cleavage of a metal–metal bond with concomitant movement of a terminal CO to a bridging site. Such a transformation would open a coordination site for a two-electron donor such as CO. A similar mechanism, i.e., Scheme I, may be proposed here.[8] Further quantitative flash and continuous photolysis studies currently in progress should better illuminate the mechanism of this unusual transformation.

Acknowledgment. This work was supported by the National Science Foundation. Ruthenium used in these studies was provided on loan by Johnson Matthey, Inc.

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(8) According to this proposal the isomerization depicted in eq 2 should also be facilitated by other two-electron donor ligands. In this context, it is notable that at P_{CO} = 0.0 the Φ_2 has a value 1.4 × 10^{-3} in THF solution, over an order of magnitude larger than under the same conditions in cyclohexane solution.

Thermochemical Study of the Lewis Acid Promoted Carbonyl Insertion Reaction

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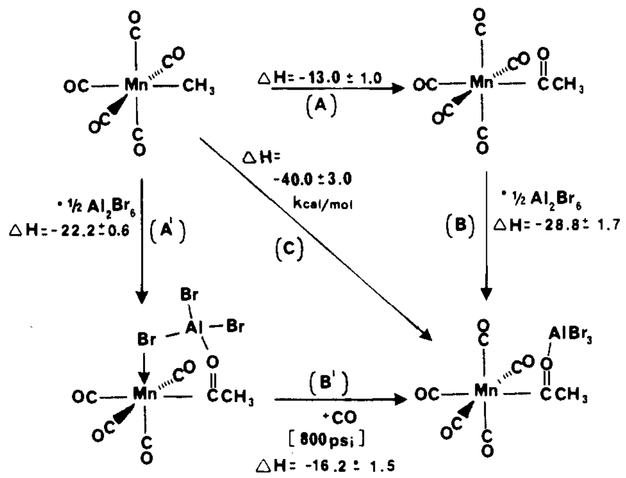
Interaction of Lewis acids with transition-metal alkyl carbonyl complexes has been shown to promote carbonyl insertion.[1] This effect combines both thermodynamic and kinetic factors. Since studies of homogeneous model systems can provide important information about heterogeneous catalysts, we have begun investigation of the thermodynamic effects of Lewis acids on carbonyl insertion. This is part of a general program of solution calorimetric studies of organotransition-metal complexes.[2]

Shriver and co-workers[1] have reported synthetic, structural, and kinetic details of the interaction of aluminum halides with methylmanganese pentacarbonyl. Cotton and Calderazzo previously determined the enthalpy of carbonylation of $CH_3Mn(CO)_5$ (reaction A in Scheme I) by measuring the temperature variation of the equilibrium constant ($\Delta H = -12.6$ kcal/mol in bis(β-ethoxyethyl)ether[3]). Using calorimetric techniques similar to those reported earlier[2] and a newly developed high-pressure cell, we have repeated this measurement[4a] and completed the thermochemical cycle shown in Scheme I. To our knowledge this represents the first thermochemical assessment of the role of Lewis acids in the promotion of this important reaction.

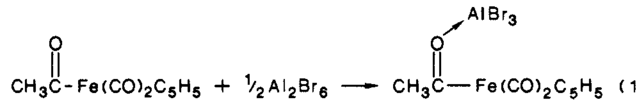
Scheme I



Reaction of $H_3C(O)$–$Mn(CO)_5$ (reaction B) with ${}^1/_2Al_2Br_6$ in toluene solution at 25 °C is rapid and exothermic, $\Delta H = -28.8 \pm 1.7$ kcal/mol.[4b] In order to compare this result to the heat of adduct formation with other transition-metal complexes, we measured the enthalpy of reaction of the iron acyl complex shown in reaction 1. The enthalpy of this reaction ($\Delta H = -30.6 \pm 2.1$ kcal/mol (25 °C, toluene solution)) is similar to that for the analogous reaction with manganese acyl and suggests that the transition metal plays only a minor role in determining the stability of the aluminum bromide–carbonyl adduct. The heat of reaction 2 was measured in order to compare the stabilities of the organometallic aluminum bromide adduct with those of organic analogues. The enthalpy of reaction 2 at 25 °C, with all species

$$(C_6H_5)_2C{=}O + {}^1/_2Al_2Br_6 \rightarrow (C_6H_5)_2C{=}O{\rightarrow}AlBr_3 \quad (2)$$

in toluene solution, is -24.5 ± 0.5 kcal/mol, in agreement with previously reported values.[5]



$$CH_3\overset{O}{\overset{\|}{C}}\text{-}Fe(CO)_2C_5H_5 + {}^1/_2Al_2Br_6 \longrightarrow CH_3\overset{O\text{–}AlBr_3}{\overset{\|}{C}}\text{—}Fe(CO)_2C_5H_5$$

(1)

Aluminum bromide adduct formation with more electron rich carbonyl compounds, such as $C_6H_5C(O)N(C_6H_5)_2$ is more exothermic ($\Delta H = -27.4$ kcal/mol[5]) and agrees, within 10%, with the values obtained for the transition-metal complexes. Thus, it appears that it may be possible to estimate the interaction of Lewis acids with transition-metal complexes by consideration of the interaction of an appropriate organic model compound with the relevant Lewis acid. It should also be noted that our data are based on reaction with ${}^1/_2Al_2Br_6$. Calculation based on reaction with the more powerful Lewis acid, $AlBr_3$, requires addition of -13.3 kcal/mol to the values reported herein.[6]

Reaction of $CH_3Mn(CO)_5$ with ${}^1/_2Al_2Br_6$, reaction A′ in Scheme I, is exothermic by 22.2 ± 0.6 kcal/mol in toluene solution

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(4) (a) The value we obtained, -13.4 ± 1.0 kcal/mol at 30 °C in THF, agrees well with that reported earlier by others.[3] In Scheme I, we adopt an average value of -13.0 ± 1.0 kcal/mol. Details of the high-pressure calorimetry will be published later. (b) In a typical reaction, a glass ampule containing approximately 0.1 g of the complex was broken into a solution of 25 g of Al_2Br_6 (purified by high-vacuum sublimination) in 400 mL of dry toluene by using the calorimetric system previously described.[2] (c) A similar value was obtained for the enthalpy of reaction B′ (Scheme I) in toluene solution. However, due to formation of precipitate in some of the reactions, greater accuracy was obtained in CH_2Cl_2 solution where no precipitation was observed.

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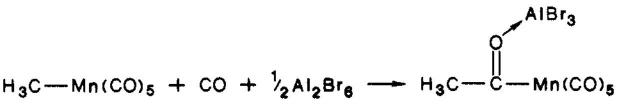
at 25 °C. This reaction involves carbonyl insertion, formation of the carbonyl oxygen–aluminum bond, and also creation of a dative bond between one of the bromine atoms and manganese. In the second step of this arm of the cycle (reaction B′) the Br–Mn bond is cleaved by CO. The enthalpy of this reaction in CH_2Cl_2 solution, −16.2 ± 1.5 kcal/mol, can be used to estimate the Mn–Br bond strength. A recent estimate of the Mn–CO bond strength is 36 ± 2 kcal/mol,[7] which implies that the Mn–Br bond strength (for the Mn–Br dative bond[8]) is on the order of 20 kcal/mol. The diagonal reaction in Scheme I, carbonyl insertion coupled with formation of the Lewis adduct, is calculated to be exothermic by 41.8 ± 2.7 kcal/mol by summing the enthalpies of reactions A + B and 38.4 ± 2.1 kcal/mol by summing the reactions of A′ + B′. Considering the extremely air-sensitive nature of the reactants, this agreement is good and we believe the average value of −40 ± 3 kcal/mol adequately defines the enthalpy of reaction 3.

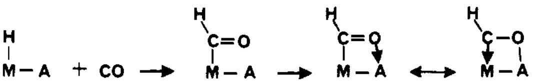


$$H_3C{-}Mn(CO)_5 + CO + \tfrac{1}{2}Al_2Br_6 \longrightarrow H_3C{-}\overset{\overset{O\rightarrow AlBr_3}{\|}}{C}{-}Mn(CO)_5 \qquad (3)$$

It has long been held that failure to observe carbonyl insertion into metal–hydrogen bonds is due to thermodynamic factors.[9] Recently, it has been shown that for gas-phase formyl insertion shown in reaction 4, $\Delta H = +10.3 \pm 7.4$ kcal/mol.[9] It is clear

$$H\text{-}Fe(CO)_4^- + CO \rightarrow H\text{-}C({=}O)\text{-}Fe(CO)_4^- \qquad (4)$$

that, in the absence of competing side reactions,[10] the presence of a strong Lewis acid such as aluminum bromide would be sufficient to overcome such a barrier. This is of interest since interaction with Lewis acidic supports may enhance the insertion of carbon monoxide into transition-metal hydrogen bonds either through formation of Lewis acid adducts or possibly through hydroxy carbene complexes[11] as shown in reaction 5. Oxophilic



(5)

metals such as thorium have been shown to undergo carbonyl insertion forming η^2-formyls. Complete kinetic and thermodynamic data for this reaction are known, and the thorium–oxygen interaction is estimated to be on the order of 5 kcal/mol.[12] This is clearly lower than the interaction with the external Lewis acid, Al_2Br_6.

In summary, the thermodynamic cycle in Scheme I illustrates the range of thermodynamic effects that can be expected when carbonyl insertion is coupled to formation of Lewis acid adducts. The role of the transition metal in determining the strengths of these bonds appears minor. The approximation that stabilization of other insertion products can be modeled by known thermochemical data for organic substrates appears to be justified. Additional experimental work is in progress to test this hypothesis.

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Effect of Structural Disorder on Organic Superconductors: A Neutron Diffraction Study of "High-T_c" β^*-$(BEDT\text{-}TTF)_2I_3$ at 4.5 K and 1.5 kbar

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Received May 28, 1986

Synthetic organic metals based on bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF, $C_{10}S_8H_8$, or abbreviated ET) offer a unique opportunity to systematically study structure–property relationships.[1] Salts of ET typically contain two-dimensional networks of intermolecular intra- and interstack S···S contacts of 3.60 ± 0.1 Å (the van der Waal radii sum) which provide the electron conduction pathways. Within the nearly isostructural (triclinic space group $P\bar{1}$, $Z = 2$) series β-$(ET)_2X$, $X = I_3^-$, I_2Br^-, AuI_2^-, and IBr_2^-, all are ambient-pressure superconductors at low temperatures except for the I_2Br^- salt, which remains metallic down to at least 0.45 K.[2] Since the central atoms of the anions are located on crystallographic inversion centers, the I_2Br^- salt is randomly disordered ($I{-}I{-}Br^-$ and $Br{-}I{-}I^-$), and it has been proposed that the resulting variation of local potentials in the ET network prevents the onset of superconductivity.[2a]

β-$(ET)_2I_3$ is also structurally disordered, but in this case the disorder involves only one ethylene group on one end of the ET molecule. The terminal $-C_2H_4$ group has two conformations, labeled A and B in Figure 1b, in the crystal above 200 K.[3] Below 200 K satellite reflections appear in the neutron[4a] and X-ray[4b] diffraction patterns which have been analyzed in terms of rigid-body sinusoidal displacive modulations of the ET molecules and the I_3^- anions about their average positions in the unit cell.[4b,c] Because this results in fluctuations in intermolecular distances from one unit cell to another, it was proposed[4c] that, in order to avoid unfavorable H···I contacts, the site occupancies corresponding to the A and B conformations of the ET molecules would become ordered with the same periodicity of the modulation. Recent structure–property correlations and calculations indicate[1a] that the superconducting transition temperature at ambient pressure for β-$(ET)_2I_3$ ($T_c = 1.4$ K) is anomalously low with respect to β-$(ET)_2IBr_2$ ($T_c = 2.8$ K) and β-$(ET)_2AuI_2$ ($T_c = 5$ K), so that, even though the low-temperature structure is ordered, the incommensurate periodic variations in the local potentials may increase electron-pair scattering and prevent the onset of superconductivity in β-$(ET)_2I_3$ above 1.4 K.

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