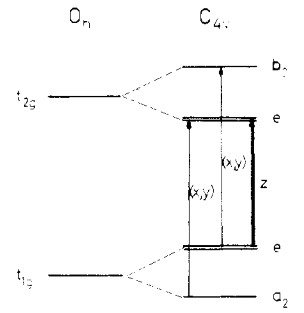

Figure 3. Schematic representation of the lowest energy charge-transfer transition in approximate C_{4v} symmetry.

order of several hundred wavenumbers are therefore expected. The observed bandwidths are too large to resolve them in the absorption spectrum.

Some of the absorption bands in Figure 2 show pronounced linear dichroism. The dichroism is particularly well resolved in the first band at 23040 cm^{-1}, which we assign to the $t_{1g} \rightarrow t_{2g}$ (O_h notation) one-electron transition: it is polarized completely parallel to Fe–O. This may be rationalized as follows.

We assume idealized C_{4v} symmetry for the complex with z parallel to Fe–O. This is an approximation, since the complexes are, in reality, quite strongly distorted in the crystals.[1] Through the substitution of one axial chloride by oxygen, the t_{1g} and t_{2g} orbitals are split into tetragonal components as shown in Figure 3. There are three formally allowed one-electron transitions, two x, y polarized and one z polarized. From the relative disposition of donor and acceptor orbitals[14] it is easy to see that only one can acquire intensity in a ligand to metal charge-transfer mechanism: $e(t_{1g}) \rightarrow e(t_{2g})$. This transition is z polarized and has its origin in the predominant weight of p_x, p_y orbitals of the axial chloride (compared to the corresponding oxygen orbitals) in the donor $e(t_{1g})$ orbital. Dichroism is also observed in the higher energy part of the spectrum. But the situation is complicated by the excited-state splittings and the overlapping absorption bands.

Acknowledgment. We thank P. J. McCarthy for fruitful discussion and correspondence. The work was financially supported by the Swiss National Science Foundation (Grant No. 2.872-77).

Registry No. $Cs_2[FeCl_5(H_2O)]$, 25500-43-0; $(NH_4)_2[FeCl_5(H_2O)]$, 16774-56-4; $K_2[FeCl_5(H_2O)]$, 15132-22-6; $(NH_4)_2[InCl_5(H_2O)]$, 17949-59-6; $Cs_2Na[YCl_6]$, 27880-16-6; $Cs_2Na[FeCl_6]$, 28015-80-7.

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Bifunctional Activation of Coordinated Carbon Monoxide: A Kinetic Study of Lewis Acid Induced Alkyl Migration

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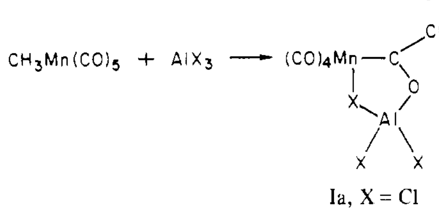
Table I. Kinetic Data for Reaction 1 at 22 °C

Lewis acid	solvent	[acid],[a] M	$[CH_3Mn(CO)_5]$,[a] M	k_{obsd}, s^{-1}
$AlBr_3$[b]	*n*-heptane	2.30×10^{-2}	9.55×10^{-4}	170[c]
$AlCl_3$[d]	benzene	6.55×10^{-4} [e]	5.65×10^{-3}	170[c]
$AlCl_2Et$[b]	*n*-heptane	1.20×10^{-2}	5.60×10^{-4}	10 ± 1[f,g]
$AlClEt_2$[b]	*n*-heptane	5.50×10^{-2}	4.04×10^{-4}	0.37 ± 0.02[f,g]

[a] Concentration after mixing. [b] Pseudo first order in acid. [c] Lower limit for k_{obsd}; see text. [d] Pseudo first order in $CH_3Mn(CO)_5$. [e] Saturated $AlCl_3$ in benzene; see ref 12. [f] Average of four or more determinations. [g] Redistribution of the alkylaluminum chloride takes places prior to insertion.

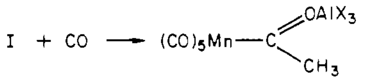
The alkyl migration (CO insertion) reaction of transition-metal complexes has been the subject of numerous synthetic and mechanistic investigations.[1] This transformation is of interest because it is a fundamental reaction of organometallic compounds as well as an important step in the commercial production of oxygenated hydrocarbons with use of transition-metal catalysts.[2] Recently we reported that molecular Lewis acids such as $AlBr_3$ induce rapid alkyl migration in $CH_3Mn(CO)_5$, $(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_3$, and $(\eta^5\text{-}C_5H_5)Mo(CO)_3CH_3$, forming cyclic adducts as seen in eq 1.[3] Upon



(1)

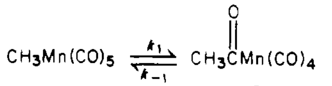
Ia, X = Cl
b, X = Br

exposure to subatmospheric pressures of CO, the cyclic complex I undergoes further reaction, eq 2, which has been the subject of a kinetic study.[3]



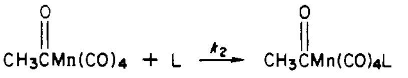
(2)

A critical question in understaning reaction 1 is whether the Lewis acid facilitates the methyl migration or simply captures the coordinatively unsaturated intermediate II, which as shown in eq 3a appears to be formed in the conventional CO insertion



$$CH_3Mn(CO)_5 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CH_3\overset{\overset{\displaystyle O}{\|}}{C}Mn(CO)_4 \qquad (3a)$$

II



$$CH_3\overset{\overset{\displaystyle O}{\|}}{C}Mn(CO)_4 + L \xrightarrow{k_2} CH_3\overset{\overset{\displaystyle O}{\|}}{C}Mn(CO)_4L \qquad (3b)$$

reaction.[1] Although II has never been directly observed, the kinetic evidence for its existence is strong.[1] Our previous work showed that the rate of reaction 1 was too rapid to measure by classical kinetic techniques.[3] In the present research, we have applied the much faster stopped-flow technique in the investigation of reaction 1.

Experimental Section

Kinetic runs were carried out at 22 °C with an Applied Photophysics Model 1705 stopped-flow spectrophotometer modified for work with air-sensitive compounds. Reactants were prepared and purified as previously described.[3] Solvents were dried by using Na/K alloy and degassed by multiple freeze–pump–thaw cycles on a high-vacuum line. The cyclic acetyl product I absorbs light in the near-UV region, whereas the starting materials are essentially transparent.[4] The

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[2] Parshall, G. W. "Homogeneous Catalysis"; Wiley: New York, 1980

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[4] For Ia, λ_{max} = 370 nm (shoulder), ϵ = 580 M^{-1} cm^{-1}; for Ib, λ_{max} = 370 nm (shoulder), ϵ = 820 M^{-1} cm^{-1}.

experimental details of the kinetic runs are given in Table I.

Results

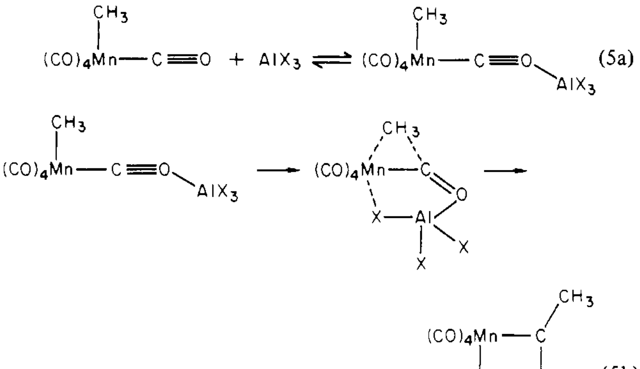
For both $AlBr_3$ and $AlCl_3$, the reaction was complete in the time of mixing, ca. 5 ms. Calculated and observed absorbance changes agreed to within 5%. Because of the sensitivity of $AlCl_3$ and $AlBr_3$ to water, it was not possible to use lower acid concentrations than those listed in Table I. Although the rate of reaction was measurable for $AlCl_2Et$ ($k_{obsd} = 10 \pm 1$ s^{-1}) and $AlClEt_2$ ($k_{obsd} = 0.37 \pm 0.02$ s^{-1}), infrared, NMR, and UV-vis spectroscopy showed that Ia was formed, presumably following redistribution of the alkylaluminum chloride.[5] For example, NMR data indicate that only one-third of $CH_3Mn(CO)_5$ reacts to form an acetyl product in a benzene solution containing equimolar amounts of $AlClEt_2$ and $CH_3Mn(CO)_5$. Similarly, the IR spectrum of the reaction product obtained following addition of excess $AlClEt_2$ to $CH_3Mn(CO)_5$ is identical with that of Ia prepared from $AlCl_3$.[3] This implies that the rate-determining redistribution (eq 4) of $AlClEt_2$

$$3AlClEt_2 \rightleftharpoons AlCl_3 + 2AlEt_3 \qquad (4)$$

occurs before the alkyl migration reaction of interest. Nevertheless, the overall reaction to form Ia is significantly faster than that observed in the absence of a Lewis acid. Attempts to promote reaction 1 with other Lewis acids resulted in alkyl cleavage for BCl_3,[3] BBr_3,[3] Ph_2BBr, and $GaCl_3$,[6] while no reaction was observed for $(i\text{-PrO})_3Al$, Et_2AlOEt, $InCl_3$, or $LaCl_3$.

Discussion

A lower limit can now be placed on the rate of reaction 1. Since the reaction was complete within the time required for mixing in the stopped-flow spectrophotometry, a reasonable estimate of the half-life would be less than 4 ms, corresponding to a $k_{obsd} > 170$ s^{-1}. This can be compared to the k_1 value of 2×10^{-6} s^{-1} observed for eq 3a with L = cyclohexylamine in mesitylene solution at 25.5 °C.[7] (Under similar conditions, k_1 in hexane is too small to measure.) This large rate enhancement (ca. 10^8) indicates that the Lewis acid is involved in the primary alkyl migration step (eq 3a) and does not merely intercept the coordinatively unsaturated intermediate (eq 3b) in the mechanism outlined above. One possible mechanism for this rate enhancement is coordination of the Lewis acid to the oxygen atom of a terminal carbonyl in $CH_3Mn(CO)_5$, thereby affording the reaction scheme (5a) and (5b). Although there is no direct experimental evidence for the preequilibrium (5a), Lewis acid adducts are well-known for cyclopentadienyl, anionic, and donor-substituted metal carbonyls.[8] In these systems, the bifunctionally coordinated CO exhibits a greatly reduced CO stretching frequency and bond order. In addition, extended Hückel molecular orbital calculations on the alkyl migration reaction carried out by Berke and Hoffmann[9] indicate that coordination of an electrophile such as H^+ or Li^+ to a terminal carbonyl stabilizes the transition state (eq 3a) by ca. 3 kcal/mol. We[10] have previously observed a small rate enhancement of methyl migration in the presence of carboxylic acids, and Collman et al.[11] reported a 2400-fold increase in the alkyl migration rate in $RFe(CO)_4^-M^+$ when M^+ is changed from $((C_6H_5)_3P)_2N^+$ to Li^+. Although the observed rate enhancement for $AlBr_3$ requires a significantly larger reduction in the activation energy than that calculated by Berke and Hoffmann, their arguments are in qualitative agreement with the present result.



(5a)

(5b)

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Registry No. Ia, 74417-97-3; Ib, 72319-91-6; $CH_3Mn(CO)_5$, 13601-24-6; $AlBr_3$, 7727-15-3; $AlCl_3$, 7446-70-0; $AlCl_2Et$, 563-43-9; $AlClEt_2$, 96-10-6.

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Improved Synthesis of Some Molybdenum and Tungsten Tetrahydrides

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Polyhydride complexes of the type MH_xL_y ($x \gtrsim 3$) have been increasingly studied recently.[1] We have considered the tertiary phosphine tetrahydrides of molybdenum and tungsten as possible sources of highly reactive, highly ligand-deficient species, but a detailed study of their chemistry has required that we develop better synthetic routes to these compounds.

The most common method to date of preparing molybdenum and tungsten tetrahydrides is $NaBH_4$ reduction of MCl_4L_2 (M = Mo or W; L = tertiary phosphine) in ethanol in the presence of excess phosphine (eq 1, 2).[2-5] The yields of the last step

$$MoCl_5 \xrightarrow{CH_3CN} \underset{80\%}{MoCl_4(CH_3CN)_2} \xrightarrow[CH_2Cl_2]{2L} \underset{50\%}{MoCl_4L_2} \xrightarrow[\substack{2L \\ EtOH}]{NaBH_4} \underset{15\%}{MoH_4L_4} \qquad (1)$$

$$WCl_6 \xrightarrow[\substack{Zn \\ CH_2Cl_2}]{PPh_3} \underset{35\%}{WCl_4(PPh_3)_2} \xrightarrow[CH_2Cl_2]{2L} \underset{90\%}{WCl_4L_2} \xrightarrow[\substack{2L \\ EtOH}]{NaBH_4} \underset{15\%}{WH_4L_4} \qquad (2)$$

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