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A MECHANISTIC INVESTIGATION OF THE DECACARBONYLDIMANGANESE-CATALYZED CARBONYLATION OF AMINES

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Summary

The $Mn_2(CO)_{10}$-catalyzed reactions of n-butylamine and cyclohexylamine with CO to give the corresponding ureas have been examined under a variety of conditions of temperature, CO pressure, reaction time, solvent and potential co-catalysts. With the diamines, ethylenediamine and 1,4-diaminobutane, there was no catalyzed reaction with CO. On the other hand, 1,3-diaminopropane gave 1,4,5,6-tetrahydropyrimidine, and 1,6-diaminohexane yielded a polyurea. In an effort to elucidate the mechanism of these reactions, several stoichiometric reactions were carried out. The reaction of $Mn_2(CO)_{10}$ with primary aliphatic amines proceeds to give a carbamoyl complex as follows:

$$Mn_2(CO)_{10} + 3\ RNH_2 \rightleftharpoons \textit{cis}\text{-}Mn(CO)_4(NH_2R)(CONHR) + RNH_3^+ + Mn(CO)_5^-$$

Under CO pressure the isolated carbamoyl complex reacted to give the urea as follows:

$$\textit{cis}\text{-}Mn(CO)_4(NH_2R)(CONHR) + CO \rightarrow (RNH)_2C{=}O + HMn(CO)_5$$

The mechanism of this latter reaction is proposed to involve the intermediate formation of the organic isocyanate RNCO. These reactions are discussed as part of an overall mechanism for the $Mn_2(CO)_{10}$-catalyzed formation of ureas. The mechanism successfully accounts for factors which affect the yields of the reaction. Other metal carbonyl complexes, $Re_2(CO)_{10}$, $(\eta\text{-}CH_3C_5H_4)Mn(CO)_3$ and $[\eta\text{-}C_5H_5Cr(CO)_3]_2$, did not catalyze the reactions.

Introduction

A variety of metal complexes are known [1,2] to catalyze the reactions of CO with organic amines. Depending upon the conditions, the products of these reactions may be formamides (HCONHR), oxamides (RHNOC—CONHR), or ureas ($(RNH)_2C{=}O$). Although partial mechanisms have been postulated for these reactions, very little evidence is available to support them [2]. Therefore, we have undertaken a mechanistic investigation of a catalytic reaction first described by Calderazzo [3]. He noted that $Mn_2(CO)_{10}$ catalyzes the reaction of CO with primary aliphatic amines to yield 1,3-dialkylureas (eq. 1).

$$2\,RNH_2 + CO \xrightarrow{Mn_2(CO)_{10}} RNH{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}NHR + H_2 \qquad (1)$$

Although some mechanistic possibilities were proposed, further study was necessary. In the present paper, we report studies which account for a large number of features of this reaction.

Experimental

General. Decacarbonyldimanganese was used as obtained from Pressure Chemical Co. The *cis*-$Mn(CO)_4(NH_2R)(CONHR)$ complexes [4], $HMn(CO)_5$ [5], $Mn(CO)_5^-$ [5], $Mn(CO)_5Br$ [6] and $[C_5H_5Cr(CO)_3]_2$ [7] were prepared according to literature procedures. Amines were distilled from KOH before use. Tetrahydrofuran (THF) was distilled from $LiAlH_4$; other reagent grade solvents were used without further purification. All operations were performed under atmospheres of CO or prepurified N_2.

Catalytic reactions. These were carried out in a manner similar to that used by Calderazzo [3]. A 300 ml stainless steel bomb was charged with the amine, solvent catalyst, and a magnetic stirring bar. The bomb was flushed by bubbling N_2 through the reaction solution. The bomb was then closed and charged with CO which had been purified by passing it through a stainless steel trap at −95° C (toluene N_2 slush) under tank pressure to remove any $Fe(CO)_5$ present. The pressure conditions given in the Tables refer to the room temperature CO pressures before the bomb temperature was increased. The bomb was heated in an oil bath with magnetic stirring to the reaction temperatures listed in the Tables. After the desired reaction times, the bomb was allowed to cool to room temperature, and the pressure was released. Dicyclohexylurea was collected by filtration of the reaction solution; other dialkylureas were isolated by concentrating the reaction solutions and cooling to −20° C, followed by filtration. The products were washed well with hexane and dried in a vacuum. They were identified by their melting points [3] and infrared spectra. Other products of the reactions were obtained by fractionally distilling the filtrate.

Kinetic studies

Thermostatted reactions between $Mn_2(CO)_{10}$ (5×10^{-3} *M*) and large excesses of n-$BuNH_2$ in benzene solvent were performed in foil-wrapped 25 ml volumetric flasks loaded under N_2 and capped with rubber septum stoppers. The absorbance of the 2045 cm^{-1} IR band of $Mn_2(CO)_{10}$ was periodically measured on samples withdrawn by syringe. Plots of $\ln(A - A_\infty)$ vs. time were linear with slopes of k_{obsd}.

Results and discussion

Yields of the catalytic reactions under various conditions. Reactions of CO with primary aliphatic amines catalyzed by $Mn_2(CO)_{10}$ were carried out accord-

TABLE 1. REACTIONS WITH VARIOUS PRIMARY AMINES[a]

Amine	CO Pressure (atm)	Urea Yield (%)
Cyclohexylamine, 27.5g	96.6	72
n-Butylamine, 22.2g	91.1	56
Benzylamine, 24.5g	81.6	82

[a] 0.65g $Mn_2(CO)_{10}$, 20-22 h, 195°C in 25-30 ml hexane solvent.

ing to eq. 1 using a variety of conditions. Yields of the ureas (based on the amount of amine used) obtained under these conditions are given in Tables 1—5.

Cyclohexyl-, n-butyl-, and benzyl-amines all give good yields of their ureas under conditions given in Table 1. The yields increase with increasing temperature (Table 2) and CO pressure (Table 3) as illustrated for cyclohexylamine. Table 4 shows that the reaction of cyclohexylamine does not give more urea product even if the reaction is allowed to continue beyond 12 h when the reaction is run at 195—200° C, 0.65 g $Mn_2(CO)_{10}$, and 47.6 or 95.2 atm CO pressure. This result suggests that the reaction has reached equilibrium within 12 h under these conditions. The catalyst has not been inactivated, however, since the urea product may be filtered from the reaction mixture and the catalytic solution be used to catalyze a second and even a third reaction of amine and CO.

The yields are only slightly dependent on whether the solvent is benzene, THF, or cyclohexane (Table 5); they are lower when the reacting cyclohexylamine is also used as the solvent.

In Table 6 are shown the results of studies with several different metal carbonyl catalysts. In addition to $Mn_2(CO)_{10}$, $HMn(CO)_5$ is also very active and presumably catalyzes the reaction by the same mechanism (to be discussed later). On the other hand, the methylcyclopentadienyl complex, $(CH_3C_5H_4)Mn(CO)_3$, is apparently too inert to be converted to a catalytic form. The analogous $Re_2(CO)_{10}$ and also $[C_5H_5Cr(CO)_3]_2$ are not active.

TABLE 2. EFFECT OF TEMPERATURE ON THE CYCLOHEXYLAMINE REACTION[a]

Temperature (°C)	CO Pressure (atm)	Urea Yield (%)
195	96.6	72
165	88.4	28

[a] 27.5g cyclohexylamine, 0.65g $Mn_2(CO)_{10}$, 30 ml hexane solvent for 21-22 h.

TABLE 3. EFFECT OF CO PRESSURE ON THE CYCLOHEXYLAMINE REACTION[a]

CO Pressure (atm)	Urea Yield (%)
37.8	38
47.6	53
95.2	81

[a] 21.8g cyclohexylamine, 0.65g $Mn_2(CO)_{10}$, 25 ml benzene solvent, 200° for 12 h.

TABLE 4. EFFECT OF TIME ON THE CYCLOHEXYLAMINE REACTION[a]

TIME (h)	CO Pressure (atm)	Urea Yield (%)
12[b]	47.6	53
24[b]	47.6	56
12[c]	95.2	72
24[c]	95.2	72

[a] 21.8g cyclohexylamine, 0.65g $Mn_2(CO)_{10}$, 195-200°.

[b] 25 ml benzene solvent.

[c] 25 ml hexane solvent.

TABLE 5. EFFECT OF SOLVENT ON THE CYCLOHEXYLAMINE REACTION[a]

Solvent (25 ml)	Urea Yield (%)
Benzene	53
Tetrahydrofuran	48
Cyclohexane	47
———	23

[a] 21.8g cyclohexylamine, 0.65g $Mn_2(CO)_{10}$, 47.6 atm CO, 195-200°, 12 h.

TABLE 6. EFFECT OF VARIOUS METAL COMPLEX CATALYSTS ON THE CARBONYLATION REACTION[a]

Amine	Complex	Urea Yield (%)
CyNH$_2$, 27.5g	Mn$_2$(CO)$_{10}$, 0.65g	72
n-BuNH$_2$, 55.5g	HMn(CO)$_5$, ~1.5g	58
CyNH$_2$, 21.8g	Re$_2$(CO)$_{10}$, 0.40g	--
CyNH$_2$, 21.8g	(CH$_3$C$_5$H$_4$)Mn(CO)$_3$, 0.50g	--
CyNH$_2$, 24.5g	[C$_5$H$_5$Cr(CO)$_3$]$_2$, 0.25g	--

[a] 95.2 - 96.6 atm CO, 180-200° in hydrocarbon solvent, 22-24 h.

Listed in Table 7 are some reactions which were performed in the presence of various added compounds. It was reported previously that secondary amines are not carbonylated using the Mn$_2$(CO)$_{10}$ catalyst [3]. We find now that the carbonylation of primary amines is actually inhibited by added diethylamine,

TABLE 7. EFFECT OF ADDED COMPOUNDS ON THE Mn$_2$(CO)$_{10}$-CATALYZED CARBONYLATION OF PRIMARY AMINES[a]

Amine	Compounds Added	Urea Yield (%)
CyNH$_2$, 8.7g[b]	Et$_2$NH, 7.1g	--
i-PrNH$_2$, 10.4g[b]	Et$_2$NH, 10.6g	--
CyNH$_2$, 8.7g[b]	TMEDA,[c] 9.0g	13.5
CyNH$_2$, 27.5g[b]	H$_2$O, 1.0g	28
i-PrNH$_2$, 20.8g	EtOH, 15.7g	13
CyNH$_2$, 30.4g[b]	CH$_3$(CH$_2$)$_6$CO$_2$H, 4.0g	19
CyNH$_2$, 21.8g	Cyclohexene, 20.2g[d]	71
CyNH$_2$, 27.5g[b]	———	72

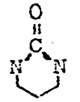
[a] Unless noted otherwise, reactions performed at 195-200° with 0.65g Mn$_2$(CO)$_{10}$ under an initial CO pressure of 95.2 - 96.6 atm for 20-24 h.

[b] 25-30 ml hexane solvent.

[c] N,N,N',N'-tetramethylethylenediamine.

[d] 80.2 atm CO.

TABLE 8. $Mn_2(CO)_{10}$ - CATALYZED CARBONYLATIONS OF DIAMINES[a]

Diamine	Products
$H_2N(CH_2)_2NH_2$	no reaction
$H_2N(CH_2)_3NH_2$	, 60%, , 6%
$Me_2N(CH_2)_3NH_2$	$Me_2N(CH_2)_3NH(O)CH$, 59%
$H_2N(CH_2)_4NH_2$	no reaction
$H_2N(CH_2)_6NH_2$	polyurea, 31%

[a] At 180-200°C in hexane, ~95 atm CO, 0.65g $Mn_2(CO)_{10}$, for 20 h.

and to a lesser extent by a tertiary diamine, *N,N,N′,N′*-tetramethylethylenediamine. Small quantities of H_2O and octanoic acid cause a lowering of the yield, and using ethanol as a solvent also reduces the yield of the 1,3-dialkylurea. Cyclohexene appears to act as an inert solvent, although it was hoped that the olefin might itself be a reactant. It had been shown by others [8] that $Mn_2(CO)_{10}$ catalyzes the reaction of CO and H_2 with cyclohexene under conditions similar to those used in the $Mn_2(CO)_{10}$-catalyzed amine carbonylation reactions. Other than the urea and small amounts of alkylformamide [3], no other products were detected in any of these reactions.

Several reactions of diamines with CO (~95 atm) at 180—200° C in hexane for 20 h in the presence of 0.65 g of $Mn_2(CO)_{10}$ were examined (Table 8). Surprisingly no reaction was observed with either ethylenediamine or 1,4-diaminobutane. With 1,6-diaminohexane an insoluble product was isolated whose IR spectrum indicated that it was a polyurea. In this diamine, the amino groups react as normal primary aliphatic amines.

With 1,3-diaminopropane, a low yield (6%) of the cyclic urea was obtained (Table 8). The major product (60%) was 1,4,5,6-tetrahydropyrimidine which appears to result from the formamide $H_2N(CH_2)_3NH(O)CH$ which is initially formed in the catalytic reaction. However, under the conditions of the reaction and on distillation during work-up, it is known [9] to lose H_2O to give the tetrahydropyrimidine product. It should be noted that tetrahydropyrimidine was also formed in the absence of $Mn_2(CO)_{10}$; however, there was an induction period of approximately 20 h which did not occur in the presence of $Mn_2(CO)_{10}$. Support for the initial formation of a formamide in the 1,3-diaminopropane reaction comes from the related reaction of $Me_2N(CH_2)_3NH_2$ which gives a 59% yield of the formamide $Me_2N(CH_2)_3NH(O)CH$ [10].

Except for 1,6-diaminohexane, the shorter-chain diamines do not give normal urea formation. The ability of these diamines to form 5-, 6- and 7-membered chelate rings is presumably responsible for the different products. It is not entirely clear, however, why different products (formamides) are generated in the 1,3-diaminopropane reactions.

Mechanism of catalysis. Reaction of $Mn_2(CO)_{10}$ *with* RNH_2

As a first step in exploring the mechanism of catalytic reaction (eq. 1) the reaction of $Mn_2(CO)_{10}$ with primary aliphatic amines was examined. It had previously been reported [11] that $Mn_2(CO)_{10}$ reacts immediately with neat n-butylamine at room temperature to give $[Mn(CO)_5(NH_2Bu)^+][Mn(CO)_5^-]$. The anion was precipitated as its $Ni(o\text{-phen})_3^{2+}$ salt, but the cation was not isolated. Since we had shown [4,12] earlier that other cations of the type $Mn(CO)_5(NH_2R)^+$ react immediately with amines to give the carbamoyl complexes *cis*-$Mn(CO)_4(NH_2R)(CONHR)$, it seemed unlikely that $Mn(CO)_5(NH_2Bu)^+$ would exist in the n-$BuNH_2$ solution. Repeating this reaction, we find that it proceeds instantaneously and quantitatively as follows:

$$Mn_2(CO)_{10} + 3\,n\text{-}BuNH_2 \rightleftharpoons cis\text{-}Mn(CO)_4(NH_2Bu)(CONHBu) + BuNH_3^+ + Mn(CO)_5^- \tag{2}$$

The infrared spectrum of the solution agrees with that reported originally [11]; however, the peaks clearly indicate that the products are *cis*-$Mn(CO)_4(NH_2Bu)(CONHBu)$ (2065w, 1971vs, 1921s cm^{-1}) and $Mn(CO)_5^-$ (2020w, 1904s, 1872 cm^{-1}) in butylamine solvent. There is no evidence for the cation [4], $[Mn(CO)_5(NH_2Bu)^+]$. Although evaporation of the butylamine reverses eq. 2 to leave $Mn_2(CO)_{10}$, the $Mn(CO)_5^-$ can be precipitated as $PPN[Mn(CO)_5]$ [13] by adding an aqueous solution of bis(triphenylphosphine)iminium chloride (PPN^+Cl^-) to the butylamine solution. Vacuum evaporation of the solvents from the filtrate yielded *cis*-$Mn(CO)_4(NH_2Bu)(CONHBu)$.

Although reaction 2 is very rapid in pure amine, dilution with a hydrocarbon solvent causes the rate to drop sharply. Kinetic studies of reaction 2 in benzene solvent (Table 9, Fig. 1) show that at 24.5 and 40.0° C the reaction follows the

TABLE 9. RATE CONSTANTS FOR THE REACTION OF $Mn_2(CO)_{10}$ WITH n-$BuNH_2$ IN BENZENE ACCORDING TO EQUATION 2

	[n-$BuNH_2$] (M)	$10^4 k_{obsd}$ (s^{-1})
24.5°	3.00	15.3
	2.97	16.3
	2.66	9.17
	2.33	4.32
	2.20	3.27
	2.09	2.60
	1.90	1.68
40.0°	3.14	17.4
	2.75	8.89
	2.47	5.19
	2.19	2.98

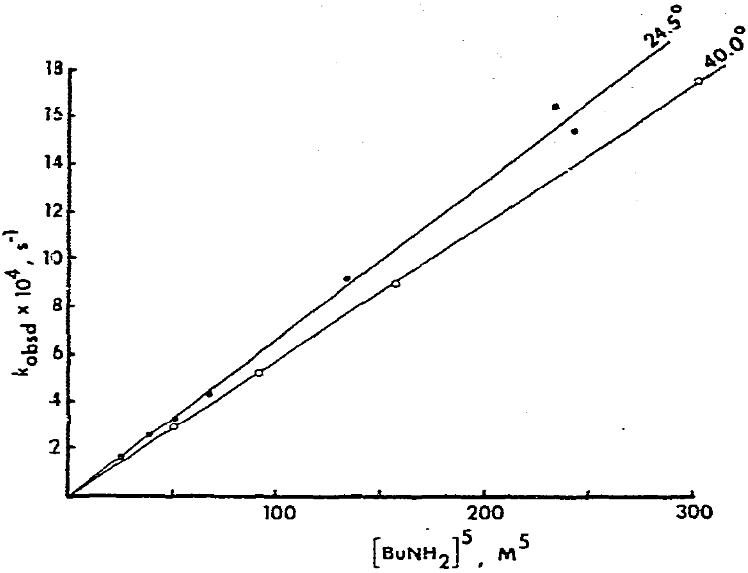


Fig. 1. Plot of k_{obsd} vs. $[n\text{-}BuNH_2]^5$ for the reaction of $Mn_2(CO)_{10}$ with $n\text{-}BuNH_2$ in benzene solvent according to eq. 2.

rate law given in eq. 3. The reaction is slightly faster at the lower temperature. Preliminary runs at 0 and 60° C gave results which indicated that the amine dependence at these temperatures drops to less than fifth order, although it remains above third order.

$$-\frac{d[Mn_2(CO)_{10}]}{dt} = k[Mn_2(CO)_{10}][BuNH_2]^5 \qquad (3)$$

Reactions of $Mn_2(CO)_{10}$ with cyclohexylamine were attempted at temperatures of 100 and 160° C in decalin solution, but plots of $\ln(A - A_\infty)$ vs. time showed curvature. This is probably due to decomposition of $Mn_2(CO)_{10}$ which has been observed [14] in this temperature range in the absence of amine. Although detailed kinetic studies were not carried out, it is clear that reaction 2 is not instantaneous at these high temperatures and could be rate-determining in the catalytic reaction, especially toward the end of a reaction when the amine concentration is low.

Two mechanisms for reaction 2 might be considered. First, one in which heterolytic cleavage of the Mn—Mn bond occurs to give $Mn(CO)_5^-$ and $Mn(CO)_5(NH_2R)^+$ followed by reaction of $Mn(CO)_5(NH_2R)^+$ with additional amine to give *cis*-$Mn(CO)_4(NH_2R)(CONHR)$ is possible (eq. 4).

$$\begin{tikzcd} Mn_2(CO)_{10} + NH_2R \arrow[r, "\text{slow}"] & Mn(CO)_5^- + Mn(CO)_5(NH_2R)^+ \arrow[d, "\begin{array}{l}2\ NH_2R \\ \text{fast}\end{array}"] \\ & RNH_3^+ + cis\text{-}Mn(CO)_4(NH_2R)(CONHR) \end{tikzcd} \qquad (4)$$

The second step in this sequence is known [4] to be very fast at room temperature and therefore cannot be the rate-determining step. Thus, the first step must be rate-determining in this scheme. While there is ample evidence [15,16] to suggest the possible occurrence of the first step, the position of the equilibrium is not known. If the reverse of step one is slow as compared to the 2nd step, the 5th order amine dependence must be associated with the first step; a mechanism requiring a 5th order amine dependence for this step seems unlikely. On the other hand, if the reverse of the first step is faster than the second step, the overall 5th order would be made up of the order for the second step (which is likely to be 2nd order; see below) and that for the first step (which must then be 3rd order). All of the available kinetic data are therefore consistent with this mechanism.

A second possible mechanism (eq. 5) is basically the reverse of 4, i.e., initial formation of the carbamoyl group on the dimer followed by heterolysis of the Mn—Mn bond:

$$\begin{tikzcd}[column sep=small] \mathrm{Mn_2(CO)_{10} + 2\,NH_2R \rightleftharpoons NH_3R^+ + (OC)_5Mn{-}Mn(CO)_4(CONHR)^-} \arrow[d, "\mathrm{RNH_2}"] \\ \mathrm{(OC)_5Mn^- + \mathit{cis}\text{-}Mn(CO)_4(NH_2R)(CONHR)} \end{tikzcd} \tag{5}$$

Amines are known to attack CO carbon atoms in complexes where the carbon is sufficiently positive; this occurs [17,18] when the C—O stretching force constants, k(CO), are greater than approximately 16.0 mdyn/Å. While the k(CO) value (16.5 mdyn/Å) [19] for the equatorial CO groups of $Mn_2(CO)_{10}$ is sufficiently high to allow carbamoyl complex formation (first step of eq. 5), it is low enough to suggest that the equilibrium should lie to the left. This may account for the lack of any observed intermediates in the infrared spectra of the reaction solutions. For more weakly nucleophilic amines such as aniline, this equilibrium would be even less favorable and would be expected to reduce the overall rate of reaction. This step may be the reason why the yields of 1,3-diphenylurea obtained in the catalyzed reaction [3] of aniline and CO are much lower than those obtained with alkylamines.

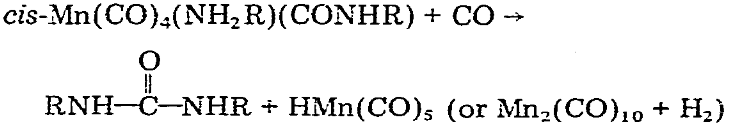
Carbamoyl complex formation is generally a rapid process [17,18,20,21]; therefore, the first step in eq. 5 will presumably be a rapid equilibrium. Since this equilibrium accounts for 2 of the 5 order dependence on amine concentration, the second step must be responsible for 3 orders. Although there are no kinetic studies of amine heterolyses of metal—metal bonds, it is possible that the attacking nucleophile is a hydrogen bonded dimer ($(RNH_2)_2$), where hydrogen bonding enhances the nucleophilicity of the attacking nitrogen. Such nucleophiles have been postulated previously [22—25]. Moreover, the hydrogen-bonding ΔH associated with the equilibrium, $2\ RNH_2 \rightleftharpoons (RNH_2)_2$, is known [25] to be negative which means that increasing temperature will decrease the amount of dimer. In this reaction, an increase in temperature would then contribute to a decrease in the rate of reaction. If this decrease outweighed activation parameters associated with either of the steps in eq. 5, the overall rate of reaction should decrease as the temperature is increased. That this is observed is consistent with the involvement of the $(RNH_2)_2$ nucleophile. The mechanism for the reaction of a metal carbene complex with amines has also been interpreted [24] in this manner to account for the observed negative activation energy.

While a $(RNH_2)_2$ nucleophile accounts for 2 of the 3-order dependence on $[RNH_2]$, the other order could be associated with hydrogen bonding of an amine proton to the departing $Mn(CO)_5^-$ anion. There is no precedent for this interaction and clearly more studies are required of reactions involving amine-induced heterolyses of metal—metal bonds. The metal—metal bond heterolysis step in the first mechanism (eq. 4) also could proceed by a mechanism involving nucleophilic attack by $(RNH_2)_2$ and RNH_2-assisted departure of $Mn(CO)_5^-$.

We have not considered mechanisms in which the carbamoyl group is formed by insertion of CO into a metal—amine bond. Although this has been considered [26] as a step in the formation of formamides in the reaction of $Co_2(CO)_8$ with amines, there is no direct evidence [26] for such an insertion. On the other hand, attack of an amine on coordinated CO groups is thoroughly documented [17, 20,23] and is the most reasonable route for the formation of carbamoyl ligands.

The reactions of secondary amines, diethylamine and piperidine, with $Mn_2(CO)_{10}$ were much more complicated than represented by eq. 2. Although infrared spectra of some reaction solutions suggested that carbamoyl complexes were formed, further reactions occurred rapidly yielding other products [11]. Difficulties in this reaction may account for the inability of $Mn_2(CO)_{10}$ to catalyze the formation of ureas from secondary amines.

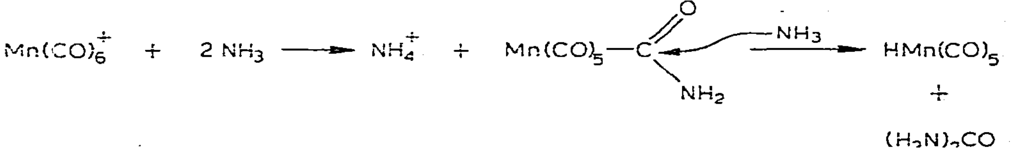
Reactions of cis-Mn(CO)₄(NH₂R)(CONHR). Since *cis*-$Mn(CO)_4(NH_2R)(CONHR)$ forms as soon as $Mn_2(CO)_{10}$ and amine are mixed, even before the catalytic reactions are pressured with CO, it was of interest to know if and how this complex reacted with CO and amine. When the cyclohexylamine complex, *cis*-$Mn(CO)_4(NH_2Cy)(CONHCy)$, was subjected to 68 atm of CO pressure at room temperature in hexane solvent, the carbamoyl complex disappeared completely within 24 h and 1,3-dicyclohexylurea was isolated in approximately 25% yield. An infrared spectrum of the solution showed that the manganese was in the form of $HMn(CO)_5$ and $Mn_2(CO)_{10}$. The former complex disappeared with longer reaction times; it appears that the decomposition of $HMn(CO)_5$ gives $Mn_2(CO)_{10}$ and H_2 even under these mild conditions, as has been observed previously [27]. Thus, this reaction appears to proceed as follows:



$$\begin{gathered} cis\text{-}Mn(CO)_4(NH_2R)(CONHR) + CO \rightarrow \\ RNH{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}NHR + HMn(CO)_5\ (\text{or } Mn_2(CO)_{10} + H_2) \end{gathered} \qquad (6)$$

It is only by this reaction with CO that the carbamoyl complex produces the urea, and this reaction is presumably the step which yields the urea in the catalytic reaction.

The mechanism of reaction 6 has not been investigated thoroughly; however, it is possible that an external amine (resulting from CO displacement of the coordinated amine) or the *cis*-coordinated amine could attack the carbamoyl carbon releasing the urea and forming the Mn—H bond. An external amine attack mechanism has been proposed [28,29] for the reaction of $Mn(CO)_6^+$ with ammonia (eq. 7).



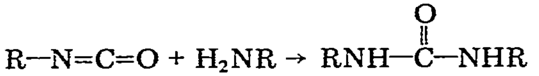
(7)

In this reaction, the proposed carbamoyl intermediate was not detected, however, its involvement is reasonable especially in view of the reactions of $Re(CO)_6^+$ with amines to give $Re(CO)_5(CONHR)$ [30].

There is no evidence to rule out the involvement of such external or intramolecular amine attack mechanisms in reaction 6; however, we feel there is greater precedent for the generation of an isocyanate intermediate as given in the following series of reactions.

$$cis\text{-}Mn(CO)_4(NH_2R)(CONHR) + CO \rightleftharpoons Mn(CO)_5(CONHR) + NH_2R \qquad (8)$$

$$Mn(CO)_5(CONHR) + NH_2R \rightleftharpoons NH_3R^+ + Mn(CO)_5^- + RN{=}C{=}O \qquad (9)$$



$$R{-}N{=}C{=}O + H_2NR \rightarrow RNH{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}NHR \qquad (10)$$

No studies have been reported for the substitution of the amine in *cis*-$Mn(CO)_4(NH_2R)(CONHR)$ to serve as a precedent for eq. 8. However, there are many examples [31] in metal carbonyl chemistry where an amine is replaced by CO. Therefore eq. 8 is a strong possibility especially under the conditions of high CO pressure existing in the catalytic reactions.

If $Mn(CO)_5(CONHR)$ is indeed formed as in eq. 8, we propose that it will react with excess amine base to deprotonate the carbamoyl proton. The resulting intermediate would then dissociate to give $Mn(CO)_5^-$ and the RNCO isocyanate as shown in eq. 9. A very similar reaction has been described [32] for a tungsten carbamoyl complex (eq. 11). An equilibrium mixture of reactants and products

$$C_5H_5W(CO)_3CONHCH_3 + Et_3N \rightleftharpoons Et_3NH^+ + C_5H_5W(CO)_3^- + CH_3{-}N{=}C{=}O \qquad (11)$$

was formed rapidly. If a primary amine (CH_3NH_2) was used in place of Et_3N, $CH_3NH_3^+C_5H_5W(CO)_3^-$ and the urea $(CH_3NH)_2C{=}O$ were the products. Presumably the initially formed $CH_3{-}N{=}C{=}O$ rapidly reacted with excess amine to give the observed urea. The position of the equilibrium in eq. 11 depends upon the nucleophilicity [33] of the metal carbonyl anion. With strong nucleophiles such as $C_5H_5Fe(CO)_2^-$, the equilibrium lies far to the left and $CpFe(CO)_2CONHCH_3$ does not react with excess amine [33]. Also for $Re(CO)_5^-$, the equilibrium lies far toward the $Re(CO)_5CONHR$ complexes [30]. This inability of $Re(CO)_5CONHR$ to react with amines may account for the inactivity of $Re_2(CO)_{10}$ as a catalyst in these reactions.

On the other hand, $Mn(CO)_5^-$ is an even weaker nucleophile than $C_5H_5W(CO)_5^-$, and we observe that it does not react even with a 50-fold excess of $CH_3{-}N{=}C{=}O$ either in the absence or presence of $Et_3NH^+Cl^-$. This strongly suggests that equilibrium 9 lies far to the right, making the conversion of the carbamoyl complex to the isocyanate very favorable.

It should be noted that it would not be possible to convert carbamoyl complexes of secondary amines, $Mn(CO)_5CONR_2$, to isocyanates according to step 9. This mechanism therefore, predicts that $Mn_2(CO)_{10}$ will not catalyze the formation of ureas from secondary amines and CO. Indeed, Calderazzo [3] originally noted that secondary amines did not react. A mechanism involving amine attack at the carbamoyl carbon should, however, give ureas even with secondary amines, although perhaps in lower yield for steric reasons. The final step (eq. 10) is well-known [34] to proceed rapidly even at room temperature.

Another variant on the mechanism given in eq. 8—10 is for isocyanate formation to occur directly from *cis*-$Mn(CO)_4(NH_2R)(CONHR)$. This seems less likely, however, since the resulting anion, $Mn(CO)_4(NH_2R)^-$, would be more nucleophilic than $Mn(CO)_5^-$ and its carbamoyl complex should be more stable than $Mn(CO)_5CONHR$.

Besides the reaction of *cis*-$Mn(CO)_4(NH_2Cy)(CONHCy)$ with CO, we also examined its reaction with excess NH_2Cy. At room temperature in hexane solvent even with high concentrations of amine, there is no reaction for days. Only upon heating to approximately 80° C does *cis*-$Mn(CO)_4(NH_2Cy)(CONHCy)$ begin to disappear. Urea is not produced in the reaction, but a new metal complex believed to be *fac*-$Mn(CO)_3(NH_2Cy)_2(CONHCy)$ is formed (eq. 12). The

$$cis\text{-}Mn(CO)_4(NH_2Cy)(CONHCy) + NH_2Cy \rightleftharpoons fac\text{-}Mn(CO)_3(NH_2Cy)_2CONHCy + CO \qquad (12)$$

n-butylamine analog was formed together with other products when $Mn_2(CO)_{10}$ reacted with excess $BuNH_2$ at 120° C in hexane. The unstable *fac*-$Mn(CO)_3(NH_2Bu)_2CONHBu$ was isolated by precipitation from CH_2Cl_2 solution with pentane. Carbon and hydrogen analyses of the difficult-to-solidify product were within 1.5% of values required for this formulation. When *fac*-$Mn(CO)_3(NH_2Cy)_2CONHCy$ in a hexane suspension was treated with 68 atm of CO pressure at 25° C, *cis*-$Mn(CO)_4(NH_2Cy)CONHCy$ and its CO-reaction products (eq. 6) were formed. This reaction supports the formulation of these bis(amine) compounds and also indicates that reaction 12 is reversible.

Since reaction 12 does not lead to any products of the catalytic reaction, it appears to be a non-productive side reaction. Since it would form at high amine concentrations, reaction 12 may account for the fact that using pure amine rather than a diluent solvent actually decreases the yield of the catalytic reaction (Table 5). Also the reduction in yield caused by the addition of tetramethylethylenediamine (TMEDA) to the catalytic reactions may be due to the formation of the unreactive chelated species, *fac*-$Mn(CO)_3(TMEDA)CONHR$. Likewise, the unreactivity of the diamines, ethylenediamine and 1,4-diaminobutane, may result from the formation of similar unreactive species. High CO pressures should reduce the concentration of the unreactive complexes and give higher yields as is observed (Table 3).

Reactions of RNH_3^+, $Mn(CO)_5^-$, $HMn(CO)_5$, *and* $Mn_2(CO)_{10}$. These species are produced in the catalytic reaction in steps described by eq. 2 and 6. In order for the reaction to be catalytic, the manganese must be reconverted back to $Mn_2(CO)_{10}$, which reacts with more amine (eq. 2) to give the key carbamoyl complex. We propose that $Mn_2(CO)_{10}$ is formed from RNH_3^+ and $Mn(CO)_5^-$ in the following reactions:

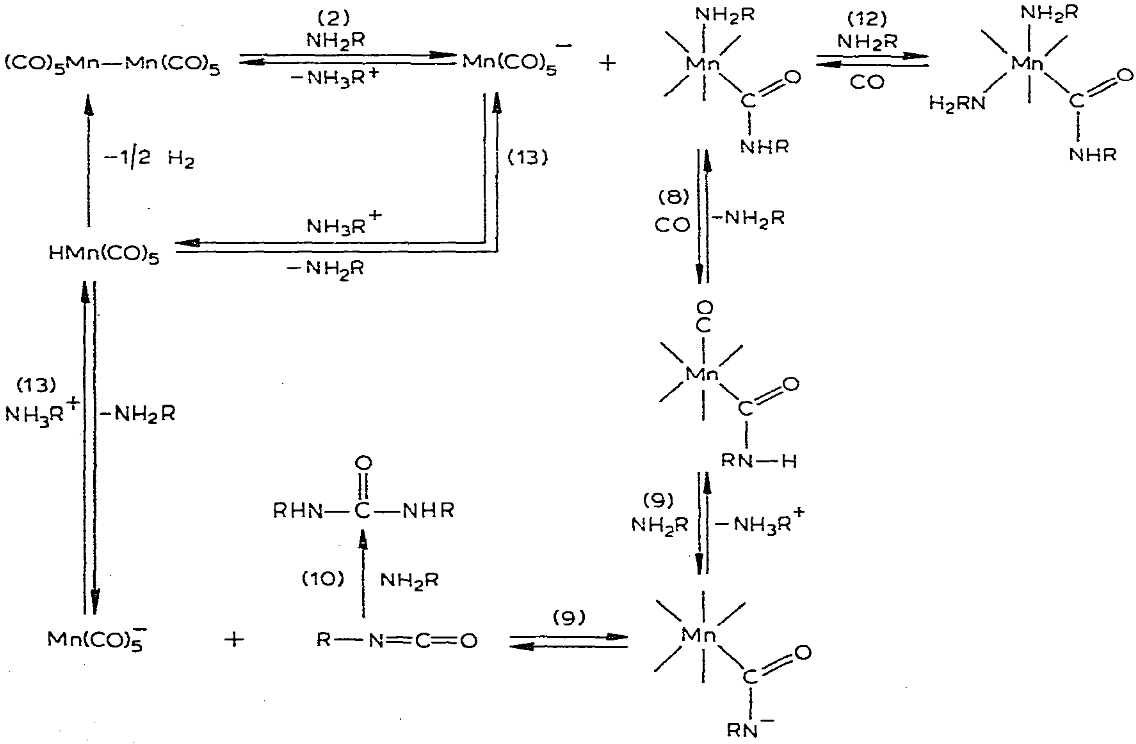
$$Mn(CO)_5^- + RNH_3^+ \overset{K_1}{\rightleftharpoons} RNH_2 + HMn(CO)_5 \xrightarrow{k} 1/2\ H_2 + 1/2\ Mn_2(CO)_{10} \qquad (13)$$

The equilibrium constant K_1 could be small because of the lower basicity of $Mn(CO)_5^-$ ($K_a = 8 \times 10^{-8}$ in H_2O [27]) as compared to RNH_2 ($K_a = 10^{-11}$ in H_2O). In the less polar organic solvents used in these catalytic reactions the formation of $HMn(CO)_5$ may be more favorable than suggested by the pK_a values in H_2O. The position of the equilibrium will also be affected by the amine concentration. This in turn will affect the rate of the reaction associated with k, which is probably irreversible under the low H_2 pressures generated in the bomb [27].

Samples withdrawn from a catalytic reaction shortly after the reaction began, when amine concentration was high, showed predominately $Mn(CO)_5^-$. At the end of a catalytic reaction, when much of the amine has been consumed, $Mn_2(CO)_{10}$ is often observed by IR. These observations are qualitatively in agreement with the shifting positions of the equilibria in eq. 13. Very little is known about the rates associated with the K_1 and k reactions. It is possible that the overall reaction represented in eq. 13 is rate-determining for the catalytic reaction especially at high amine concentrations.

Overall mechanism. Combining the individual reactions discussed above gives the overall mechanism shown in Scheme 1. Reaction numbers are those given in the discussion. As noted in the discussion, there are alternative possible mechanisms for individual steps, but we feel the present evidence best supports those given in Scheme 1.

SCHEME 1



The mechanism involves 3 key steps: (1) the reaction of $Mn_2(CO)_{10}$ to form the carbamoyl complex (eq. 2); (2) the reaction of the carbamoyl complex with CO and amine to give the urea via the organic isocyanate (eq. 8,9,10); (3) the regeneration of $Mn_2(CO)_{10}$ from $Mn(CO)_5^-$ and RNH_3^+ (eq. 13). The reaction of the carbamoyl complex with excess amine according to eq. 12 gives a catalytically inactive form of manganese.

With the exception of free RNCO, $Mn(CO)_5CONHR$ and $Mn(CO)_5CONR^-$, all of the compounds in Scheme 1, have been observed by infrared spectroscopy in reaction mixtures during or at the conclusion of a catalytic reaction. The highest concentrations of inactive *fac*-$Mn(CO)_3(NH_2R)_2CONHR$ are observed in reactions run at low CO pressures (<47.6 atm) or when the amine is not diluted by a solvent. These observations are consistent with the involvement of reaction 12 in the overall process as shown in Scheme 1.

The rate-determining step of the reaction is not clear. It was thought that the conversion of $RNH_3^+Mn(CO)_5^-$ to $Mn_2(CO)_{10}$ according to eq. 13 might be the rate-determining step; however, increasing the RNH_3^+ concentration by adding $CH_3(CH_2)_6CO_2H$ to the reaction mixture actually decreased the yield of urea (Table 7). Reaction 2 has the unusual negative activation energy which makes it proceed slower at higher temperatures. Therefore, this reaction could be rate-determining under most conditions. Although reaction 6, i.e., a combination of 8, 9, and 10, proceeds slowly at room temperature, its dependence on amine concentration, CO pressure or temperature has not been investigated. At this point, it is not possible to say whether or not it is rate-determining. While many details of the reaction remain to be elucidated, the importance of the formation and subsequent reaction of the carbamoyl complex in this reaction suggests its possible involvement in other reaction of CO and amines.

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