

Transalkylation Reaction. Homogeneous Catalytic Formation of C–N Bonds

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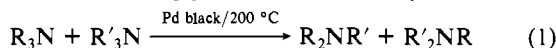
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Abstract: We have performed kinetic and mechanistic studies on homogeneous ruthenium-catalyzed transalkylation of tertiary amines. From these studies we have derived a kinetic expression for transalkylation catalysis based on initial reaction rates. We find that transalkylation proceeds most efficiently in alcoholic solvents (e.g., MeOH or EtOH), under a slight pressure of CO, with a mixed-metal, iron–ruthenium catalyst. The mechanism appears to be one in which a metal cluster of at least two and most probably three atoms binds the amine through insertion into an α C–H bond to give a metallazacyclopropane or metal–iminium complex. Nucleophilic attack by free amine on the complex, or an immediate derivative, follows, and subsequent rearrangement of the intermediate formed gives transalkylation products. The catalyst system has been tested as a synthetic tool for the oligomerization and cyclization of tertiary diamines. These preliminary studies have been quite successful. Thus, N,N,N',N' -tetramethylethylenediamine can be transformed into Me_3N and N,N' -dimethylpiperazine with good conversion and high selectivity. N,N,N',N' -Tetraethylethylenediamine can be transformed into Et_3N and the linear, perethyl, ethylenediamine dimer, trimer, tetramer, and pentamer with excellent conversions.

The catalytic formation and cleavage of carbon–nitrogen (C–N) single bonds is of considerable importance for numerous diverse areas of chemistry because of the ubiquitous presence of nitrogen-containing compounds in nature. For example, the catalytic formation of C–N bonds plays a significant role in the synthesis of pharmacologically active molecules.^{1–4} The catalytic cleavage of C–N bonds is of fundamental importance to the refining of crude oil to fuels and petrochemical feedstocks as part of the hydrotreating process.^{5–8} Catalytic C–N bond formation and cleavage are both essential to the functioning of life-controlling processes.

In general, research on the catalysis chemistry of C–N bonds has focused on the formation of C–N bonds with little attention paid to the cleavage of the C–N bond, especially in tertiary amines. When we initiated work in the area, the only available literature on catalytic C–N bond cleavage was that devoted to the hydrodenitrogenation of crude oil and coal using heterogeneous catalysts and excessive reaction conditions (above 400 °C and 1000–2000 psig H_2).^{5–8} In fact, the only evidence that one could catalyze C–N bond scission at lower temperatures was the work on Murahashi.⁹

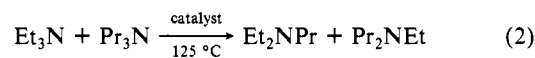
Murahashi reported that he could efficiently catalyze the exchange of alkyl groups between tertiary amines, at 200 °C, as shown in reaction 1 using palladium black catalysts. The dis-



covery^{9–11} of catalysts that cleave and reform C–N single bonds

in tertiary amines at 200 °C was in itself a considerable feat given that the average C–N bond dissociation energy for tertiary amines is ~ 75 kcal/mol.¹²

Because of the similarity between Murahashi's work on C–H activation in tertiary amines catalyzed by Pd black^{9–11} and our studies on similar reactions catalyzed by homogeneous catalysts,¹³ we attempted to catalyze reaction 1 by using homogeneous catalysts. In 1980, we published a preliminary report describing the first examples of homogeneous transition-metal-catalyzed alkyl exchange or "transalkylation" between tertiary amines (eq 2).¹⁴



catalyst = $\text{Ru}_3(\text{CO})_{12}$, $\text{Os}_3(\text{CO})_{12}$, $\text{Rh}_6(\text{CO})_{16}$, $\text{Ir}_4(\text{CO})_{12}$

These original observations provided the impetus for the development of a new and comprehensive mechanistic picture of how C–N bonds are cleaved in the industrially important hydrodenitrogenation reaction.^{15–18} In addition, we demonstrated that the homogeneous catalysts are far more active for (2) than the heterogeneous catalyst, Pd black. This higher activity allowed us to reduce transalkylation temperatures to 125 °C.

At this juncture, it occurred to us that we had achieved sufficient catalytic activity at low enough temperatures to warrant the exploration of the transalkylation reaction for organic synthesis. An examination of the literature demonstrates the potential synthetic utility of the transalkylation reaction. Mixed-alkyl amines are intermediates or are used directly in various industrial syntheses that include biocides, phase-transfer catalysts, surfactants, and polymerization catalysts.¹⁸ Moreover, if the transalkylation reaction can be applied to diamines, as shown in (3) for N,N,N',N' -tetraalkylethylenediamines, then transalkylation holds considerable potential for the preparation of tertiary and quaternary amine polymers and unusual amine macrocycles, including analogues of crown ethers, cryptands, and cryptates.^{19,20}

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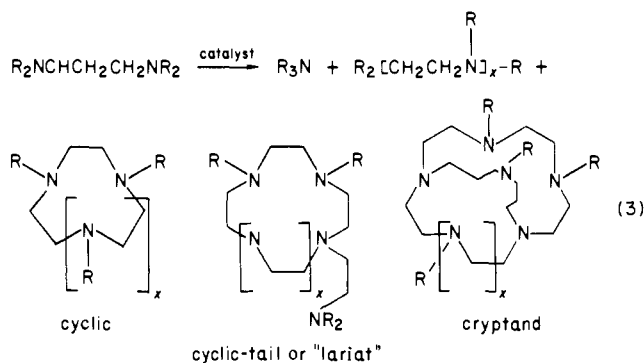
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Amine macrocycles continue to play an important role in the development of models of various bioinorganic processes, including oxygen transport,²¹ oxidation catalysis,²² and various electron-transfer processes.²³

In this context, we have undertaken kinetic and mechanistic studies of the transalkylation reaction in an effort to understand the catalysis chemistry involved, to improve the stability, selectivity, and the activity of the catalysts, in particular those based on $Ru_3(CO)_{12}$, and to explore the scope of the reaction as it applies to organic synthesis.²⁴ The results of the kinetic studies are described below.

Experimental Section

General Methods. All secondary and tertiary amines were purchased from Aldrich and distilled from CaH_2 under Ar or N_2 before use. Ethanol was purified in the same manner. Methanol was purified via distillation from $Mg(OMe)_2$ under Ar. THF, diglyme, ethyl ether, and *n*-butyl ether were purified by distillation from sodium benzophenone ketyl under N_2 and stored under N_2 before use. Catalyst precursors were purchased from Strem Chemicals and used as received. $Ru_3(CO)_{12}$ was stored in a Dri-Box under N_2 .

Analytical Procedures. Product analyses for all the kinetic studies were performed on a Hewlett-Packard 5880A reporting GC equipped with FID using a 2.5 m \times 0.325 cm column packed with 60/80 Carbowax/4% Carbowax 20 M/0.8% KOH on acid-washed Chromosorb W (supplied by Supelco). *n*-Butyl ether was used as an internal standard for GC analyses. Infrared spectra were obtained by using a Perkin-Elmer 281 IR spectrophotometer. NMR spectra were taken on a JEOL 90-MHz instrument. GC-mass spectral analyses were performed by using an LKB-9000 mass spectrometer or a Ribermag R 10 10 C.

General Reaction Procedures for Kinetic Studies. Stock solutions of amines were prepared, in appropriate solvents, with *n*-butyl ether as an internal standard. The solutions, normally 0.67 M in both Et_3N and Pr_3N unless indicated otherwise, were stored under Ar at 0 °C and analyzed before use. Magnetically stirred, 34-mL quartz-lined bomb reactors were dried by heating at 120 °C and then cooled and stored in a desiccator until used. Two general procedures were followed.

Procedure A. In a typical reaction, the required quantity of $Ru_3(CO)_{12}$, usually 0.05 mmol (32 mg) or as noted, was weighed under N_2 and transferred to a bomb reactor. The reactor was then loaded with 5 mL of stock solution. The reactor was sealed and degassed via three pressurization/depressurization cycles using 500 psig N_2 or CO and then pressurized to the desired pressure with N_2 or CO (normally 100 psig) and heated in an oil bath to 160 ± 0.5 °C. Samples were taken at appropriate times (usually 15 min) by cooling the reactor in an ice bath, depressurizing, and removing a 0.1-mL sample. The reaction was then restarted following the above procedure.

Procedure B. A second set of kinetic studies was conducted as in A but with slight modifications. In these studies, the solvent used was either ethanol, THF, or diglyme. The reaction conditions were as follows. In

the standard reactor were mixed 5 mL of dry solvent containing 1 mmol of *n*-butyl ether as an internal standard, 0.05 mmol of $Ru_3(CO)_{12}$, and 2.0 mL of a 1:1 molar ratio (6.0 mmol/6.0 mmol) of Et_3N and Pr_3N . When the reactions were studied under CO, the reactor was degassed with CO and pressurized to 100 psig CO. Otherwise the same procedure was followed with N_2 . The reactions were sampled every 0.5 h for the first 2 h and every hour thereafter until the mole percentage of mixed alkylamines approached 70% or until the mole percentage of mixed alkylamines failed to change significantly, indicating catalyst degradation.

H_2O Concentration Studies. These reactions were run as in procedure A using methanol as the only solvent and 100 psi CO. Water 0 to 100 μ L was added by syringe.

CO Pressure Studies. These reactions were run as described in procedure A with Et_3N and Pr_3N amine concentrations of 0.74 M and using methanol as the only solvent. The CO pressure was varied from 0 to 400 psig at ambient temperature.

Catalyst Concentration Studies. Reactions were run as described for procedure A in the general procedures. Experiments were conducted in methanol under 100 psig CO at 160 °C. The solutions were 0.87 M in total amine concentration with a 1:1 ratio of Et_3N/Pr_3N . $Ru_3(CO)_{12}$ concentrations were varied between 5.0×10^{-3} and 4.0×10^{-2} M.

Amine Concentration Studies. Reactions were run as in the CO pressure studies with the exception that the CO pressure was held constant at 100 psig CO. The overall amine concentration was varied from 0.2 to 3.7 M. The ratio of Et_3N to Pr_3N was maintained at 1:1. Experiments were then performed in which the ratio of Et_3N to Pr_3N was varied with the total amine concentration held constant at 1.34 M.

Temperature Studies. Reactions were run as in the CO pressure studies with the exception that the CO pressure was held constant at 100 psig CO. Rates were recorded at 130, 145, and 160 °C.

Deuterium-Exchange Studies. When procedure A was used, 5 mL of a solution containing 2.62 mmol of Pr_3N in CD_3OD was heated at 160 °C and sampled at 15-min intervals for the first hour and every half-hour afterward for 3.5 h. A 5-mL solution containing 2.62 mmol of Et_3N in CD_3OD was treated similarly. A solution of 2.62 mmol of both amines in CD_3OD was run identically. Samples were withdrawn every 10 min. The rate of deuterium incorporation into the amine molecules was followed as a function of time via mass spectral analysis. Corrections were made for natural abundance of isotopes ^{13}C , 2H , and ^{15}N .

Reaction of N,N,N',N' -Tetramethylethylenediamine. In a magnetically stirred, 34-mL, quartz-lined bomb reactor was mixed 5 mL of dry ethanol containing 1 mmol of *n*-butyl ether as internal standard for GC analyses, 64 mg (0.1 mmol) of $Ru_3(CO)_{12}$, 44 μ L of $Fe(CO)_5$ (0.3 mmol), and 2.0 mL (13.2 mmol) of N,N,N',N' -tetramethylethylenediamine. The reactor was sealed and degassed via three pressurization/depressurization cycles with 500 psig of CO and then pressurized to 100 psig with CO and heated to 160 °C for 2 h. At the end of this period the reactor was cooled, depressurized, and analyzed by GC. The GC analysis showed small amounts of Me_3N . After 120 h of reaction, approximately 7 mmol of Me_3N was formed along with 3 mmol of N,N' -dimethylpiperazine, 0.5 mmol of *N*-ethyl- N,N',N' -trimethylethyldiamine, 0.5 mmol of N,N,N',N'',N''' -pentamethyldiethylenetriamine [$Me_2NCH_2CH_2N(Me)CH_2CH_2NMe_2$], and 1.5 mmol of *N*-methyl- N' -(2-(dimethylamino)ethyl)piperazine.

Reaction of N,N,N',N' -Tetraethylethylenediamine. The same procedure as used for the tetramethyl derivative was used for tetraethylethylenediamine (2.0 mL = 9.4 mmol). After 16 h of reaction time, GC analysis showed production of 2.5 mmol of Et_3N . After an additional 84 h of reaction time, 4.2 mmol of Et_3N was produced along with four other major products, including 1.7 mmol of N,N,N',N'',N''' -pentaethyldiethylenetriamine [$Et_2NCH_2CH_2N(Et)CH_2CH_2NEt_2$], 0.8 mmol of N,N,N',N'',N''',N'''' -hexaethyltriethylenetetramine [$Et_2N[CH_2CH_2N(Et)]_2CH_2CH_2NEt_2$], 0.1 mmol of the perethyltetraethylenepentamine, traces of the pentaethylenhexamine, and traces of N,N' -diethylpiperazine and N,N',N'' -triethyl-1,4,7-triazacyclononane. We also observed the formation of 0.1 mmol of *N*-*n*-butyl- N,N',N' -triethylethylenediamine.

Results

A rational approach to exploring the synthetic utility of a neat reaction is to develop a kinetic and mechanistic understanding of the reaction to fully appreciate the reaction's potential. In our preliminary studies, the transalkylation reactions were run in neat amine at 125–150 °C. The use of the neat reactant as the solvent is not an appropriate approach to undertaking kinetic studies; consequently, our first objective was to find a useful solvent system.

Solvent Survey. In our original studies with neat amines, reaction 2, we consistently obtained 50–58 mol % mixed alkylamines.

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Table I. Initial Rates and Final Mole Percentages for Transalkylation in Various Solvents

solvent ^a	initial rates ^b		final mol % mixed alkylamines	final time, h
	N ₂ ^c	100 psi CO		
THF	80	2.4	48	3
diglyme	45	4.3	40	7
diethyl ether	19	7	47	4
methanol	22	63 (160 °C)	63, 70	4
		13 (145 °C)		
		5.6 (130 °C)		
ethanol	18	28	61	16
		46 ^d	64 ^d	4.5

^a Reactions were run as in procedure A of the Experimental Section for diethyl ether and methanol and as in procedure B for THF, diglyme, and ethanol. Reactions solutions in diethyl ether and methanol were 0.67 M in each amine and 0.76 M for the other solvents. ^b Initial rates are defined as turnover frequency (TF), where TF is defined as moles of Et₂NPr/mole of catalyst precursor per hour. ^c In the absence of CO pressure, the catalyst will decompose in all solvents. Evidence of catalyst decomposition is usually visible after 1 h. ^d In mixed-metal catalyst systems 0.15 mmol of Fe(CO)₅ was added to the standard reaction.

Although these percentages were always less than those obtained by Murahashi with palladium black at 200 °C (60–65 mol % mixed alkylamines),⁹ we assumed that this was simply a result of the differences in reaction temperatures. These results seemed to be confirmed by our studies of ether solvents, using Ru₃(CO)₁₂ as the catalyst precursor (see Table I), in that the final distribution of amines was similar. Moreover, the initial rates in all cases were comparable (see Table I). On testing alcohol solvents, we found that alcohols promote rapid catalyst degradation.

In an attempt to prevent catalyst degradation in the alcohol solvents, the reactions were run under 100 psig CO. CO not only eliminated catalyst degradation, it also significantly improved the reaction rate, and the final distribution reached 62–65 mol % mixed alkylamines in 3–4 h at 160 °C. This is a considerable improvement when compared with the 60–65% obtained by Murahashi after 16 h at 200 °C. Backtracking, we found that catalyst degradation also occurs in the ether solvents although at a slower rate. The use of CO with the ether solvents significantly diminishes transalkylation catalysis rather than enhancing it.

As a result of this survey, we concentrated on the use of alcohol solvents, mainly methanol, in our kinetic and synthetic studies.

Deuterium-Exchange Studies. To establish a relationship between our previous studies of deuterium exchange on the alkyl groups of Et₃N and Pr₃N using neat amines and D₂O, we examined the rate of D for H exchange of these amines in CD₃OD. The pertinent results of these studies give the initial rate of appearance of Pr₃N-*d*_x in CD₃OD [defined as turnover frequency (TF) where TF = moles of deuterated amine produced/mole of Ru₃(CO)₁₂ per hour] TF = 273 ± 17, and the initial rate of appearance of Et₃N-*d*_x was found to be 250 ± 15. In each case, the major deuterated products were the same as those observed previously: Pr₂NCHDCHDCH₃, Pr₂NCHDCH₂CH₃, Et₂NCHDCHD₂, and Et₂NCHDCD₃.

CO Pressure Studies. With the discovery that added CO would facilitate catalysis of the transalkylation reaction in alcoholic solvents, we attempted to establish the effect of changes in CO pressure on catalyst activity and optimize the effect. The results of this study are shown in Figure 1. There appears to be an initial rate enhancement as the CO pressure increases to approximately 100 psig. Any further increases in CO pressure cause a rapid decline in catalyst activity.

Catalyst Concentration Studies. We have previously shown that valuable information on catalyst nuclearity can be obtained by studying the effects of catalyst concentration on relative catalyst activity. The plot shown in Figure 2 illustrates this approach.

The results shown in Figure 2 indicate that the product yield is not linearly dependent on catalyst concentration. Moreover, the plot shown in Figure 2 is indicative of a cluster-catalyzed

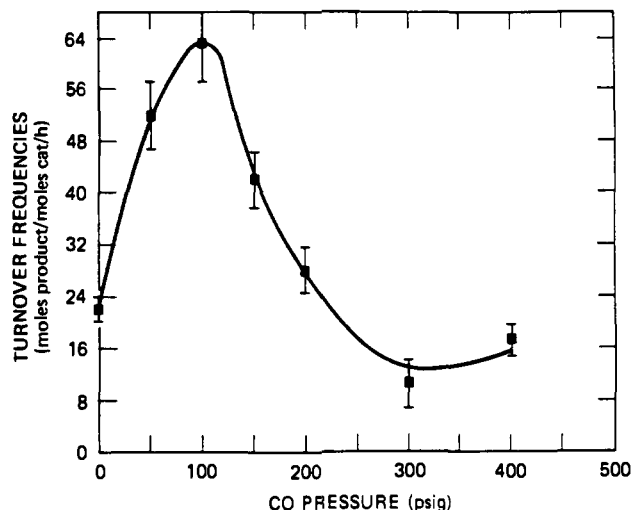


Figure 1. Plot of the initial rates of transalkylation as a function of CO pressure. Initial rates are defined as the turnover frequency (TF) = moles of Et₂NPr produced/mole of Ru₃(CO)₁₂/per hour. Reactions were run in methanol under CO, at 160 °C; total volume was maintained at 5.0 mL; [Et₃N] = [Pr₃N] = 0.74 M.

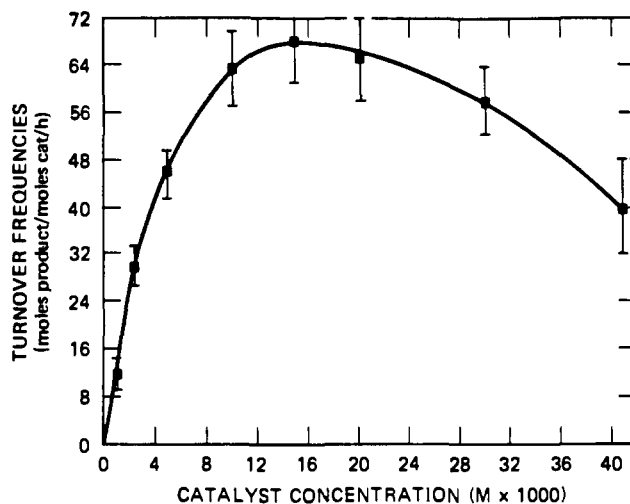


Figure 2. Plot of the initial rates of transalkylation as a function of catalyst concentration. Initial rates are defined as the turnover frequency (TF) = moles of Et₂NPr produced/mole of Ru₃(CO)₁₂ per hour. Reactions were run in methanol under 100 psig CO, at 160 °C; total volume was maintained at 5.0 mL; [Et₃N] = [Pr₃N] = 0.74 M.

reaction; however, further substantiation will be necessary to obtain confirmation (see the Mixed-Metal Catalysts section).

Amine Concentration Studies. Amine concentration studies were performed in two ways. In one set of studies, initial rates were measured as a function of the mole percent of Et₃N while the total amine concentration (Et₃N and Pr₃N) and other variables were kept constant. The results of these experiments are shown in Figure 3.

In a second set of experiments, initial rates were measured as a function of changes in the total amine concentration while the ratio of Et₃N/Pr₃N was kept constant at 1:1. The results of both studies were used to develop transalkylation rate expressions (presented below).

Water Concentration Studies. In an attempt to determine whether or not water plays a role in the reaction as suggested previously,¹⁴ we studied the effect of added water. The results of this study, shown in Figure 4, indicate that the presence of water, even at low concentrations, diminishes the systems ability to catalyze transalkylation.

Temperature Studies. Reaction rate data were obtained for reaction 2 run in methanol at several temperatures, as recorded in Table I. These data allow us to calculate the energy of activation, $E_a = 24.8 \pm 2$ kcal/mol.

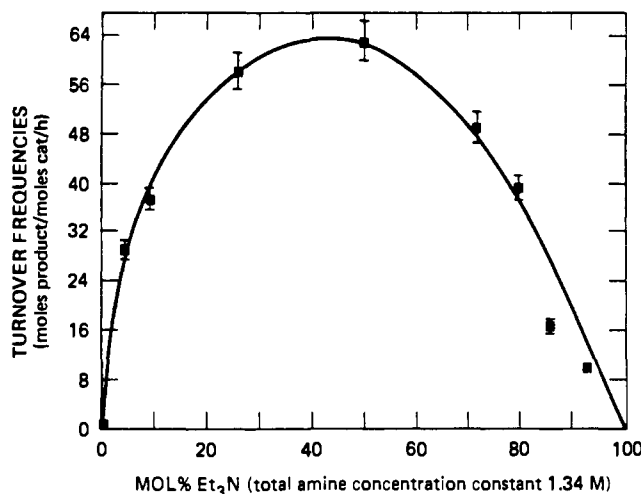


Figure 3. Initial catalytic rates as a function of the ratio of Et₃N to Pr₃N. Initial rates are defined as the turnover frequency (TF) = moles of Et₂NPr produced/mole of Ru₃(CO)₁₂ per hour. Reactions were run in methanol with 0.05 mmol of Ru₃(CO)₁₂, under 100 psig CO, at 160 °C; volume was 5.0 mL; total amine concentration was maintained at 1.34 M.

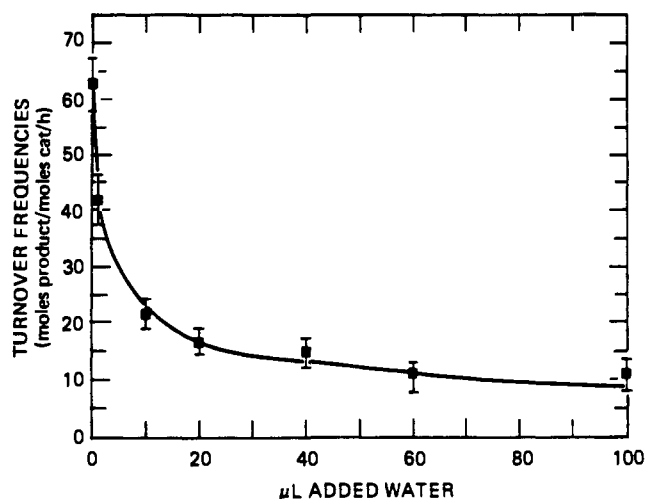
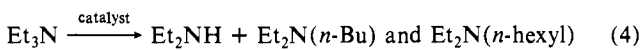


Figure 4. Initial rates of transalkylation as a function of added water. Initial rates are defined as the turnover frequency (TF) = moles of Et₂NPr produced/mole of Ru₃(CO)₁₂ per hour. Reactions were run in methanol under 100 psig CO, at 160 °C; total volume was maintained at 5.0 mL; [Et₃N] = [Pr₃N] = 0.74 M.

Mixed-Metal Catalysts. We previously reported the synergistic effects obtainable via the addition of iron carbonyl to ruthenium-cluster-catalyzed reactions such as the water-gas shift reaction,²⁵ hydroformylation, and aminomethylation.^{26,27} Without any understanding of the processes involved, we attempted to obtain similar rate enhancements in transalkylation catalysis through the use of iron carbonyls. As recorded in Table I, we did observe rate enhancements when iron carbonyl was added, despite the fact that iron carbonyl by itself is not catalytically active (although see below).

Other Products. In addition to the transalkylation reaction, we observed another reaction that consumes Et₃N irreversibly. The remarkable reaction, (4), which we discuss elsewhere,²⁸



proceeds very slowly under the conditions used in the kinetic

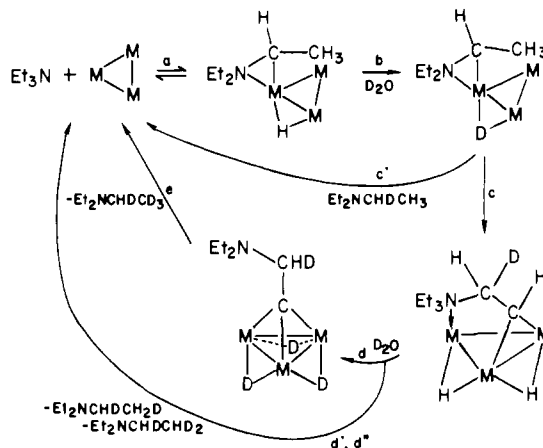
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Scheme I

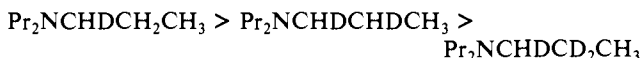


studies, except at high catalyst concentration.

Discussion

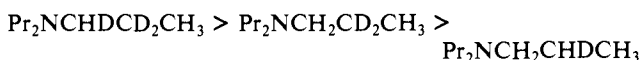
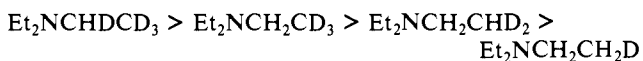
To develop a complete mechanistic and kinetic picture of ruthenium-promoted transalkylation catalysis based on the results presented above, we need to briefly discuss our previous studies on catalytic C-H activation/D for H exchange in tertiary amines. These studies show that C-H activation is a prerequisite to transalkylation catalysis.

Scheme I illustrates the proposed mechanism for C-H activation/D for H exchange in Et₃N as catalyzed by ruthenium, osmium, and Pd black. A similar scheme has been used to illustrate rhodium-catalyzed deuteration of Et₃N. The major products in ruthenium-, osmium-, or Pd-black-catalyzed deuteration of Et₃N and Pr₃N are



We call this the $\alpha\beta\beta$ activation/exchange mechanism because one α hydrogen always undergoes C-H activation/D for H exchange before any β hydrogens exchange.

In contrast, homogeneous rhodium-catalyzed and heterogeneous molybdenum-catalyzed C-H activations/D for H exchanges of Et₃N and Pr₃N proceed by the $\beta\beta\alpha$ mechanism; that is, the first hydrogen exchanged is always a β hydrogen and the last hydrogen exchanged is always one α hydrogen. For $\beta\beta\alpha$ exchange, we observe the following deuterated products:



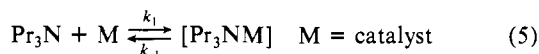
A key point, which appears to be related to the current work, is that ruthenium-catalyzed deuteration of Et₃N proceeds via pathways d and e (Scheme I) more often than by pathway c, whereas the reverse is true for exchange in Pr₃N.

The above observations permit us to develop both a kinetic and a mechanistic understanding of the events that occur during transalkylation. We can begin by deriving kinetic expressions that conform to the experimental observations.

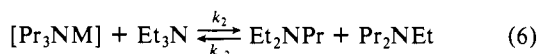
Kinetic Studies

Rate Expression. To develop a useful kinetic expression for ruthenium-promoted transalkylation catalysis in the Et₃N/Pr₃N model system, we must first consider potential amine-catalyst interactions. From the D for H exchange studies, we know that exchange can occur without transalkylation. These results indicate that amine, either Et₃N or Pr₃N, can reversibly bind to the catalyst before transalkylation. This suggests a preequilibrium such as

that shown in (5) for Pr_3N .



Pr_3NM can then react further with Et_3N to give products



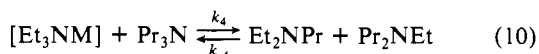
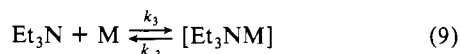
Initially, the back reaction, k_{-2} , does not contribute to the rate of reaction; thus, assuming a steady state for $[\text{Pr}_3\text{NM}]$, we can write an expression for the appearance of the product Et_2NPr :

$$d[\text{Et}_2\text{NPr}]/dt = k_1 k_2 [\text{Pr}_3\text{N}] [\text{Et}_3\text{N}] [\text{M}] / (k_{-1} + k_2 [\text{Et}_3\text{N}]) \quad (7)$$

For constant $[\text{M}]$ and P_{CO} , (7) simplifies to (8). Alternatively,

$$d[\text{Et}_2\text{NPr}]/dt = k_1 k_2 [\text{Pr}_3\text{N}] [\text{Et}_3\text{N}] / (k_{-1} + k_2 [\text{Et}_3\text{N}]) \quad (8)$$

Et_3N can bind to the catalyst, (9), before transalkylation, (10).



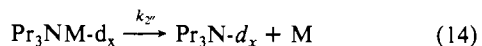
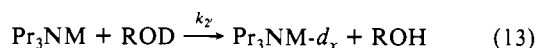
In analogy to (8), we obtain (11). The complete forward rate

$$d[\text{Et}_2\text{NPr}]/dt = k_3 k_4 [\text{Pr}_3\text{N}] [\text{Et}_3\text{N}] / (k_{-3} + k_4 [\text{Pr}_3\text{N}]) \quad (11)$$

expression for all amine concentrations, at constant $[\text{M}]$ and CO pressure, is given by

$$d[\text{Et}_2\text{NPr}]/dt = k_1 k_2 [\text{Pr}_3\text{N}] [\text{Et}_3\text{N}] / (k_{-1} + k_2 [\text{Et}_3\text{N}]) + k_3 k_4 [\text{Et}_3\text{N}] [\text{Pr}_3\text{N}] / (k_{-3} + k_4 [\text{Pr}_3\text{N}]) \quad (12)$$

Reasonable values for k_{-1} and k_{-3} can be derived from the deuteration studies. Consider the following reactions for Pr_3N deuteration:



An expression for $[\text{Pr}_3\text{NM}]$ concentration can be written as

$$d[\text{Pr}_3\text{NM}]/dt = k_1 [\text{Pr}_3\text{N}] [\text{M}] - k_{-1} [\text{Pr}_3\text{NM}] - k_2' [\text{Pr}_3\text{NM}] [\text{ROD}] \quad (15)$$

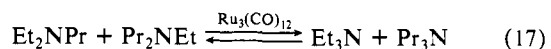
If a steady state is assumed in which all available metal is complexed as Pr_3NM , then $d[\text{Pr}_3\text{NM}]/dt = 0$ and $k_1 > k_{-1}$ or k_2' . The rate of appearance of deuterated Pr_3N is given by (16). If

$$d[\text{Pr}_3\text{N-d}_x]/dt = k_2'' [\text{Pr}_3\text{NM-d}_x] \quad (16)$$

$k_2'' > k_2'$, then the rate of appearance of deuterated Pr_3N is a measure of the rate of release of Pr_3N from the complex. Because we observe no transalkylation products which are undeuterated in this experiment, k_2'' must be greater than k_2' . If we disregard deuterium isotope effects, then there is no a priori reason why the release of deuterated amine would be different from undeuterated amine and k_{-1} can be approximated by k_2'' . Then from our deuteration studies, $k_{-1} \approx 283 \text{ h}^{-1}$, and a similar analysis for Et_3N gives $k_{-3} \approx 250 \text{ h}^{-1}$.

Multivariate analysis using all the amine concentration data and the values for k_{-1} and k_{-3} as starting points gives the best fit with the following rate constants: $k_1 = 125 \text{ h}^{-1}$, $k_{-1} = 273 \text{ h}^{-1}$, $k_2 = 547 \text{ h}^{-1} \text{ M}^{-1}$, $k_3 = 40 \text{ h}^{-1}$, $k_{-3} = 250 \text{ h}^{-1}$, $k_4 = 202 \text{ h}^{-1} \text{ M}^{-1}$, at a constant catalyst concentration of 0.01 M [defined as added $\text{Ru}_3(\text{CO})_{12}$] and a constant CO pressure of 100 psig. The line drawn through the data points of Figure 5 is the rate predicted from (12) using the optimized values for k_1 – k_4 .

We briefly examined the kinetics of the reverse of reaction 2, i.e., reaction 17.



We find that the initial turnover frequency for the back reaction is $19 \pm 3 \text{ h}^{-1}$ ($[\text{Et}_2\text{NPr}] = 0.5 \text{ M}$ and $[\text{Pr}_2\text{NEt}] = 0.46 \text{ M}$, under

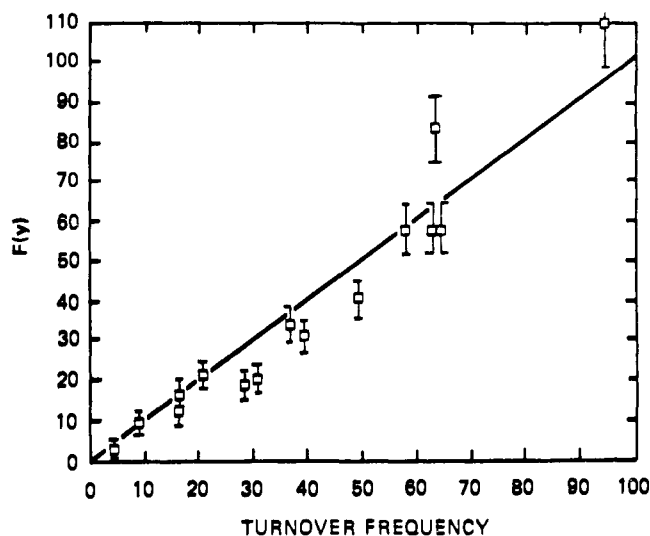


Figure 5. Initial rates of transalkylation as a function of $F(y)$ where $F(y) = [(k_1 k_2 [\text{Et}_3\text{N}] [\text{Pr}_3\text{N}]) / (k_{-1} + k_2 [\text{Pr}_3\text{N}])] + [(k_3 k_4 [\text{Et}_3\text{N}] [\text{Pr}_3\text{N}]) / (k_{-3} + k_4 [\text{Pr}_3\text{N}])]$ and k_1 and 125; $k_{-1} = 273$; $k_2 = 547$; $k_3 = 40$; $k_{-3} = 250$; $k_4 = 202$. Initial rates are defined as the turnover frequency (TF) = moles of Et_2NPr produced/mole of $\text{Ru}_3(\text{CO})_{12}$ per hour. Reactions were run in methanol under 100 psig CO, at 160 °C; total volume was maintained at 5.0 mL.

standard conditions). Based on this result, a rate expression for (17) similar to (12) can be written as in (18).²⁹

$$19 \text{ h}^{-1} = d[\text{Pr}_2\text{NEt}]/dt = k_5 k_6 [\text{Pr}_2\text{NEt}] [\text{Et}_2\text{NPr}] / (k_{-5} + k_6 [\text{Et}_2\text{NPr}]) + k_7 k_8 [\text{Et}_2\text{NPr}] [\text{Pr}_2\text{NEt}] / (k_{-7} + k_8 [\text{Pr}_2\text{NEt}]) \quad (18)$$

At equilibrium, the forward rate in reaction 2 must equal the reverse reaction rate or the forward rate for reaction 18. Murahashi suggests that transalkylation equilibria approach a statistical distribution of alkylamines (73.3 mol % mixed alkylamines).⁹ However, transalkylation, as it occurs in (2) at 160 °C, consistently falls short (66–70 mol % mixed alkylamines) of the true statistical value. Furthermore, Murahashi never obtains higher than 66 mol % mixed alkylamines even though his experiments are performed at 200 °C. Consequently, we choose to consider 68 mol % mixed alkylamines as the true equilibrium mixture. Thus, for the reaction run at initial total amine concentration of $\sim 1.00 \text{ M}$ ($[\text{Et}_3\text{N}] = [\text{Pr}_3\text{N}]$), the equilibrium concentrations will be $[\text{Et}_2\text{NPr}] = [\text{Pr}_2\text{NEt}] = 0.34 \text{ M}$ and $[\text{Et}_3\text{N}] = [\text{Pr}_3\text{N}] = 0.16 \text{ M}$.

If we assume that k_6 and k_8 are similar to k_4 , we can approximate (18) by (19).

$$d[\text{Pr}_2\text{NEt}]/dt = (k_5 k_6 / k_{-5} + k_7 k_8 / k_{-7}) [\text{Pr}_2\text{NEt}] [\text{Et}_2\text{NPr}] \quad (19)$$

If the initial TF rate at $[\text{Et}_2\text{NPr}] = [\text{Pr}_2\text{NEt}] = \sim 0.50 \text{ M}$ is $19 \pm 3 \text{ h}^{-1}$, we can solve (19) for $k_5 k_6 / k_{-5} + k_7 k_8 / k_{-7} = 76 \text{ M}^{-1} \text{ h}^{-1}$. Therefore, at equilibrium, the TF for the back reaction (17) calculated from (19) is $\sim 8.8 \text{ h}^{-1}$.

The equilibrium TF for the forward reaction, (2), calculated from (12) by using the optimized values for the various rate constants, is 5 h^{-1} ; this value agrees with the calculated back reaction within the limits imposed by experimental error. Therefore, the kinetic behavior of reaction 2 can be predicted by using eq 12.

The results plotted in Figures 1 and 2 indicate that reaction 2 exhibits a complex rate dependence on both catalyst concentration and CO pressure; as such, the development of an exact rate expression for initial rates that allows for variations in catalyst concentration and CO pressure does not seem profitable at the present time. However, the effects of changes in CO pressure

(29) Where k_5 , k_{-5} , and k_6 correspond to transalkylation in which Pr_2NEt first binds to catalyst and k_7 , k_{-7} , and k_8 correspond to transalkylation where Et_2NPr binds first to catalyst.

and catalyst concentration on reaction rates are especially valuable in identifying some of the important mechanistic features of transalkylation catalysis.

Catalytic Cycle

Because tertiary amines and especially Et_3N can be readily oxidized by using various procedures, including electron transfer, to give the free iminium ion,³⁰ reaction 20, and because mecha-

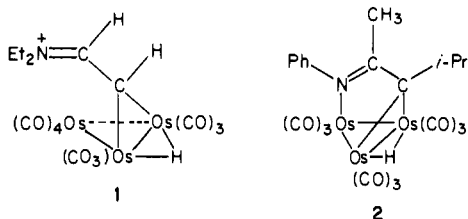


nisms that describe both D for H and transalkylation catalysis based on iminium intermediates can be written, the only role for M, the active metal complex, may be to serve as oxidant to generate free iminium. We do not believe that free iminium ions are actually involved in either catalytic cycle for the following reasons.

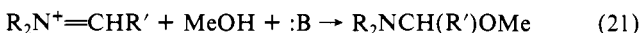
First, a free iminium must always give products containing at least one α deuterium; therefore, a free iminium species cannot generate the $\beta\beta\alpha$ deuterium-exchange pattern observed in the rhodium- or molybdenum-catalyzed reactions.

Second, if free iminium species are responsible for the products observed in the ruthenium-, osmium-, and Pd-black-catalyzed reactions, then the relative ratios of the deuterated products formed at low conversions should be the same. In the results published in ref 13 and 15, the initial ratios of the Et_3N -deuterated products for ruthenium, osmium, and Pd black are not particularly similar.

Third, the osmium-iminium complex **1**, isolated from the reaction of Et_3N with $\text{Os}_3(\text{CO})_{12}$,³¹ and the structurally characterized imine complex **2**³² conform to our proposed intermediates in $\alpha\beta\beta$ C-H activation/D for H exchange.



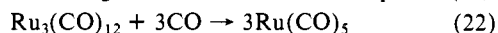
Fourth, although free iminium ions react rapidly in basic MeOH to give stable ether complexes, reaction 21,³³ GC-MS does not reveal the formation of such products under any reaction conditions thus far studied.



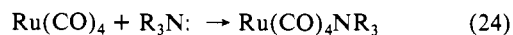
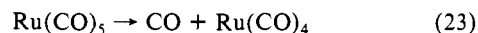
Fifth, added H_2O should promote transalkylation via iminium hydrolysis previously proposed.¹⁴ Under the conditions studied here, addition of H_2O even in small amounts only decreases the rate of transalkylation, as shown in Figure 4 (above). Thus, we conclude that both ruthenium-catalyzed C-H activation/D for H exchange and transalkylation must proceed through metal-amine complexes.

Below we discuss the sequence of events that leads to formation of these complexes and the transformations that occur during the catalytic cycle(s).

CO Pressure and Solvent Studies. Initiation of the catalytic cycle must begin with the creation of at least one site of unsaturation on the catalyst precursor. Two potential pathways to coordinative unsaturation can be envisioned based on the results of the CO pressure studies (Figure 1). One pathway involves formation of mononuclear catalyst species and the other pathway involves cluster species. If catalysis is promoted by mononuclear species, then the data are consistent, with the first step being CO-promoted cluster fragmentation to mononuclear species, (22).



This would account for the rate increases at low CO pressure. The mononuclear species then loses CO to become coordinatively unsaturated, (23), and catalytically active, (24). Reaction 23 would



be susceptible to CO inhibition and would account for the rate decreases observed at higher CO pressures.

Alternatively, if catalysis is promoted by a cluster species derived from $\text{Ru}_3(\text{CO})_{12}$, then the data are consistent with this species, being susceptible to decomposition at low concentrations of free CO. The decreases observed in catalyst activity that occur concurrent with continuing increases in CO pressure can then be explained in two ways. First, because catalyst activity depends on the formation of a coordinatively unsaturated site and because CO will compete with amine for these sites, a delicate balance will exist between catalyst stability and activity such that, at some point, increases in CO pressure will reduce catalyst activity. Second, if the cluster is susceptible to fragmentation, as in (22), and if the cluster is the only active species, then increases in CO pressure will eventually reduce the overall concentration of active catalyst species, thereby decreasing catalyst activity.

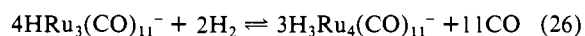
The latter explanation seems most likely because the catalyst does, in fact, decompose in all solvents in the absence of CO and only maintains its stability under CO pressure. Moreover, the results of the catalyst concentration studies point to the existence of a cluster catalyst.

The observation that low pressures of CO stabilize the catalyst system in both alcoholic and ether solvents but diminish catalyst activity in the ether solvent can be explained in terms of the formation of neutral vs. anionic clusters and the dissolution of these species in the various solvents. In alcoholic solvents, the catalyst precursor rapidly reacts to form homogeneous solutions containing anionic cluster species, including $\text{HRu}_3(\text{CO})_{11}^-$, $\text{H}_3\text{Ru}_4(\text{CO})_{11}^-$ (identified by IR), and other less stable species. In ether solvents in the absence of CO, the catalyst precursor reacts to give two phase solutions in which the major soluble species is $\text{Ru}_3(\text{CO})_{12}$ and an oily red precipitate that contains ammonium salts of the anionic species found in the alcoholic solutions. Under CO, the ether solutions become homogeneous but contain mostly neutral ruthenium carbonyls. In fact, $\text{Ru}_3(\text{CO})_{12}$ precipitates out when these solutions are allowed to stand overnight at room temperature.

These results suggest that the true catalyst species are anionic in nature, and their formation and stabilization are favored in protic solvents. In contrast, ether solvents must favor the formation and stabilization of catalytically inactive neutral carbonyls.

Catalyst Concentration Studies. Catalyst concentration studies should, as we have discussed at length elsewhere,³⁴ provide an indication of equilibria occurring between clusters and fragments. The catalyst concentration studies (Figure 2) show that the relative rate of catalysis increases with increasing amounts of added $\text{Ru}_3(\text{CO})_{12}$ up to a concentration of approximately 0.015 M and then begins to decline. As discussed previously, these results suggest that the active catalyst complex is a polynuclear species.

At concentrations above 0.015 M, the decrease in catalyst activity can be attributed to the formation of higher clusters that are either inactive or much less active than the smaller clusters. An example of this type of behavior is found in studies of ruthenium-catalyzed hydroformylation under water-gas shift conditions where equilibrium 22 is coupled to (25) and (26).^{18,35} In



this case, work by Suss-Fink et al. shows that the $\text{HRu}_3(\text{CO})_{11}^-$ species is the active catalyst and not the tetranuclear species. In keeping with these observations, in reaction 2 we observe formation of catalytically inactive $\text{Ru}_6\text{C}(\text{CO})_{16}^{2-}$ in high yield after extended

(30) Schanze, K. S.; Giannotti, C.; Whitten, D. G. *J. Am. Chem. Soc.* **1983**, *105*, 6326-6327 and references cited therein.

(31) Shapley, J. R.; Tachikawa, M.; Churchill, M. R.; Lashewyck, R. A. *J. Organomet. Chem.* **1978**, *167*, C39.

(32) Adams, R. D.; Selegue, J. P. *Inorg. Chem.* **1980**, *19*, 1795-1801.

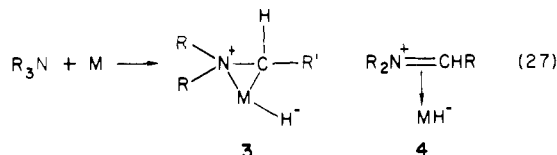
(33) Shono, T.; Matsumura, Y.; Inoue, K.; Ohmizu, H.; Kashimura, S. *J. Am. Chem. Soc.* **1983**, *104*, 5753-5757.

(34) Laine, R. M. *J. Mol. Catal.* **1982**, *14*, 137.

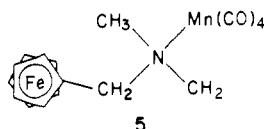
(35) Suss-Fink, G.; Reiner, J. *J. Mol. Catal.* **1982**, *16*, 231-242 and private communication.

reaction periods.³⁶ This observation proves that higher cluster species do form in the reaction solution. The question of the nuclearity of the active catalyst species is discussed in greater detail below.

C-H Bond Activation and Alkyl Transfer. Once a site of coordinative unsaturation forms, it is possible for an amine to bind at that site. Our D for H exchange studies indicate that following coordination of the amine-nitrogen electron pair, such as in (24), the metal can insert into an α C-H bond as shown in (27). We

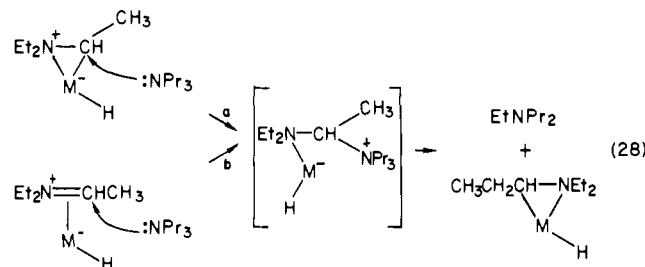


have previously argued that one cannot distinguish between the formation of a metallazacyclopropane, **3**, and an iminium ion complex, **4**.¹⁷ Both types of complexes are known to form in reactions of amines with transition metals. Kaesz et al.³⁷ have reported the formation of metallazacyclopropane, **5**, from re-

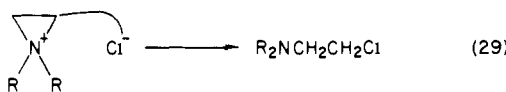


actions of dimethylferrocenylamine with $MeMn(CO)_5$, whereas Shapley et al.³¹ have reported the formation of the iminium osmium complex, **1**, from the reaction of Et_3N with $Os_3(CO)_{12}$, and Adams and Selegue³² have reported the formation of **2**, an imine complex, from the reaction of $H_2Os_3(CO)_{10}$ with an azadiene.

Two divergent steps leading to transalkylation could follow the insertion reaction. The simplest step, mechanistically, would be nucleophilic attack of free amine at the electron deficient carbon in either **3** or **4**, reaction 28, to give an intermediate monoammonium diaminomethane. Both reactions are conceivable



given that aziridinium compounds are susceptible to ring opening via attack by nucleophiles as weak as the chloride ion, (29).³⁸



Moreover, even imines, normally less electrophilic than the iminium species, are readily susceptible to attack by amine nucleophiles, (30), as evidenced by the works of Garrou,³⁹ Nicoletti,⁴⁰ Murahashi,²⁴ and Khai,⁴¹ thus providing support for pathway b of (28).

The fact that transalkylation is faster when Pr_3N binds to the active catalyst rather than when Et_3N binds to the catalyst suggests

(36) Product was identified by single-crystal X-ray diffraction studies, Wilson, R. B., Jr.; Cho, B. R.; Laine, R. M.; Fredricks, M., unpublished work.

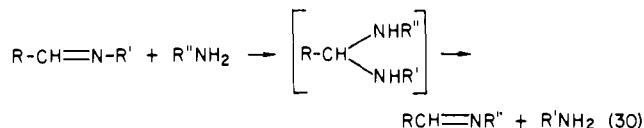
(37) Crawford, S. S.; Knobler, C. B.; Kaesz, H. D. *Inorg. Chem.* **1977**, *16*, 3201-3207.

(38) Cannon, J. G.; Gangjee, A.; Long, J. P.; Allen, A. J. *J. Med. Chem.* **1976**, *19*, 934.

(39) Jung, C. W.; Fellman, J. D.; Garrou, P. E. *Organometallics* **1983**, *2*, 1042-1044.

(40) De Angelis, F.; Grgurina, I.; Nicoletti, R. *Synthesis* **1979**, 70.

(41) Khai, B. T.; Concilio, C.; Porzi, G. *J. Org. Chem.* **1981**, *46*, 1759 and references cited therein.



that the difference in transalkylation reaction rates does not arise as a consequence of the nucleophilicity or steric bulk of the incoming (uncomplexed) amine. However, it appears to arise as a consequence of the relative stabilities of the intermediate complexes that form based on the fact that $k_1k_2 > k_3k_4$ even though $k_1k_{-1} > k_3k_{-3}$.

If the lifetime (relative concentration) of the metallazacyclopropane is greater for the Pr_3N complex than it is for the Et_3N complex, then alkyl transfer will proceed at a greater rate via the Pr_3N complex. The fact that the major deuteration products for Pr_3N , in the absence of transalkylation, are $Pr_2NCHDEt$ and $Pr_2NCHDCHDCH_3$ supports the idea that the Pr_3N metallazacyclopropane complex is preferred relative to a bridging carbene complex, e.g., **1**. For Et_3N , the major deuteration products are $Et_2NCHDCHD_2$ and $Et_2NCHDCD_3$. This suggests that for Et_3N a bridging carbene complex analogous to **1** is preferred to the metallacyclopropane complex. It also suggests that metallazacyclopropane species are the reactive intermediates in transalkylation.

At present, the exact process by which both alkyl groups are transferred between the two reacting nitrogen centers remains uncertain. It seems reasonable that the formation of at least one of the new C-N bonds occurs by nucleophilic attack of the uncomplexed amine on an α carbon bound to a metal, giving the monoammonium salt of a diaminomethane. When transalkylation is run in CD_3OD , extensive deuteration of the starting amines occurs before significant quantities of transalkylation products form. The transalkylation products that do form initially are selectively deuterated. Thus, at low conversions we observe mostly $Et_2NPr-d_{1,2}$ and $Pr_2NEt-d_{3,4}$. Because $Et_2NPr-d_{1,2}$ must arise from Et_3N and $Pr_2NEt-d_{3,4}$ from Pr_3N , which normally form $Et_3N-d_{3,4}$ and $Pr_3N-d_{1,2}$, we conclude that the transferred alkyl group is the one that originally binds to the cluster. A further conclusion is that both amines must bind and undergo C-H activation during or before the alkyl-transfer step in order for both products to be deuterated.

Still another mechanism for transalkylation is also possible. In this mechanism the metallazacyclopropane intermediate **3** opens up to give a metal-bound amide and a carbene, $Et_2N-M_x=CHCH_3$, which subsequently undergoes attack by Pr_3N to give $Et_2N-M_x=CHCH_2CH_3$ and Pr_2NEt . Work by Angelici et al.⁴² on reactions of metal-carbene complexes with nucleophiles suggests that such a mechanism is possible. Moreover, recent work by Balch et al.⁴³ shows that ruthenium can break carbon-nitrogen bonds to give a metal-carbene species.

Catalyst Nuclearity. We have previously shown that there is an exceptionally good correlation between the catalytic reactivity patterns of palladium black in its reactions with tertiary amines and those of homogeneous ruthenium and osmium catalysts with the same amines;¹⁵ therefore, Murahashi's mechanistic arguments concerning Pd-black-catalyzed D for H exchange and transalkylation catalysis^{9-11,24} have considerable bearing on the work described here.

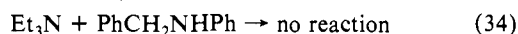
Murahashi proposes that catalytic activation of tertiary amines by palladium black is initiated by formation of a palladium-iminium complex.^{9,11,24} Catalytic deuteration of tertiary amines then proceeds via reversible isomerization of the initially formed palladium-iminium complex to a palladium-enamine complex as shown in Scheme II.

There appear to be two difficulties with this conceptualization. First, it is reasonable to envision the formation of **6** in the context of a normal organometallic complex of palladium because it would be an 18-electron species. However, **6** presumably depicts the

(42) Motschi, H.; Angelici, R. J. *Organometallics* **1982**, *1*, 343-349.

(43) Chan, Y.-W.; Wood, F. E.; Renner, M. W.; Hope, H.; Balch, A. L. *J. Am. Chem. Soc.* **1984**, *106*, 3380-3381.

transalkylation in anhydrous alcoholic media. However, in aqueous media the reaction does proceed but not in the absence of benzaniline or benzaldehyde.



$\text{Fe}(\text{CO})_5$ does not catalyze C for H exchange on aliphatic amines.⁴⁹ Consequently, in (35) benzaldehyde must activate the catalyst and/or the amine to promote transalkylation perhaps by electron transfer. We have independently noted that we can promote transalkylation and reaction (35) by using *ruthenium catalysts and water* with mononuclear ruthenium catalysts.⁴⁹ Deuteration and product selectivity studies reveal an additional and different transalkylation mechanism that can be promoted in the presence of H_2O . This mechanism appears to be quite different from the mechanism described here, which works best

(49) Blum, Y.; Wilson, R. B.; Laine, R. M.; Shvo, Y., unpublished results.

in the *absence of water* (see Figure 4) and under CO.

We will report on the second mechanism together with some anomalies noted in the above studies at a later date.⁴⁹

Acknowledgment. We thank Prof. H. Kaesz for graciously sending us a copy of his manuscript before publication, Prof. C. P. Casey for several enlightening comments on the proposed mechanism, and Dr. Ripudaman Malhotra for many valuable discussions. The major portion of this work was generously supported by the Army Research Office through Contract DAAG29-81-K-0086. A portion of this work was supported through NSF Chemical Engineering Grant 82-19541.

Registry No. $\text{Ru}_3(\text{CO})_{12}$, 15243-33-1; $\text{Fe}(\text{CO})_5$, 13463-40-6; Me_3N , 75-50-3; Et_3N , 121-44-8; Pr_3N , 102-69-2; *N,N,N',N'*-tetramethylethylenediamine, 110-18-9; *N,N*-dimethylpiperazine, 106-58-1; *N,N,N',N'*-tetraethylethylenediamine, 150-77-6; *N,N,N',N',N''*-pentaethyldiethylenetriamine, 24426-21-9; *N,N,N',N',N'',N'''*-hexaethyldiethylenetetramine, 24426-32-2; perethyltetraethylenepentamine, 93783-07-4.

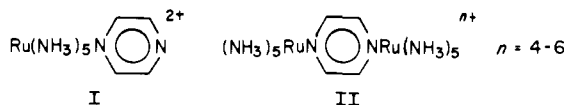
Aqueous Solution Chemistry of μ -Pyrazinepentaammineruthenium(II,III) Pentacyanoferrate(II,III): Formation, Redox Reactions, and Intervalence Properties¹

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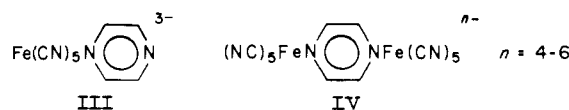
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Abstract: Several pyrazine (pz) bridged binuclear complexes of the general formula $(\text{NC})_5\text{MpzM}'(\text{NH}_3)_5^n$ were prepared in aqueous solution via the substitution reactions $\text{M}(\text{CN})_5\text{OH}_2^{m-} + \text{M}'(\text{NH}_3)_5\text{pz}^{n+} = (\text{NC})_5\text{MpzM}'(\text{NH}_3)_5^n$, where $\text{M} = \text{Fe}(\text{II,III})$ or $\text{Co}(\text{II,III})$ and $\text{M}' = \text{Ru}(\text{II,III})$ or $\text{Rh}(\text{III})$. All the complexes containing Fe(II) and/or Ru(II) are intensely colored substances, displaying a metal-to-ligand charge-transfer band in the 500–600-nm region. Rate constants for the formation and dissociation of the binuclear complexes with $\text{M} = \text{Fe}(\text{II})$ were measured. Selected redox reactions of two of the binuclear complexes, namely, $(\text{NC})_5\text{FepzRu}(\text{NH}_3)_5^n$ (V) ($n = 1-, 0$), were studied in some detail. Cyclic voltammetry of V ($n = 1-$) shows that its oxidation proceeds in two one-electron steps at 0.72 and 0.49 V, respectively. Chemical oxidation of V ($n = 1-$) with peroxydisulfate (second-order reaction with rate constant $(3.79 \pm 0.04) \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ at 25 °C, pH 4.28, and ionic strength 0.10 M) yields V ($n = 0$). The latter complex exhibits its metal-to-ligand charge-transfer band at 590 nm with molar absorbance $\sim 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ and an intervalence band (in D_2O) at 1650 nm with molar absorbance $1.55 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ and half-width $0.43 \mu\text{m}^{-1}$. Spectroscopic, electrochemical, and kinetic data on V ($n = 0$) are interpreted on the basis of a trapped valence formulation containing the localized oxidation states Fe(II) and Ru(III). The stability of the mixed valence state V ($n = 0$) with respect to electronic isomerization (V with $n = 0$ but with localized valences Fe(III) and Ru(II)) and with respect to disproportionation to form the isoivalent states V ($n = 1-$) and V ($n = 1+$) is discussed in some detail.

The feature that dominates the chemistry of the pentaammineruthenium(II) moiety is its ability to enter into π -bonding interactions with appropriate ligands, e.g., dinitrogen,² pyridines,³ and nitriles.⁴ One of the consequences of the π -donating ability of $\text{Ru}(\text{NH}_3)_5^{2+}$ is the increased basicity² of the remote nitrogen atom in I. This led to the syntheses⁵ of the binuclear complexes



II. Since then a great deal of work has been devoted to this system, in particular to the mixed valence ion with $n = 5$.⁶ The nitrogen heterocyclic chemistry³ of $\text{Ru}(\text{NH}_3)_5^{2+}$ has been duplicated⁷ with the isoelectronic moiety $\text{Fe}(\text{CN})_5^{3-}$. In particular, the basicity of the remote nitrogen in III was noted,⁷ and the syntheses of the binuclear complexes IV were reported.⁸



In the work referenced above, the primary concerns have been synthetic and structural.⁶ In particular, the electronic structures of the mixed valence ions have been the subject of much work.⁶ In view of our long standing interest in the dynamic solution

(1) This work was supported by Grants CHE 79709253 and CHE 8203887 from the National Science Foundation.

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