a,b,e}$	2.64 (s)			
I	$\overline{\mathrm{Mn(C(OAlBr}}\mathrm{Br_2)CH_3)(CO)_4}{}^{a}$	2.33 (s)			
II	$\mathrm{Mn(C(OAlBr_3)CH_3)(CO)_5}{}^{b}$	3.35 (s)			
III	$\overline{\mathrm{Mn(C(OAlCl}}\mathrm{Cl_2)CH_3)(CO)_4}{}^{a}$	2.32 (s)			
IV	$\mathrm{Mn(C(OAlCl_3)CH_3)(CO)_5}$	3.32 (s)			
V	$\overline{\mathrm{Mn(C(OBF}}\mathrm{F_2)CH_3)(CO)_4}{}^{a}$	2.39 (s)			
	$\mathrm{Mn(CH_2C_6H_5)(CO)_5}{}^{a}$		2.18 (s)	6.89 (asym)	
	$\mathrm{Mn(C(O)CH_2C_6H_5)(CO)_5}{}^{d}$		4.24 (s)	7.23 (asym)	
VII	$\overline{\mathrm{Mn(C(OAlBr}}\mathrm{Br_2)CH_2C_6H_5)(CO)_4}{}^{a}$		4.02 (s)	6.91 (br, s)	
VIII	$\mathrm{Mn(C(OAlBr_3)CH_2C_6H_5)(CO)_5}{}^{b}$		4.56 (s)	7.31 (br, s)	
	$(\eta^5\text{-}C_5H_5)\mathrm{Fe(CH_3)(CO)_2}{}^{a}$	0.27 (s)			4.06 (s)
	$(\eta_5\text{-}C_5H_5)\mathrm{Fe(C(O)CH_3)(CO)_2}{}^{e}$	2.35 (s)			4.13 (s)
IX	$(\eta^5\text{-}C_5H_5)\overline{\mathrm{Fe(C(OAlBr}}\mathrm{Br_2)CH_3)(CO)}{}^{a}$	2.23 (s)			3.84 (s)
X	$(\eta^5\text{-}C_5H_5)\mathrm{Fe(C(OAlBr_3)CH_3)(CO)_2}{}^{a}$	2.59 (s)			4.11 (s)
	$(\eta^5\text{-}C_5H_5)\mathrm{Mo(CH_3)(CO)_3}{}^{a}$	0.35 (s)			4.53 (s)
	$(\eta^5\text{-}C_5H_5)\mathrm{Mo(C(O)CH_3)(CO)_3}{}^{a,e}$	2.44 (s)			4.68 (s)
XI	$(\eta^5\text{-}C_5H_5)\overline{\mathrm{Mo(C(OAlBr}}\mathrm{Br_2)CH_3)(CO)_2}$	2.28 (s)			4.56 (s)
XII	$(\eta^5\text{-}C_5H_5)\mathrm{Mo(C(OAlBr_3)CH_3)(CO)_3}$	2.81 (s)			4.70 (s)

[a] Toluene-d_8 solution. [b] CD_2Cl_2 solution. [c] Given in ppm downfield from $(CH_3)_4Si$. [d] Heptane solution, see ref 27. [e] These samples were obtained by hydrolyzing the Lewis acid adducts; observed spectra agree with literature values.

apparent large formation constant for the cyclic insertion product containing $AlBr_3$ or $AlCl_3$. Also, attempts to follow this reaction by BF_3 uptake were frustrated by BF_3 diffusion-limiting conditions at both room temperature and low temperatures. However, a lower limit was established for the reaction rate by an NMR experiment which demonstrated that the formation of $\overline{\mathrm{Mn(C(OAlBr}}\mathrm{Br_2)CH_3)(CO)_4}$ was greater than 90% complete in less than 40 s (the time of mixing and measurement) when 0.5 mL of 0.2 M $AlBr_3$ in toluene was mixed with 0.5 mL of 0.2 M $Mn(CH_3)(CO)_5$ in toluene at room temperature. The average value of k_1 for $Mn(CH_3)(CO)_5$ in eq 2 (calculated from data compiled by Calderazzo)[3] is 6.4×10^{-4} s^{-1}. If the reaction between $AlBr_3$ and $Mn(CH_3)(CO)_5$ occurs by the mechanism shown in eq 6, then a time of ca. 3.6×10^3 s would be required for the

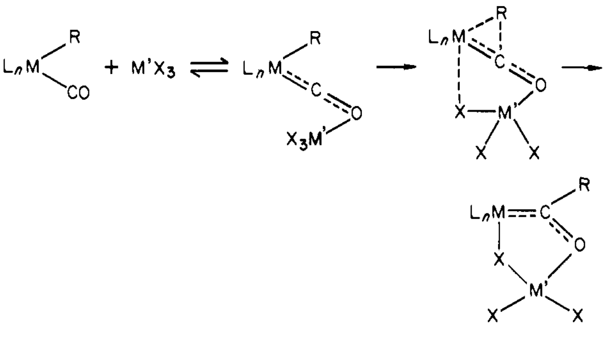


(6)

reaction to reach 90% completion (eq 7). (The immediate color change which is observed when $Mn(CH_3)(CO)_5$ and $AlBr_3$ are mixed indicates the reaction rate is significantly faster than the limit given here.) Since the observed reaction time is much less

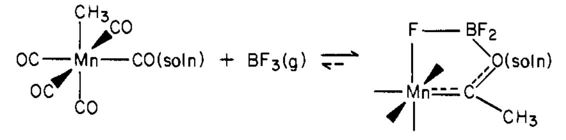
$$t = \left(\frac{1}{k_1}\right)\frac{[Mn(CH_3)(CO)_5]_0}{[Mn(CH_3)(CO)_5]t} = \frac{1}{6.4 \times 10^{-4}} \ln 10 = 3.6 \times 10^3 \text{ s} \quad (7)$$

than that predicted by the mechanism of eq 6, it appears that the Lewis acid assists in the primary alkyl migration step, perhaps as outlined in eq 8. Berke and Hoffmann have employed extended Huckel calculations to estimate that the transition state for CH_3 migration is stabilized by ca. 3 kcal/mol when the electrophile H^+ or Li^+ is attached to the carbonyl oxygen.[26] This would amount to an increase in rate at 20 °C by a factor of 160. It is probable that the qualitative aspects outlined by Berke and Hoffmann apply to the strong Lewis acid assisted reactions.



(8)

When BF_3 was allowed to interact with $Mn(CH_3)(CO)_5$ (eq 9), an equilibrium was established. The ready reversibility of this reaction probably arises from three factors: (1) BF_3 is a weaker acid than $AlBr_3$ and thus interacts less strongly with the acetyl oxygen, (2) fluoride is a poorer ligand than bromide toward the soft Mn(I) center, and (3) the high volatility of BF_3 favors dissociation of the complex.



(9)

$K = 7.6 \times 10^{-2}$ torr^{-1}

In contrast with BF_3, BCl_3 and BBr_3 primarily gave no acetyl products but, instead, caused cleavage of the metal–alkyl bond yielding $MnX(CO)_5$ (X = Cl, Br). In the reaction with BCl_3, IR and NMR spectra indicate that $\overline{Mn(C(OBCl}Cl_2)CH_3)(CO)_4$ was present as a minor component, i.e., terminal CO bands at 2110, 2032, and 1979 cm^{-1}, a presumed O-coordinated acetyl band at 1363 cm^{-1} and CH_3 ^1H NMR at δ 2.24. In agreement with this interpretation, hydrolysis produced $Mn(CH_3)(CO)_5$. However, reaction with CO did not yield the expected $Mn(C(OBCl_3)CH_3)(CO)_5$. Fischer has reported evidence for the formation of $\overline{Mn(C(OBBr}Br_2)CH_3)(CO)_4$ at low temperatures (by a reaction quite different from the CO insertion discussed here).[27] In our reactions we did not explore the possibility of employing low temperatures to stabilize the product.

Aluminum alkyls, which are weaker Lewis acids than the group 3 halides and have no electron-rich ligand to fill an empty coordination site, produced various results. No detectable reaction occurred between $Al(CH_3)_3$ and $Mn(CH_3)(CO)_5$. The addition of excess $Al(i\text{-}C_4H_9)_3$ to $Mn(CH_3)(CO)_5$ produced a brown solution with a very complex IR spectrum. Treatment of this brown solution with CO and subsequent hydrolysis produced a complex mixture of components which appeared to include $Mn_2(CO)_{10}$ and isovaleric acid.

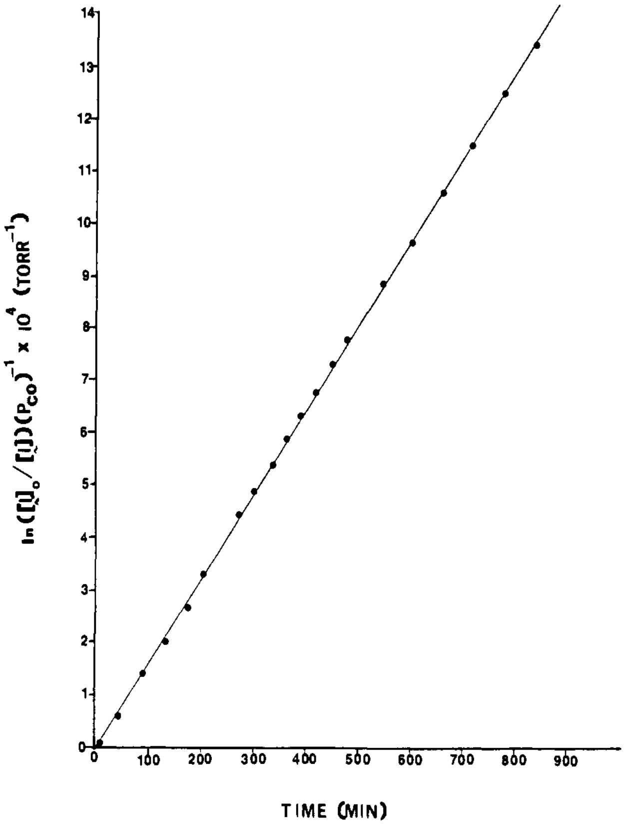
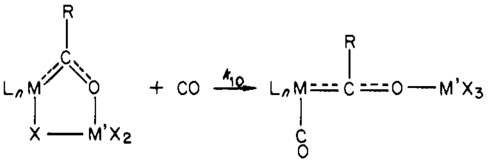


Figure 3. (ln ($[\overline{Mn(C(OAlBr}Br_2)CH_3)(CO)_4]_0/[\overline{Mn(C(OAlBr}Br_2)CH_3)(CO)_4]_t$))$(P_{CO})^{-1}$ vs. time for the reaction of $\overline{Mn(C(OAlBr}Br_2)CH_3)(CO)_4$ (0.881 mmol) with CO (572 torr) in toluene solution (2.9 mL at 20.0 ± 0.1 °C.

CO Addition to Cyclic Insertion Products. As indicated in eq 10, the action of CO on the cyclic Lewis acid coordinated metal acyls (compounds I, III, V, VII, IX, and XI in Table IV) produces simple acyclic Lewis acid coordinated acyls (compounds II, IV, VI, VIII, X, and XII in Table IV). The net effect of this reaction is substitution of a CO ligand for a halogen in the coordination sphere of the metal.



(10)

The initial rate data for CO uptake were found to be first order in both $\overline{Mn(C(OAlBr}Br_2)CH_3)(CO)_4$ concentration and CO pressure, with an overall second-order rate constant, k_{10}, of 2.5×10^{-8} s^{-1} torr^{-1}. As an independent check, the CO uptake was monitored under conditions which were pseudo-first-order with respect to $\overline{Mn(C(OAlBr}Br_2)CH_3)(CO)_4$ (I). The second-order rate plot shown in Figure 3 yields a value of $k_{10} = 2.7 \times 10^{-8}$ s^{-1} torr^{-1}, which is in good agreement with the value determined above from initial rates. From published CO solubility data[28] the average of these rate constants may be expressed in more conventional units: $k_{13} = 2.7 \times 10^{-3}$ M^{-1} s^{-1}.

The second-order rate law is consistent with either a simple S_N2 displacement of Br by CO or the reversible formation of a coordinatively unsaturated intermediate which then reacts with the incoming CO (eq 11). The mechanism of eq 11 is similar to that proposed for the simple CO insertion of $Mn(CH_3)(CO)_5$ in the absence of Lewis acid (eq 2), which displays second-order kinetics

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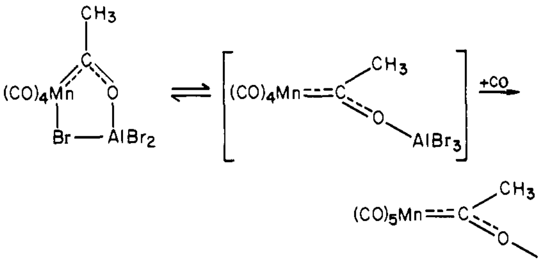
[26] H. Berke and R. Hoffmann, *J. Am. Chem. Soc.*, **100**, 7224–7236 (1978).

[27] E. O. Fischer, *Adv. Organomet. Chem.*, **14**, 1–32 (1976).

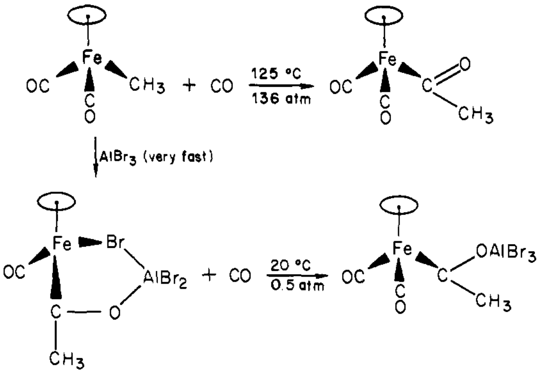
[28] A. Seidell and W. F. Linke, "Solubilities of Inorganic and Metal-Organic Compounds", 4th ed., Vol. 1, Van Nostrand, New York, 1958, pp 457–458.



(11)

when, as is the case with CO, the concentration of incoming ligand is low.[3]

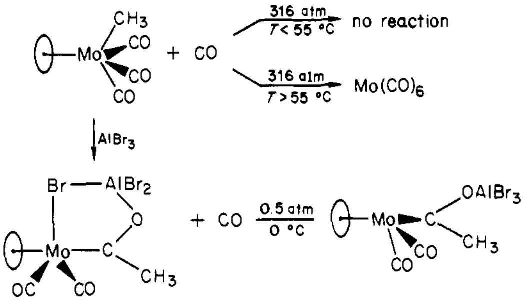
The complete rate equation was determined only for reaction of $Mn(C(OAlBrBr_2)CH_3)(CO)_4$. Other complexes are compared in Table VI on the basis of their initial rates of carbon monoxide uptake. One interesting result is that in all cases the Lewis acid adducts react more rapidly than the parent $L_nM(R)(CO)$ species, in some cases orders of magnitude more rapidly. Under the rather mild reaction conditions employed, $Mn(CH_3)(CO)_5$ is the only one of the four parent compounds selected for study that reacts with CO at a detectable rate. Literature reports of the carbonylation reactions of $Mn(C_6H_5CH_2)(CO)_5$ and $(\eta^5\text{-}C_5H_5)Fe(CH_3)(CO)_2$ are sketchy and sometimes contradictory.[29-31] It is clear, however, that very severe conditions of pressure and/or temperature are required to achieve significant reaction rates. In the absence of Lewis acid these rates were too slow to be observable under our conditions. In the corresponding Lewis acid complexes, $Mn(C(OAlBrBr_2)CH_2C_6H_5)(CO)_4$ and $(\eta^5\text{-}C_5H_5)Fe(C(OAlBrBr_2)CH_3)(CO)$, CO insertion has already occurred because of the stabilizing effect of the acid, and subsequent CO addition occurs at an appreciable rate (eq 12a,b).



(12a)

(12b)

The molybdenum system presents an interesting case. Although the parent methyl compound, $(\eta^5\text{-}C_5H_5)Mo(CH_3)(CO)_3$, is stable, the corresponding acetyl compound, $(\eta^5\text{-}C_5H_5)Mo(C(O)CH_3)(CO)_3$, is not.[32] Barnett reported that a mixture of $(\eta^5\text{-}C_5H_5)Mo(C(O)CH_3)(CO)_3$ and $(\eta^5\text{-}C_5H_5)MoCl(CO)_3$ was produced by the reaction of $[(\eta^5\text{-}C_5H_5)Mo(CO)_3]^-$ with $CH_3C(O)Cl$.[33] The acetyl complex was isolated as a yellow oil, but it was thermally unstable and rapidly decomposed. Here, too, literature reports of the carbonylation reaction are contradictory,[29,31] but the most recent observations of King et al.[31] (eq 13a), indicate that the direct insertion reaction cannot be achieved at 316 atm. In striking contrast to the behavior of its parent compound, $(\eta^5\text{-}C_5H_5)Mo(C(OAlBrBr_2)CH_3)(CO)_2$, reacts with CO under mild conditions at a very rapid rate, and the acetyl product, $(\eta^5\text{-}C_5H_5)Mo(C(OAlBr_3)CH_3)(CO)_3$, is thermally stable (eq 13b). In this system the Lewis acid not only lowers the activation energy barrier for CO insertion but also stabilizes the acetyl product, thus making the reaction thermodynamically favorable.



(13a)

(13b)

The stable cyclic insertion product $(\eta^5\text{-}C_5H_5)Mo(C(OAlBrBr_2)CH_3)(CO)_2$ was hydrolyzed under mild conditions and the simple acetyl $(\eta^5\text{-}C_5H_5)(Mo(C(O)CH_3)(CO)_2$ was identified by IR.[32,33] This compound decomposes to give $(\eta^5\text{-}C_5H_5)Mo(CH_3)(CO)_3$ plus other unidentified products.

All of the reactions described above consume Lewis acid stoichiometrically. Attempts to carry out the reactions with a catalytic amount of Lewis acid were unsuccessful. In an experiment using 0.3 mmol of $AlBr_3$ and 0.9 mmol of $(\eta^5\text{-}C_5H_5)Fe(CH_3)(CO)_2$, the observed CO uptake did not exceed 0.3 mmol. This indicates that the Lewis acid is bound so tightly to the acyl product that an insignificant amount is available to react with the excess alkyl complex.

Examination of Table VI reveals that there is a general correlation between the observed stability of a Lewis acid adduct and the rate of its reaction with CO. Adduct stability in toluene solution increases in the order $(\eta^5\text{-}C_5H_5)Mo(C(OAlBrBr_2)\cdot CH_3)(CO)_2 < Mn(C(OBFF_2)CH_3)(CO)_4 < (\eta^5\text{-}C_5H_5)Fe(C(OAlBrBr_2)CH_3)(CO) < Mn(C(OAlClCl_2)CH_3)(CO)_4 \approx Mn(C(OAlBrBr_2)CH_2C_6H_5)(CO)_4 \approx Mn(C(OAlBrBr_2)CH_3)(CO)_4$. The relative placement of $(\eta^5\text{-}C_5H_5)Mo(C(OAlBrBr_2)CH_3)(CO)_2$ and $Mn(C(OBFF_2)CH_3)(CO)_4$ is somewhat arbitrary because the two complexes show different types of instability: the Mo complex decomposes irreversibly while the Mn complex decomposes reversibly. The rate with which the adduct reacts with CO decreases in the order $(\eta^5\text{-}C_5H_5)Mo(C(OAlBrBr_2)CH_3)(CO)_2 \gg Mn(C(OBFF_2)CH_3)(CO)_4 > Mn(C(OAlClCl_2)CH_3)(CO)_4 > (\eta^5\text{-}C_5H_5)Fe(C(OAlBrBr_2)CH_3)(CO) > Mn(C(OAlBrBr_2)CH_2C_6H_5)(CO)_4 > Mn(C(OAlBrBr_2)CH_3)(CO)_4$. The two series are roughly inverse, indicating that reaction rate decreases with increasing adduct stability. This is a reasonable correlation if adduct stability reflects the ease with which the halogen atom leaves the coordination sphere of the metal. Within the series of acetylmanganese–Lewis acid adducts there is a strict correlation between initial rate and predicted adduct stability. The manganese metal has a formal oxidation state of +1 and is thus a soft acid. On the basis of a simple hard–soft acid–base model and of general stabilities of organometallic halides, the fluoro compound should be less stable than the chloro compound, which should be less stable than the bromo compound.[34]

Included for comparison in Table VI are three systems in which there is no apparent interaction between the Lewis acid and $Mn(CH_3)(CO)_5$. Germanium tetrachloride, $B(C_6H_5)F_2$, and $Mg(oleate)_2$ are weak Lewis acids, and they do not induce the acyl group formation observed in eq 5. These acids have a relatively small effect on the rate of reaction between $Mn(CH_3)(CO)_5$ and CO. The weakest acid, $Mg(oleate)_2$, causes no rate en-

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[29] T. H. Coffield, J. Kozikowski, and R. D. Closson, *Spec. Publ. Chem. Soc.*, No. **13**, 126 (1959).

[30] F. Calderazzo and F. A. Cotton, *Proc. Int. Conf. Coord. Chem., 7th*, 296–297 (1967).

[31] R. B. King, A. D. King, Jr., M. Z. Iqbal, and C. C. Frazier, *J. Am. Chem. Soc.*, **100**, 1687–1694 (1978).

[32] K. W. Barnett and D. W. Slocum, *J. Organomet. Chem.*, **44**, 1–37 (1972).

[33] K. W. Barnett, Ph.D. Thesis, University of Wisconsin, 1967.

[34] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions", 2nd ed., Wiley, New York, 1967, pp 24–25.

Table VI. Rate of Carbon Monoxide Uptake for Toluene Solutions of Alkylmetal Complexes and Acylmetal–Lewis Acid Complexes[a]

	complex	10^6(initial rate), M s^{-1}
	$Mn(CH_3)(CO)_5$	0.18
	$Mn(CH_3)(CO)_5$ + Mg(oleate)$_2$[b]	0.16
	$Mn(CH_3)(CO)_5$ + $GeCl_4$[b]	0.22
	$Mn(CH_3)(CO)_5$ + $B(C_6H_5)F_2$[b]	0.32
I	$Mn(C(OAlBrBr_2)CH_3)(CO)_4$	0.72
III	$Mn(C(OAlClCl_2)CH_3)(CO)_4$	4.2
V	$Mn(C(OBFF_2)CH_3)(CO)_4$	7.8
	$Mn(CH_2C_6H_5)(CO)_5$	*c*
VII	$Mn(C(OAlBrBr_2)CH_2C_6H_5)(CO)_4$	1.6
	$(\eta^5\text{-}C_6H_5)Fe(CH_3)(CO)_2$	*c*
IX	$(\eta^5\text{-}C_5H_5)Fe(C(OAlBrBr_2)CH_3)(CO)$	2.5
	$(\eta^5\text{-}C_5H_5)Mo(CH_3)(CO)_3$	*c*
XI	$(\eta^5\text{-}C_5H_5)Mo(C(OAlBrBr_2)CH_3)(CO)_2$	35
XIII	$[NEt_4][W(C_6H_5)(CO)_5]$[d]	0.021
	$[NEt_4][W(C_6H_5)(CO)_5]$[d] + $Al(C_6H_5)$[e]	2.4

[a] [Metal complex] = 1.00 ± 0.005 M in toluene; $t = 20.0 \pm 0.1$ °C; $P_{CO} = 383 \pm 17$ torr. [b] [Lewis acid] = 0.10 ± 0.01 M. [c] No reaction. [d] [Metal complex] = 0.070 ± 0.005 M in CH_2Cl_2; $t = 17.9 \pm 0.1$ °C; $P_{CO} = 300 \pm 13$ torr. [e] [Lewis acid] = 0.065 ± 0.005 M.

hancement; the stronger acids, $B(C_6H_5)F_2$ and $GeCl_4$, cause small rate enhancements, which indicates that they effect only slight stabilization of the coordinatively unsaturated intermediate in eq 2.

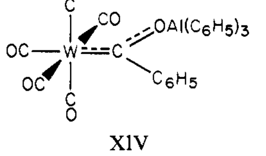
Lewis Acid Promoted Insertion for $[W(C_6H_5)(CO)_5]^-$. The action of CO and a variety of Lewis acids on $[W(C_6H_5)(CO)_5]^-$ was investigated to explore molecular Lewis acid insertion reactions in an anionic metal–aryl system. In the absence of Lewis acid this tungsten complex is known to undergo very slow CO insertion.[16] The aluminum and boron halide Lewis acids did not produce promising results; however, triphenylaluminum caused a large rate of enhancement of CO uptake (eq 14). However,

$$[NEt_4][W(C_6H_5)(CO)_5] + Al(C_6H_5)_3 + CO \xrightarrow[CH_2Cl_2]{} [NEt_4][W(C(OAl(C_6H_5)_3)C_6H_5)(CO)_5] \quad (14)$$

in the absence of CO the Lewis acid does not induce the insertion reaction, as judged by infrared spectra of the solution. Presumably the fact that C_6H_5 is not a good bridging ligand prevents the formation of a cyclic product of the type observed for boron or aluminum halides acting on the neutral metal carbonyl alkyls.

Initial rates of CO uptake were determined for the assisted and unassisted reactions (Table VI), and these show a Lewis acid rate enhancement on the order of 10^2. For example, the reaction was complete (≥90%) in 42 h in the presence of Lewis acid, but in the absence of acid only 18% completion was attained in 7 days.

Infrared spectra of the product shows that the triphenylaluminum promoted reaction also leads to $W(CO)_6$ by-product. Aside from this impurity, the infrared data support structure XIV; thus the characteristic low-frequency band of a Lewis acid coordinated acyl was observed at 1395 cm^{-1} and ca. 40 cm^{-1} increase in the terminal CO stretching frequencies was observed. The identity of XIV was confirmed by the reaction of $[NEt_4][W(C(O)C_6H_5)(CO)_5]$ with $Al(C_6H_5)_3$. In addition, a base displacement reaction (eq 15) was performed on XIV to generate the benzoyl complex, free from Lewis acid.



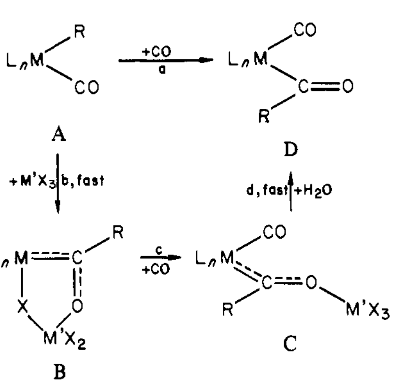
XIV

$$[NEt_4][W(C(OAl(C_6H_5)_3)C_6H_5)(CO)_5] + NHMe_2 \rightarrow NHMe_2{\cdot}Al(C_6H_5)_3 + [NEt_4][W(C(O)C_6H_5)(CO)_5] \quad (15)$$

Attempted Lewis Acid Promoted Formyl Formation. We have investigated the interaction of Lewis acids with $MnH(CO)_5$ and other hydride metal carbonyls, with the thought that the Lewis acid might promote a hydride migration to give an acid stabilized formyl complex. As yet, these experiments have not met with success.

Summary

The preceding discussion illustrates that Lewis acids can have a profound effect on the kinetics and thermodynamics of carbon monoxide insertion reactions. Strictly speaking, it is not correct to say that strong Lewis acids merely increase the rate at which an alkylmetal carbonyl complex reacts with CO to produce the corresponding acyl complex, because the Lewis acid induces a CO insertion reaction even in the absence of added CO. Lewis acid coordination does, however, provide an alternate route from the simple alkyl to the simple acyl complex by way of two fast intermediate steps (eq 16, steps b, c, d). This route enables a convenient synthesis of acyl complexes which cannot otherwise be easily prepared from the corresponding alkyl complexes, e.g., $(\eta^5\text{-}C_5H_5)Fe(C(O)CH_3)(CO)_2$, $(\eta^5\text{-}C_5H_5)Mo(C(O)CH_3)(CO)_3$, and $Mn(C(O)CH_2C_6H_5)(CO)_5$, and stabilization of the acyl group by Lewis acid coordination allows the isolation and storage of complexes which would otherwise decompose, e.g., $(\eta^5\text{-}C_5H_5)Mo(C(OAlBr_3)CH_3)(CO)_3$.



(16)

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Supplementary Material Available: Anisotropic thermal parameters (Table D1) and a list of calculated and observed structure factor amplitudes (Table D2) (15 pages). Ordering information is given on any current masthead page.