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Cis Labilization of Ligand Dissociation. 7. Substitution Reactions of Acetonitrilepentacarbonylmanganese(I). Cis Labilization via Nucleophilic Attack at Metal-Bound CO[1]

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Abstract: Reaction of acetonitrilepentacarbonylmanganese(I) tetrafluoroborate, $[Mn(CO)_5(CH_3CN)]BF_4$, with pyridine in CH_3NO_2 solvent yields $Mn(CO)_3(NC_5H_5)_3^+$ and CO_2 as products. Reduction of 1 mol of solvent is shown to occur. Reaction is inhibited by added pyridinium tetrafluoroborate. Pentacarbonylpyridinemanganese(I) tetrafluoroborate, $[Mn(CO)_5(NC_5H_5)]BF_4$, reacts with pyridine in CH_3NO_2 solvent to afford the same products, but at a somewhat slower rate. These and other evidences suggest that reaction proceeds via a rate-determining attack of the aci anion of solvent, $CH_2NO_2^-$, at the carbon of metal-bound CO. In acetonitrile, reaction of $[Mn(CO)_5(CH_3CN)]BF_4$ with pyridine affords $[Mn(CO)_5(NC_5H_5)]BF_4$ as principal product. The reaction rate is much faster than for reaction of $[Mn(CO)_5(CH_3CN)]BF_4$ with triphenylphosphine. A nucleophilic attack of pyridine at metal-bound CO to produce a cis-labilizing adduct ligand appears to precede the rate-determining loss of CH_3CN. Reactions of $[Mn(CO)_5(CH_3CN)]BF_4$ with triphenylphosphine in acetonitrile, to yield principally $Mn(CO)_5PPh_3^+$, with CD_3CN to yield $Mn(CO)_5CD_3CN^+ + Mn(CO)_3(CD_3CN)_3^+$, or with CH_3CN to yield $Mn(CO)_3(CH_3CN)_3^+$ all proceed at comparable rates. Dissociative loss of CO ($k(35\ ^\circ C) = 1.2 \pm 0.6 \times 10^{-6}\ s^{-1}$) is slower than loss of CH_3CN ($k(35\ ^\circ C) = 4.2 \pm 1.0 \times 10^{-6}\ s^{-1}$). The rate of substitution of $[Mn(CO)_6]BF_4$ by PPh_3 in acetic anhydride proceeds via dissociative loss of CO ($k(35\ ^\circ C) = 5.2 \pm 0.6 \times 10^{-7}\ s^{-1}$). These comparative rates suggest than CH_3CN is only slightly labilizing in $Mn(CO)_5CH_3CN^+$. Reaction of $[Mn(CO)_5(CH_3CN)]BF_4$ with pyridine in wet acetonitrile leads to formation of additional products such as $Mn(CO)_5^-$ and dinuclear manganese species, that can be related to nucleophilic attack of OH^- at metal-bound CO.

It is now reasonably well established that in substituted metal carbonyl compounds, for a large class of ligands, the positions cis to these ligands are labilized with respect to dissociation. The evidences for this are of two forms. Systematic comparisons of rate constants indicate that many ligands, upon replacement for CO, labilize the complex toward ligand loss relative to CO as reference ligand.[2] From studies of both thermal and photochemical reactions of such substituted carbonyls, it can be established that ligand entry into a coordinatively unsaturated intermediate leads to formation of the cis product.[3-6] In the case where the entering ligand is labeled CO, the principle of microscopic reversibility requires that the stereochemistry of ligand entry into the coordinatively unsaturated intermediate be the same as that for dissociative loss of CO in a thermal reaction.

Reaction pathways involving nucleophilic attack at carbon in metal carbonyls have been demonstrated in several systems. Examples include nucleophiles derived from alkoxides,[7] organolithium compounds,[8,9] Grignard reagents,[10,11] amines,[12-16] halides,[17,18] pseudohalides,[19-21] and OH^-.[22-24] Nucleophilic attack occurs most readily in carbonyl complexes in which the metal-bound carbon carries a slight positive charge. Interaction of the nucleophile with carbonyl may lead to a stable product, or may be manifested in the form of isotope exchange, as in the case of ^{18}O exchange of metal carbonyl cations in aqueous base.[22,23] One can imagine, however, that interaction of a base with suitable metal carbonyl moieties might result in formation of an intermediate acid–base adduct not sufficiently stable to be isolated, nor present in sufficiently large concentration to permit ready detection.[13] Nevertheless, the formation of such an acid–base adduct could have important consequences for the kinetics of substitution reactions of such a metal center, inasmuch as the resulting adduct might possess strongly cis-labilizing character.[25]

The cation $Mn(CO)_5(CH_3CN)^+$ is an appropriate choice for studying the connections between nucleophilic attack at CO and ligand substitution. It readily undergoes substitution, and evidence exists that the substitution process is mediated by attack at CO. For example, in the reaction of $Mn(CO)_5(CH_3CN)^+$ with NH_2CH_3, the product is *cis*-$Mn(CO)_4(NH_2CH_3)[C(O)NH(CH_3)]$.[16] Similarly $Mn(CO)_5NH_2R^+$ reacts rapidly with NH_2R' to afford *cis*-$Mn(CO)_4NH_2R'[C(O)NHR']$.[26] Attack at CO and

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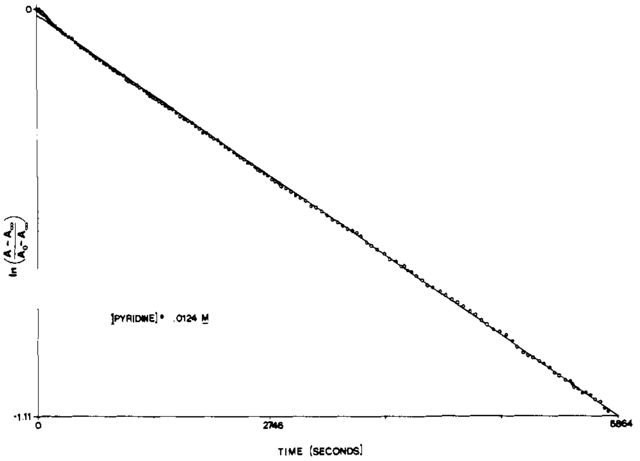

Figure 1. First-order plot for disappearance of $Mn(CO)_5(CH_3CN)^+$ upon reaction with pyridine in CH_3NO_2 solvent, 31.8 °C. The absorbance observed is the band at 2073 cm^{-1} due to the E mode CO stretching vibration.

substitution are clearly related in these reactions.

In this paper we report the results of a study of the substitution reactions of acetonitrilepentacarbonylmanganese(I), $Mn(CO)_5(CH_3CN)^+$, under various conditions in nitromethane or acetonitrile as solvent. The results demonstrate the existence of a strong labilizing effect resulting from nucleophilic attack at metal-bound CO. In addition, an unexpected oxidation–reduction reaction occurs as a result of the initial nucleophilic attack at metal-bound CO in basic CH_3NO_2 solutions.

Results and Discussion

Nitromethane as Solvent. In the absence of an assisting nucleophile, the rate of ligand loss from $Mn(CO)_5(NC_5H_5)^+$ or $Mn(CO)_5(CH_3CN)^+$ in nitroalkane solution is very low. For example, we observed that no ^{13}CO exchange with either cation occurred in nitroethane solvent after 72 h at 30 °C. Similarly, the salt $[Mn(CO)_5(CH_3CN)]BF_4$ is stable in dry CH_3NO_2 solution for 1 week or more at room temperature without evident decomposition. However, upon addition of pyridine the following unexpected reaction occurs rapidly:

$$Mn(CO)_5(CH_3CN)^+ + CH_3NO_2 + 3NC_5H_5 \rightarrow Mn(CO)_3(NC_5H_5)_3^+ + CO + CO_2 + CH_2NOH \quad (1)$$

When pyridine is present in excess, the disappearance of $Mn(CO)_5(CH_3CN)^+$ accurately follows a first-order rate law, as illustrated in Figure 1. The stoichiometry of the reaction was determined from isolation and characterization of $[Mn(CO)_3(NC_5H_5)_3]BF_4$, and by quantitative gas chromatographic analysis of the gaseous products. It is noteworthy that one overall result of the reaction is reduction of nitromethane solvent by 1 mol of CO. To establish that solvent reduction has indeed occurred ^{18}O-labeled CH_3NO_2 was prepared and employed as solvent. The evolved CO_2 was analyzed mass spectrometrically and found to contain ^{18}O in amounts that require that one oxygen of the CO_2 is derived from the solvent (Experimental Section). Unfortunately, it was not possible to isolate or otherwise identify the organic product, formaldoxime, CH_2NOH. This compound is not stable under the basic conditions of the reaction, and probably polymerizes rapidly.[27] We were not able to identify the organic residues, which, as the reaction is run, are present in very low concentrations. However, the labeling experiment just described, along with other evidence regarding the reaction to be described below, establishes clearly that reduction of the solvent molecule has occurred.

The mechanism suggested for the reaction is displayed in Scheme I.

Scheme I

$$CH_3NO_2 + NC_5H_5 \underset{}{\overset{K}{\rightleftharpoons}} HNC_5H_5^+ + CH_2NO_2^- \quad (2)$$

$$CH_2NO_2^- + Mn(CO)_5(CH_3CN)^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} cis\text{-}Mn(CO)_4(CH_3CN)Z \quad (3)$$

$$cis\text{-}Mn(CO)_4(CH_3CN)Z \xrightarrow{k_4} Mn(CO)_4Z + CH_3CN \quad (4)$$

$$Mn(CO)_4Z + NC_5H_5 \xrightarrow{k_5} cis\text{-}Mn(CO)_4(NC_5H_5)Z \quad (5)$$

$$cis\text{-}Mn(CO)_4(NC_5H_5)Z \xrightarrow{k_6} Mn(CO)_3(NC_5H_5)Z + CO \quad (6)$$

$$Mn(CO)_3(NC_5H_5)Z + NC_5H_5 \xrightarrow{k_7} fac\text{-}Mn(CO)_3(NC_5H_5)_2Z \quad (7)$$

$$fac\text{-}Mn(CO)_3(NC_5H_5)_2Z \xrightarrow{k_8} Mn(CO)_3(NC_5H_5)_2^+ + CO_2 + CH_2NO^- \quad (8)$$

$$Mn(CO)_3(NC_5H_5)_2^+ + NC_5H_5 \xrightarrow{k_9} fac\text{-}Mn(CO)_3(NC_5H_5)_3^+ \quad (Z = C(O)ON(O)CH_2^-) \quad (9)$$

The proposed mechanism might be varied by allowing for loss of CO_2 and CH_2NO^- at an earlier stage, e.g., following formation of cis-$Mn(CO)_4(CH_3CN)Z$, with formation of cis-$Mn(CO)_4(NC_5H_5)(CH_3CN)^+$. The presence of two cis-labilizing ligands should result in rapid further substitution to form the observed product.

It is well established that nitromethane can be deprotonated to form the conjugate base of the aci form. Thus, some $CH_2NO_2^-$ should exist in solution. There is precedent for reduction of the aci anionic form of nitromethane obtained via deprotonation by pyridine.[28] However, the mechanism proposed in that work is not applicable to the present case.

The effect of employing other nitroalkanes as solvent is not marked. The reaction rate varies in the order $CH_3NO_2 \sim C_2H_5NO_2 > i\text{-}C_3H_7NO_2$. Although the relative pK_a values for these nitroalkanes are known in aqueous medium,[29] it is not evident that these values are an appropriate indication of the relative acidities of the three compounds under the conditions of the reaction. In addition, the relative effectiveness of the aci anions in nucleophilic attack at CO is not known. Thus, these observations do not shed much light on the proposed mechanism.

To rule out water as a reactant, the solvent and pyridine were both saturated with ^{18}O-enriched water and then dried in the usual way. Reaction was carried out in the usual manner, and the evolved CO_2 analyzed mass spectrometrically. No ^{18}O enrichment was observed. This experiment rules out the possibility that traces of water present in the solvent or in the added pyridine are responsible for the evolution of CO_2 through OH^- attack at coordinated CO.[23] To further test the role of water, a solution of pyridine and water in CH_3NO_2 was reacted with $[Mn(CO)_5(CH_3CN)]BF_4$. A slight increase in overall rate of reaction was observed. However, products not seen when all solute and solvent materials were carefully dried were observed; notable among these is $Mn(CO)_5^-$. It thus appears that, although OH^- may react with $[Mn(CO)_5(CH_3CN)]BF_4$, such a reaction is not notably fast in relation to the observed reaction, and is not of significance under the conditions under which we have studied the reaction, with thoroughly dried solvent and reactant substances.

We assume that equilibrium 2 is achieved rapidly on the time scale of the experiment, and that the equilibrium constant K is small. With respect to the latter point, the equilibrium has not been evaluated as such, but potentiometric studies of various

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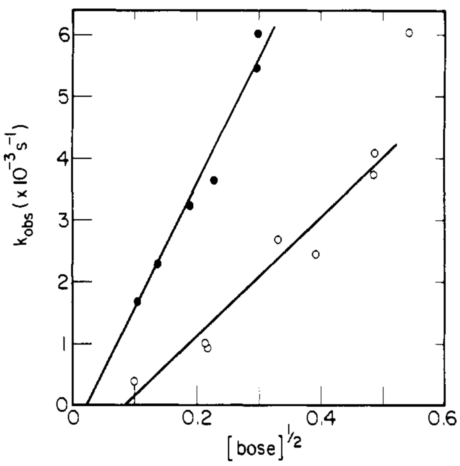

Figure 2. Graph of the pseudo-first-order rate constant, k_{obsd}, vs. $[base]^{1/2}$ for reaction with $Mn(CO)_5(CH_3CN)^+$ in CH_3NO_2 at 31.8 °C: ○ = pyridine; ● = 4-methylpylpyridine.

nitrogen bases in CH_3NO_2 are consistent with weak base behavior for pyridine and substituted pyridine.[30,31] It is noteworthy that the value of K based upon aqueous solution values of pK_a and pK_b for CH_3NO_2 and pyridine, respectively, is about 10^{-5}.

The rate at which proton transfer occurs to achieve equilibrium is not known. The rate constant for proton transfer from nitroethane to pyridine in aqueous ethanol is quite slow.[32] Deprotonation by OH^- in aqueous medium is much faster.[33] Making allowance for the expected faster rate for nitromethane as compared with nitroethane,[29b] and for the fact that our studies are at 32 °C, we expect the rate of the proton step to be fast relative to the observed overall reaction rate. The adequacy of this assumption is borne out by the observed pseudo-first-order character of the reaction when the base is present in excess (Figure 1).

If we assume that $CH_3NO_2^-$ attack, eq 3, is rate limiting, and that the reverse reaction can be neglected, the rate law is of the form

$$-d[Mn(CO)_5(CH_3CN)^+]/dt = k_1[Mn(CO)_5(CH_3CN)^+][CH_2NO_2^-] \quad (10)$$

The importance of $CH_2NO_2^-$ in the rate law was tested by adding $HNC_5H_5BF_4$. Addition of 0.1 M $HNC_5H_5BF_4$ to the reaction medium containing initially 0.25 M NC_5H_5 and 0.014 M $Mn(CO)_5(CH_3CN)^+$ caused the pseudo-first-order rate constant to decrease by a factor of about 65. This very large effect of added $HNC_5H_5^+$ demonstrates that the aci anion is involved in some step which precedes or includes the rate-determining step. Secondly, it requires that equilibrium 2 does in fact lie far to the left; it suggests that K may be on the order of 10^{-4}–10^{-5}.

We have that

$$[CH_2NO_2^-] = K[NC_5H_5]/[HNC_5H_5^+] \quad (11)$$

from which we obtain

$$-d[Mn(CO)_5(CH_3CN)^+]dt = k_1K[Mn(CO)_5(CH_3CN)^+][NC_5H_5]/[HNC_5H_5^+] \quad (12)$$

But, if K is small, $[CH_2NO_2^-] = [HNC_5H_5^+] \simeq K^{1/2}[NC_5H_5]^{1/2}$, so that

$$-d[Mn(CO)_5(CH_3CN)^+]/dt = k_1K^{1/2}[Mn(CO)_5(CH_3CN)^+][NC_5H_5]^{1/2} \quad (13)$$

Figures 2 and 3 show graphs of the observed pseudo-first-order rate constant, k_{obsd}, vs. $[base]^{1/2}$ for the bases pyridine, 4-methylpyridine, 2-methylpyridine, and N-benzylimidazole. The data agree moderately well with the expected relationship, though there is a nonzero intercept in every case. The origin of this discrepancy is not clear; it possibly arises in the experimental difficulties in evaluating the rate constants at lower base concentrations. From the observed variation in k_{obsd} with $[base]^{1/2}$ the apparent 3/2-order rate constants listed in Table I were obtained for the four bases, and compared with their aqueous solution pK_a values. For the closely analogous pyridines the relative rate constants parallel the pK_a values, as expected.

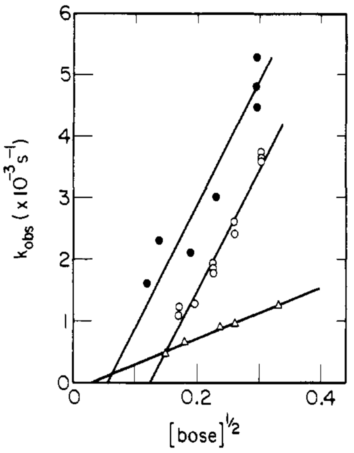

Figure 3. Graph of the pseudo-first-order rate constant, k_{obsd}, vs. $[base]^{1/2}$ for reaction with $Mn(CO)_5(CH_3CN)^+$ in CH_3NO_2 at 31.8 °C: ○ = N-benzylimidazole; ● = 2-methylpyridine. ▲ = reaction of $Mn(CO)_5NC_5H_5^+$ with pyridine.

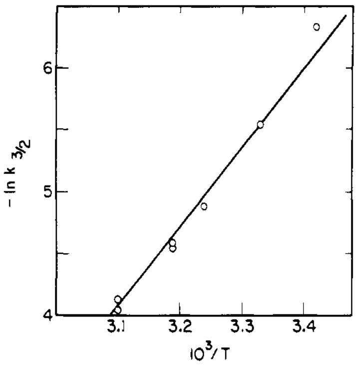

Figure 4. Ln $k_{3/2}$ vs. $1/T$ for the apparent second-order rate constant for reaction of $Mn(CO)_5(CH_3CN)^+$ with NC_5H_5 in CH_3NO_2. E_a = 83.7 kJ mol^{-1}, ln A = 27.4.

Table I. Apparent $^3/_2$-Order Rate Constant, $k_{3/2}$, Derived from Variation in k_{obsd} with $[Base]^{1/2}$ for Reaction with $Mn(CO)_5(CH_3CN^+)$ in CH_3NO_2 at 31.8 °C

base	pK_a[31]	$k_{3/2}$, $M^{-1/2}$ s^{-1}
pyridine	5.22	1.3×10^{-2}
4-methylpyridine	6.02	2.0×10^{-2}
2-methylpyridine	5.94	2.0×10^{-2}
N-benzylimidazole	6.9[a]	2.0×10^{-2}

[a] Estimated, based on values of 7.3 for N-ethylimidazole and 7.1 for N-methylimidazole.

The reaction with pyridine was studied as a function of temperature. A graph of ln $k_{3/2}$ vs. $1/T$ is shown in Figure 4. The $\Delta H^\ddagger$ value derived from these data is 81.2 kJ mol^{-1} with $\Delta S^\ddagger$ = −26 J/(K·mol). The temperature dependence of $k_{3/2}$ includes factors that affect the proton transfer preequilibrium, as well as the rate-determing step.

Attack of $CH_2NO_2^-$ on $[Mn(CO)_5(CH_3CN]BF_4$ results in formation of a new ligand, which we term the "adduct ligand", $-C(O)ON(O)CH_2^- \equiv Z$. The intermediate containing Z as ligand is not observed in the course of the reaction; thus it must react nearly as rapidly as it is formed. The reaction generates CO_2 and

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a Mn(I) compound, observed as products. We expect that Z should be a strongly cis-labilizing ligand, as observed, for example, for $CH_3C(O)$ bound to Mn.[2,35]

Equations 4–9, which describe the successive ligand loss and ligand recombination processes which lead eventually to the product, are not observable in detail. Since significant concentrations of intermediate species are not observed, the steady-state concentrations of all these intermediates must be quite low. Such low concentrations are consistent with the idea that ligand loss processes are promoted by the presence of cis-labilizing ligands such as Z or NC_5H_5. Once 2 mol of pyridine have been incorporated into the manganese carbonyl species, forming $Mn(CO)_3(NC_5H_5)_2Z$, it must break down to form CO_2 and CH_2NO^-, leaving a coordinatively unsaturated $Mn(CO)_3(NC_5H_5)_2^+$ which rapidly reacts with NC_5H_5 or, to a minor extent, CH_3CN. It is to be noted that the metal is not reduced in this step, as it is in formation of CO_2 following OH^- attack (vide infra). The buildup of electron density on the metal center as a result of pyridine substitution would be expected to facilitate the breakup of Z, as indicated in eq 8.

As an alternative to the mechanism outlined in Scheme I, attack of $CH_2NO_2^-$ at CO could result in a fast preequilibrium preceding loss of ligand from the adduct–ligand complex. If we assume that both eq 2 and 3 are rapid preequilibria, then

$$-d[Mn(CO)_5(CH_3CN)^+]/dt = k_4[Mn(CO)_4(CH_3CN)Z] = k_3KK'([CH_3NO_2][NC_5H_5]/[HNC_5H_5^+])[Mn(CO)_5(CH_3CN)^+] \quad (14)$$

where K and K' are the equilibrium constants for eq 2 and 3, respectively. This rate law is experimentally indistinguishable from eq 12. Further insight into the nature of the rate-determining step is obtained from the observation that $Mn(CO)_5(NC_5H_5)^+$ reacts with pyridine in nitromethane under the same reaction conditions to afford the same product. A graph of the observed pseudo-first-order rate constants as a function of $[NC_5H_5]^{1/2}$ is shown in Figure 3. The observed $k_{3/2}$ from these data is 4.7×10^{-3} $M^{-1/2}$ s^{-1}, about half the value observed for the reaction of $[Mn(CO)_5CH_3CN]BF_4$ (Table I). The reaction scheme for reaction of $[Mn(CO)_5(NC_5H_5)]BF_4$ with pyridine becomes equal to that for reaction of $[Mn(CO)_5CH_3CN]BF_4$ following eq 5. If attack of $CH_2NO_2^-$ on $Mn(CO)_5(NC_5H_5)^+$ were rapid, the concentration of *cis*-$Mn(CO)_4(NC_5H_5)Z$ in the early stages of the reaction would be relatively large, and one would expect that the overall reaction rate for $Mn(CO)_5(NC_5H_5)^+$ would be much greater than that for $[Mn(CO)_5CH_3CN]BF_4$. This is not observed to be the case. The observations are best accounted for by the supposition that initial attack of $CH_2NO_2^-$ on the cation, the forward reaction in eq 3, is rate determining in the reactions of both $Mn(CO)_5(CH_3CN)^+$ and $Mn(CO)_5(NC_5H_5)^+$. These reactants are present initially in comparable concentrations, and are likely to be of comparable electrophilicity toward the attacking anion. The energy-factored CO stretching force constants for $Mn(CO)_5(CH_3CN)^+$ are 17.83 and 17.05 mdyn/Å for the cis and trans CO groups, respectively.[16] The corresponding quantities for $Mn(CO)_5(NC_5H_5)^+$ are 17.67 and 16.97 mdyn/Å, respectively.[16] These values suggest that the radial CO groups of $Mn(CO)_5(NC_5H_5)^+$ may be slightly less electrophilic than those of $Mn(CO)_5(CH_3CN)^+$, consistent with the observation that the overall reaction rate for $Mn(CO)_5(NC_5H_5)^+$ is somewhat slower than that for $Mn(CO)_5(CH_3CN)^+$. However, the overall reaction rates are comparable, as expected if the rate-determining step is initial attack of $CH_2NO_2^-$, as indicated above.

Reactions in Acetonitrile. Acetonitrile is much less susceptible to deprotonation than CH_3NO_2; in Me_2SO pK_a for CH_3CN = 31.3, for CH_3NO_2 = 17.2.[36] Thus the mode of reaction observed for reaction of $Mn(CO)_5CH_3CN^+$ with pyridine in nitromethane is not expected for reaction in acetonitrile. Nevertheless, as described below, reaction of $Mn(CO)_5CH_3CN^+$ with pyridine in acetonitrile is relatively rapid.

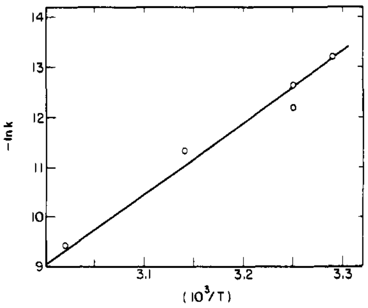

Figure 5. Ln k vs. $1/T$ for reaction of $Mn(CO)_5(CH_3CN)^+$ with solvent in CD_3CN. E_a = 119 ± 15 kJ mol^{-1}, ln A = 33.9.

As a means of assessing the rates of dissociative loss of CH_3CN or CO from $Mn(CO)_5CH_3CN^+$, the kinetics of reactions 15–17 in acetonitrile were studied. Reactions 15 and 17 were followed by observing changes in IR absorbances; reaction 16 was followed by observing changes in ^1H NMR signal intensities. The observed pseudo-first-order rate constants at 35 °C for these reactions are as follows: $k_{15} = 2.7 \pm 0.3 \times 10^{-6}$; $k_{16} = 4.2 \pm 1.0 \times 10^{-6}$; $k_{17} = 1.2 \pm 0.2 \times 10^{-6}$ s^{-1}.

$$Mn(CO)_5CH_3CN^+ + PPh_3 \xrightarrow{k_{15}} Mn(Co)_5PPh_3^+ + \text{other products} \quad (15)$$

$$Mn(CO)_5CH_3CN^+ + CD_3CN \xrightarrow{k_{16}} Mn(CO)_5CD_3CN^+ + Mn(CO)_3(CD_3CN)_3^+ \quad (16)$$

$$Mn(CO)_5CH_3CN^+ + 2CH_3CN \xrightarrow{k_{17}} Mn(CO)_3(CH_3CN)_3^+ + 2CO \quad (17)$$

Reaction 17 is a measure of the rate of CO loss. The likely mechanism is described in eq 18–21, in which reaction 18 is the slow, rate-determining step:

$$Mn(CO)_5CH_3CN^+ \rightarrow Mn(CO)_4CH_3CN^+ + CO \quad (18)$$

$$Mn(CO)_4CH_3CN^+ + CH_3CN \rightarrow Mn(CO)_4(CH_3CN)_2^+ \quad (19)$$

$$Mn(CO)_4(CH_3CN)_2^+ \rightarrow Mn(CO)_3(CH_3CN)_2^+ + CO \quad (20)$$

$$Mn(CO)_3(CH_3CN)_2^+ + CH_3CN \rightarrow Mn(CO)_3(CH_3CN)_3^+ \quad (21)$$

Reaction 20 should be faster than (18) because of the additional cis-labilizing effect of the second CH_3CN ligand.[2,3,37]

The kinetics of reaction 16 were observed as a function of temperature in the range from 30 to 58 °C. From the resulting Arrhenius plot, Figure 5, values of $\Delta H^{\ddagger}$ = 116 ± 15 kJ K^{-1} mol^{-1}, with $\Delta S^{\ddagger}$ = 23 ± 40 J K^{-1}, can be calculated.

Reactions 15 and 16 are alike in that in both cases the rate of disappearance of $Mn(CO)_5CH_3CN^+$ is determined by the combined rate of dissociative loss of CO or CH_3CN. Reaction 16 was of necessity followed using NMR rather than IR. As a result the concentration ranges employed in the two reactions are different. For this reason, and because the precision with which the reaction rate could be determined based on the NMR spectra is not very good, the agreement in rate constants between reactions 15 and 16 is reasonably good. By comparing the rate constants for reactions 15 and 16 with that for reaction 17, one can conclude that dissociative loss of CO from $Mn(CO)_5CH_3CN^+$ is slower than dissociative loss of CH_3CN, as expected.

As a basis for evaluating the labilizing effect of CH_3CN as ligand, we have attempted to study the substitution reactions of $Mn(CO)_6^+$. We chose to employ acetic anhydride as solvent, because that had been the solvent used in an earlier study of the substitution lability of this cation.[38] Attempts to study the

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substitution in acetonitrile or nitromethane were frustrated by the presence of traces of water. Even though the water levels are very low, reaction of $Mn(CO)_6^+$ with water occurs more rapidly than reaction with PPh_3. In acetic anhydride reaction with PPh_3 leads predominantly to $Mn(CO)_5PPh_3^+$ as product, although even in this case minor amounts of other species are seen. The disappearance of $Mn(CO)_6^+$ in acetic anhydride solvent at 35 °C in the presence of excess PPh_3 followed first-order kinetics, $k = 5.2 \pm 0.6 \times 10^{-7}$ s^{-1}. This figure represents an upper limit for the rate of unassisted dissociative loss of CO from $Mn(CO)_6^+$, assuming that there is no catalysis of CO loss by solvent or some nucleophilic impurity. It is interesting that CO loss from $Mn(CO)_6^+$ is only about a factor of 2 slower than CO loss from $Mn(CO)_5CH_3CN^+$. Thus, in this instance, in which CH_3CN is bound to a rather highly charged metal center, and competing with only strongly π acceptor CO ligands, it does not behave as a significant cis-labilizing ligand. However, this conclusion must be accepted with reservation because we cannot be sure that the correct rate constant for dissociative loss from $Mn(CO)_6^+$ has been measured.

In the reactions of $Mn(CO)_5(CH_3CN)^+$ in acetonitrile, labilization of the complex through nucleophilic attack at coordinated CO by solvent may contribute to an enhanced reaction rate. However, because acetonitrile is not strongly nucleophilic, the effect is not expected to be large. By contrast, the reaction of $Mn(CO)_5CH_3CN^+$ with pyridine in acetonitrile is substantially faster than the rates of the three reactions described above. Reaction proceeds smoothly in dry solvent to produce $Mn(CO)_5NC_5H_5^+$. The reaction rate is strongly dependent upon pyridine concentration (vide infra). At a pyridine concentration of 7.6×10^{-3} M, the reaction is about 100 times faster than under the same conditions with PPh_3 as ligand. It is noteworthy that the major product in the reaction is $Mn(CO)_5NC_5H_5^+$. Only traces of $Mn(CO)_3(NC_5H_5)_2(CH_3CN)^+$ and $Mn(CO)_3(NC_5H_5)_3^+$ are noted in the reaction products. The much faster rate of reaction of $Mn(CO)_5CH_3CN^+$ with pyridine, and the observed reaction product, can be accounted for in terms of a nucleophilic attack of pyridine at the carbon of a CO group cis to the coordinated acetonitrile. Such an interaction, as described earlier, produces a transient intermediate in which a CO group modified by the interaction with pyridine has become a strongly cis-labilizing ligand. The result is a more rapid loss of CH_3CN, followed by rapid uptake of pyridine. The pyridine which assumes the coordination position vacated may be that which is loosely bound to the carbonyl, or another pyridine molecule from the solvent. The reaction mechanism follows:

$$Mn(CO)_5CH_3CN^+ + NC_5H_5 \overset{K}{\rightleftharpoons} Mn(CO)_4(CH_3CN)Z'^+ \tag{22}$$

$$Mn(CO)_4(CH_3CN)Z'^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Mn(CO)_4Z'^+ + CH_3CN \tag{23}$$

$$Mn(CO)_4Z'^+ + NC_5H_5 \xrightarrow{k_2} Mn(CO)_4(NC_5H_5)Z'^+ \tag{24}$$

$$Mn(CO)_4(NC_5H_5)Z'^+ \rightarrow Mn(CO)_5NC_5H_5^+ + NC_5H_5 \tag{25}$$

$$Z' = C(O)NC_5H_5$$

The rate law for the mechanism outlined above, assuming a steady-state approximation for the concentration of $Mn(CO)_4Z'^+$, is as follows:

$$-d[Mn(CO)_5CH_3CN^+]/dt = \left(\frac{k_2k_1[NC_5H_5]^2}{k_2[NC_5H_5] + k_{-1}[CH_3CN]}\right)[Mn(CO)_5CH_3CN^+] \tag{26}$$

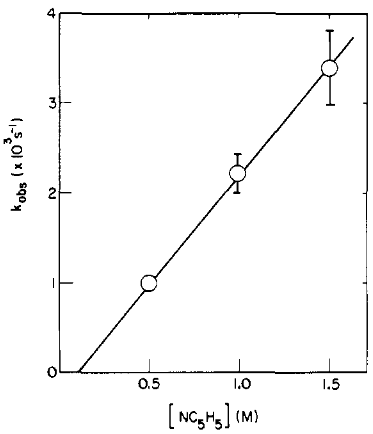

Figure 6. Variation in pseudo-first-order rate constant for reaction of NC_5H_5 with $Mn(CO)_5CH_3CN^+$ in CH_3CN solvent at 35 °C. Each datum represents the average of several kinetics runs at that ligand concentration.

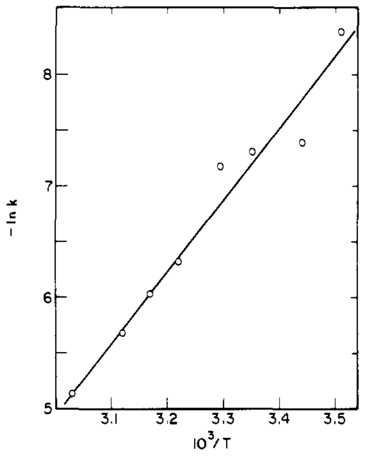

Figure 7. Ln k vs. $1/T$ for reaction of $Mn(CO)_5(CH_3CN)^+$ with NC_5H_5 in CH_3CN. $E_a = 53 \pm 3$ kJ mol^{-1}; ln A = 14.1.

The mechanism predicts a first-order dependence of the rate on $Mn(CO)_5CH_3CN^+$; the order in pyridine depends on the relative rates of recombination of the five-coordinate intermediate, $Mn(CO)_4Z'^+$ with solvent acetonitrile as compared with pyridine. In the limiting case that recombination with solvent molecules is relatively rapid the reaction should be second order in pyridine. In the alternative limiting case, when recombination of $Mn(CO)_4Z'^+$ with pyridine is relatively more rapid, the reaction is expected to be first order in pyridine. Figure 6 shows the variation in k_{obsd} with pyridine concentration. The reproducibility in these kinetic studies was unfortunately not very good, because of the need to follow the reaction by observation of a high-frequency A_1 carbonyl stretching mode at 2160 cm^{-1}, a band of low molar absorptivity. However, the data are best accommodated by the assumed first-order dependence, as shown. The second-order rate constant obtained from this graph for reaction of $Mn(CO)_5CH_3CN^+$ with pyridine at 35 °C in CH_3CN is 2.6×10^{-3} M^{-1} s^{-1}.[36]

The five-coordinate intermediate, $Mn(CO)_4Z'^+$, should be a reasonably strong electrophile, with correspondingly low selectivity toward recombination with CH_3CN or NC_5H_5.[40] The kinetics results thus strongly suggest that reaction proceeds predominantly via transfer of the bound pyridine to occupy the vacant coordination position:

$$Mn(CO)_4Z'^+ \rightarrow Mn(CO)_5NC_5H_5^+ \tag{27}$$

With this modification the rate expression for the proposed mechanism should be first order each in pyridine and Mn-

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(39) Reactions of $Mn(CO)_5(CH_3CN)^+$ with a few substituted pyridine bases in acetonitrile at 35 °C were also studied. Unfortunately, the reproducibility of the kinetic data was not very good, because of experimental limitations in the data acquisition. Nevertheless, it was possible to discern that the reactions with 4-picoline or 4-*tert*-butylpyridine are faster than the reactions with pyridine itself, as expected on the basis of inductive effects.

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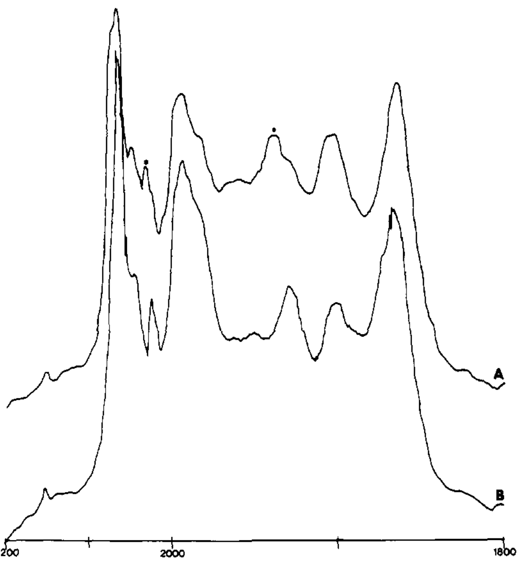

Figure 8. IR spectrum of reaction medium near completion of reaction of $[Mn(CO)_5CH_3CN]BF_4$ with pyridine in wet acetonitrile, A, as compared with a simulated spectrum, B. The simulated spectrum is obtained by computer addition of the IR spectra of the following components in approximate relative amounts indicated in parentheses: $Mn(CO)_5NC_5H_5^+$ (1); $Mn(CO)_3(CH_3CN)(NC_5H_5)_2^+$ (0.2); $Mn(CO)_5(CH_3CN)^+$ (0.2); $Mn_2(CO)_9CH_3CH$ (0.07); $Mn(CO)_5^-$ (0.03). An absorption due to excess pyridine is also corrected for. The asterisks on spectrum A denote unassigned bands.

$(CO)_5CH_3CN^+$. Migration of the nucleophile bound to coordinated CO to fill the vacant coordination position has been postulated also in other related studies.[18]

Using a pyridine concentration of 1.00 M, reaction with 0.1 M $Mn(CO)_5(CH_3CN)^+$ was studied as a function of temperature. The Arrhenius plot for the observed pseudo-first-order rate constant is shown in Figure 7. From these results we obtain $\Delta H^{\ddagger} = 50.5 \pm 3$ kJ mol^{-1}, $\Delta S^{\ddagger} = -136 \pm 4$ J K^{-1}. The rate-determining step in the mechanism is presumed to be dissociation of CH_3CN from the adduct ligand complex, eq 23. The values for $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ reflect the activation enthalpy for this process as well as for the preequilibrium, eq 22.

It is noteworthy that the activation enthalpy is much less than for unassisted loss of ligand from $Mn(CO)_5(CH_3CN)^+$, as measured by $\Delta H^{\ddagger}$ for reaction 16. On the other hand, the much more negative value for $\Delta S^{\ddagger}$ is consistent with the preequilibrium requirement, eq 22.

Effects of Water on the Reaction in Acetonitrile. The possibility exists that water in the solvent, or introduced along with pyridine, reacts with pyridine to produce hydroxide ion which can attack coordinated CO. Such a preequilibrium

$$H_2O + NC_5H_5 \rightleftarrows OH^- + HNC_5H_5^+ \tag{28}$$

would result in an inverse dependence of the reaction rate on $[HNC_5H_5^+]$. However, addition of $HNC_5H_5BF_4$ (0.14 M) to the reaction medium does not inhibit the reaction. We may thus conclude that water is not involved in the pyridine reaction in those cases in which efforts were made to exclude water from the reaction medium.

The course of the reaction of $Mn(CO)_5CH_3CN^+$ with pyridine in acetonitrile is altered upon addition of water. The major products present near completion of the reaction are $Mn(CO)_5NC_5H_5^+$, $Mn(CO)_3(NC_5H_5)_2(CH_3CN)^+$, $Mn_2(CO)_9CH_3CN$, and $Mn(CO)_5^-$. Substitution occurs rapidly in the initial stages of the reaction; both $Mn(CO)_5NC_5H_5^+$ and $Mn(CO)_3(NC_5H_5)_2(CH_3CN)^+$ grow in rapidly. However, their concentrations diminish as the reaction continues further.

Figure 8 shows the infrared spectrum of the reaction mixture near completion of the reaction (A), as compared with a simulated spectrum (B) obtained by computer addition of the digitized spectra of each of the components with approximate relative amounts as indicated in parentheses in the caption to the figure. From these results it appears that, as before, the major product in the reaction is the monosubstituted cation $Mn(CO)_5NC_5H_5^+$. However, a significant fraction of the reaction is diverted to products which can be associated with the presence of water. (Although the feature in the vicinity of 1860 cm^{-1}, due to $Mn(CO)_5^-$, is a dominant feature in the IR spectra of the reaction products, it should be kept in mind that the molar extinction coefficients for the CO stretching modes in anionic species are much greater than those of the neutral or cationic carbonyls.)

The presence of $Mn(CO)_5^-$ as a reaction product is not surprising.[23] This is probably formed via formation of the hydroxycarbonyl species via OH^- attack at a CO cis to the acetonitrile, followed by rapid CH_3CN loss. β-Hydride migration is facilitated by this ligand loss. The product of this step, $M(CO)_4H$, would rapidly incorporate any nucleophiles present to form the six-coordinate hydride. Nucleophiles present in highest abundance are CH_3CN and NC_5H_5. However, the hydride, once formed, would be subject to rapid deprotonation via reaction with pyridine. The resulting anions, $Mn(CO)_4CH_3CN^-$ or $Mn(CO)_4NC_5H_5^-$, would not be stable with respect to loss of the nitrogen ligand. They would thus be expected to rapidly convert to $Mn(CO)_5^-$ by rapid loss of the nitrogen ligand, followed by uptake of CO, or through intermolecular transfer of CO.

The amount of $Mn(CO)_5^-$ formed during reaction increases with the amount of water added. It appears that the concentration of $Mn(CO)_5^-$ builds up initially, but decreases in the latter stages of the reaction. Similarly, the concentrations of the cationic species, $Mn(CO)_5NC_5H_5^+$ and $Mn(CO)_3(NC_5H_5)_2(CH_3CN)^+$, initially increase rapidly but then diminish as the reaction continues. There is no concomitant increase in the absorbances due to the dinuclear species as reaction proceeds. The formation of dinuclear Mn(0) species during reaction can be accounted for in terms of an outer-sphere electron-transfer reaction involving the cationic and anionic species present. Thus, $Mn(CO)_5CH_3CN^+$ reacts rapidly with $Mn(CO)_5^-$ in dry acetonitrile to form $Mn_2(CO)_{10}$. The reaction is faster than the rates we have measured here for loss of CH_3CN from $Mn(CO)_5CH_3CN^+$, indicating that it probably involves an outer-sphere electron transfer. Reaction can be visualized as follows:

$$Mn(CO)_5^- + Mn(CO)_5CH_3CN^+ \rightarrow Mn(CO)_5\cdot + Mn(CO)_5CH_3CN\cdot \tag{29}$$

Since $Mn(CO)_5CH_3CN\cdot$ contains 19 electrons in the valence orbitals of the metal, it should rapidly lose CH_3CN to form $Mn(CO)_5\cdot$ which rapidly couples to form the observed product, or, in this reaction medium, goes on to other reactions. Variously substituted dinuclear manganese species might form, depending upon the ambient concentrations of ligands. All of the radicals formed through the outer-sphere electron-transfer reactions are expected to be quite labile relative to their expected lifetimes with respect to recombination reaction.

Small quantities of paramagnetic species are also formed in the course of the reaction. The EPR spectrum of the reaction mixture in frozen acetonitrile at 77 K is very similar to that of a material precipitated from a solution of $Mn(BF_4)_2$ in acetonitrile by addition of pyridine. Both EPR spectra show nitrogen as well as manganese hyperfine. It is not clear how a Mn(II) species might arise. It may simply be due to traces of impurities; on the other hand, on outer-sphere electron transfer from an electron-rich species such as $Mn(CO)_3(NC_5H_5)_2(CH_3CN)^+$ to $Mn(CO)_5\cdot$ is not out of the question.

Experimental Section

Materials. $Mn_2(CO)_{10}$ was obtained from Pressure Chemical and sublimed before use. Reagent-grade pyridine was used as supplied in syntheses. For kinetics experiments it was stirred for several hours over CaH_2, then distilled off CaH_2. The distillate was stored over activated 3 Å molecular sieves in a glovebox with continuously purified N_2 atmosphere. 2-Methyl- and 4-methylpyridine were similarly purified; 4-*tert*-butylpyridine (Aldrich) was dried over 3 Å molecular sieves before use. *N*-Benzylimidazole (Aldrich) was sublimed before use. Triphenylphosphine (PPh_3) was mixed with $LiAlH_4$ and the mixture fused. After 12 h in the molten state PPh_3 was distilled under vacuum and collected on a water-cooled cold finger.

All solvents employed were saturated with N_2 gas purge before use. Acetic anhydride was stirred over sodium wire for several days, then fractionally distilled. Nitromethane (Aldrich Spectro Grade) was thoroughly dried with 3 Å molecular sieves in the glovebox.[41] GC–mass spectral analysis revealed only small quantities of high nitroalkanes as impurities. Other nitroalkanes employed as solvents were also subjected only to drying with 3 Å molecular sieve. Acetonitrile (Mallinckrodt AR) was similarly dried over 3 Å molecular sieve in the glovebox before use.

Acetonitrilepentacarbonylmanganese(I) tetrafluoroborate, $[Mn(CO)_5(CH_3CN)]BF_4$, was prepared by dissolving $Mn_2(CO)_{10}$ (3.0 g, 7.7 mmol) in 100 mL of CH_3CN. $NOBF_4$ was added in small (ca. 0.1 g) amounts until the solution turned a pale yellow-green, and further additions produced no further gas evolution. (This usually required an excess of $NOBF_4$, ca. 4.0 g, 34 mmol.) The solution volume was reduced, and diethyl ether added. The precipitate that formed was filtered under nitrogen and vacuum dried. This material was normally recrystallized several times in the glovebox, using an acetone–diethyl ether mixture.

Pentacarbonylpyridinemanganese(I) tetrafluoroborate, $[Mn(CO)_5(NC_5H_5)]BF_4$, was prepared by a literature method.[16] **Pentacarbonylhydridomanganese(I),** $HMn(CO)_5$, was prepared by acidification of $Mn(CO)_5^-$.[42]

Acetonitrilenonacarbonyldimanganese, $Mn_2(CO)_9(CH_3CN)$, was prepared via a reported method.[43]

Tricarbonyltripyridinemanganese(I) tetrafluoroborate, $[Mn(CO)_3(NC_5H_5)_3]BF_4$, was prepared by a literature method. Reaction of this substance with CH_3CN in acetonitrile solvent led to formation of $Mn(CO)_3(NC_5H_5)_2(CH_3CN)^+$ ion, identified by its IR spectrum in the CO stretching region.[16]

Hexacarbonylmanganese(I) tetrafluoroborate, $[Mn(CO)_6]BF_4$, was prepared as described elsewhere.[44] It was recrystallized as described above for $[Mn(CO)_5(CH_3CN)]BF_4$. The IR spectrum of this product in CH_3CN solution revealed a single band at 2090 cm^{-1}.

^{18}O-Enriched nitromethane, $CH_3N^{18}O_2$, was prepared by modification of a literature procedure.[45] To prepare needed ^{18}O-enriched $NaNO_2$, 1.5 g of $NaNO_2$ was dissolved in 2 mL of 50% isotopic enrichment $H_2{}^{18}O$ (Norsk Hydro). Concentrated HCl was added to adjust pH to 4–5. The mixture was allowed to stand for several hours to effect complete isotopic mixing between solute and solvent.[46] About 4 mL of concentrated HCl was then added and the resultant solution added to 2.5 g of $Na(ClCH_2CO_2)$ in 2 mL of water, in a 10-mL round-bottom flask to which a short-path distillation apparatus was attached. The mixture was warmed with heated air to initiate reaction and to distill over the CH_3NO_2 as it formed. The distillation was carried out in stages with separation of the water layer and use of excess NaCl to effect more complete separation. The wet CH_3NO_2 recovered was dried over 3 Å molecular sieve.

Kinetics Experiments. Reactions of $Mn(CO)_5(CH_3CN)^+$ with CH_3CN or PPh_3 in CH_3CN were carried out in sealed, jacketed flasks maintained at constant temperature by circulation of ethylene glycol solution from a constant-temperature bath. Samples for IR analysis were withdrawn using Hamilton gas-tight syringes. Reaction of $Mn(CO)_5(CH_3CN)^+$ with CD_3CN was monitored using a Varian EM-390 NMR spectrometer. Dried, purified CD_3CN, with C_6H_6 as internal standard, was used as solvent. The NMR tubes were sealed off on a vacuum line and kept continuously cold until reaction was initiated by immersing the tubes in a constant-temperature bath. They were withdrawn at intervals of 8–12 h for observation of NMR spectra. The integrals of the ^1H signals due to $Mn(CO)_5(CH_3CN)^+$ and the C_6H_6 internal standard were employed to assess progress of the reaction.

Faster reactions were monitored in the IR using a simple stopped-flow device similar to that described earlier.[47] For reactions carried out in CH_3NO_2 solvent the concentration of $Mn(CO)_5(CH_3CN)^+$ was typically 0.005 M. The disappearance of the carbonyl stretching bond at 2073 cm^{-1} due to $Mn(CO)_5(CH_3CN)^+$ served as a convenient monitor of the progress of reaction. However, reaction of $Mn(CO)_5(CH_3CN)^+$ with NC_5H_5 in CH_3CN as solvent leads to $Mn(CO)_5(NC_5H_5)^+$ as product. This substance exhibits an E mode CO stretch essentially coincident with the analogous 2073-cm^{-1} band due to reactant. Hence it was necessary to monitor the much less intense A_1 mode due to reactant at 2160 cm^{-1}.

A study of ^{13}CO exchange with $Mn(CO)_5CH_3CN^+$ or $Mn(CO)_5(NC_5H_5)^+$ in $C_6H_5NO_2$ was carried out using techniques described elsewhere.[48]

All IR spectral work was carried out using a Beckman Model 4240, outfitted with a homemade ADC for transcription of spectra or absorbance vs. time data to magnetic cassette tape. The tapes were read into a DEC PDP-11/10 minicomputer for workup of the kinetics data.

GC and GC–Mass Spectrometric Results. Reaction products of $Mn(CO)_5(CH_3CN)^+$ reaction with NC_5H_5 were analyzed using an F and M instrument with thermal conductivity detector. A column 2 m in length, 1/4-in. o.d. copper tubing packed with Porapak Q, was employed for analysis for CO and CO_2. The ^{18}O content of the CO_2 produced in the reaction of $Mn(CO)_5(CH_3CN)^+$ with NC_5H_5 in labeled CH_3NO_2 was determined in a GC–mass spectrometer experiment using a 3-m glass column with Porapak Q on a Varian MAT 311A GC–MS system. Comparison of the relative intensities of the mass 63 and 61 peaks showed that the CH_3NO_2 contained 42% $CH_3N^{16}O^{18}O$. The relative intensities of the mass 44 and 46 peaks corresponded to 19% $C^{16}O^{18}O$. Thus, the ^{18}O content of the product gas is about 0.5 that of solvent, as expected for the mechanism proposed.

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