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ORGANOMETALLICS IN HIGH ENERGY CHEMISTRY

Final Report

October 1983

By: Richard M. Laine, Donald A. Levins,
and Clifford D. Bedford

Prepared for:

U.S. ARMY RESEARCH OFFICE
P.O. Box 12211
Research Triangle Park, NC 27709

Attention: Dr. G. Ronald Husk

Contract No. DAAG29-81-K-0086

SRI International Project PYU-3545

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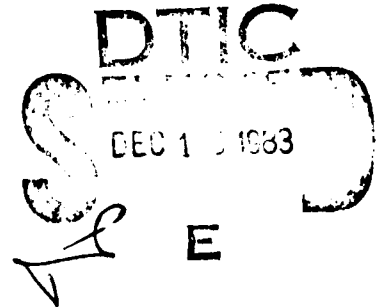and Clifford D. Bedford

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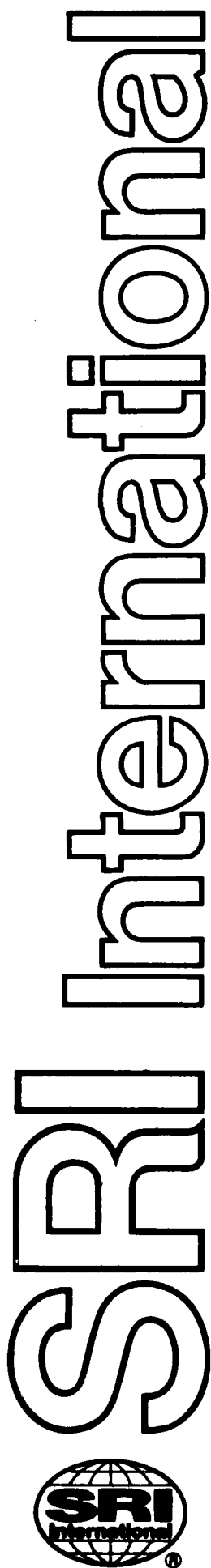SRI International Project PYU-3545

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catalysis	ruthenium	aluminates
homogeneous	silicon-nitrogen bonds	
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transalkylation	polysilazanes	→ Developed Are

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We have developed new synthetic strategies for the synthesis of polymethylene-imine precursors to RDX and HMX through the use of homogeneous catalysts based on ruthenium and; ruthenium and iron mixtures. These catalysts have proved effective for the oligomerization and cyclization of tertiary diaminoalkanes at temperatures and rates superior to the heterogeneous palladium black catalyzed reactions previously reported. Under somewhat different conditions, these same catalysts will cleave and reform Si-N bonds. Activation of Si-N bonds has been found useful in several organic syntheses. In an effort to understand why palladium black is →

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was Developed.

less effective than the homogeneous catalysts, ~~we have developed~~ an understanding of how Lindlar catalysts function. In addition, ~~we have been able to develop~~ a comprehensive picture of how other heterogeneous catalysts especially hydrodenitrogenation catalysts interact with nitrogen containing organics was peveloped.
Were Explored.

In unrelated studies, ~~we have explored~~ synthetic methods for preparing nitroalkoxyaluminates with the objective of developing air and moisture stable high energy organometallics. ~~We find that~~ For β-nitro alkoxy aluminates, air and moisture sensitivity decreases significantly with increasing numbers of β-nitro groups.

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CONTENTS

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STATEMENT OF THE PROBLEM STUDIED

In the last 20 years, the fields of organometallic chemistry and homogeneous catalysis chemistry have undergone explosive growth. This growth has resulted in the synthesis of numerous new organometallic compounds and many methods of using these compounds as homogeneous catalysts for the synthesis of a tremendous variety of organic compounds. Despite the exceptional growth in these two areas, there has been little application of the discoveries in these areas to the development of new high energy compounds or to new synthetic routes to provenor the synthesis of a tremendous variety of organic compounds. Despite the exceptional growth in these two areas, there has been little application of the discoveries in these areas to the development of new high energy compounds or to new synthetic routes to proven high energy compounds.

In the past two years, we have attempted to expand the scope of organometallic synthesis to include the synthesis of high energy organometallic compounds. In addition, we have sought to apply homogeneous catalytic systems recently discovered in these laboratories to develop novel synthetic routes to polymethyleneimine compounds that can be used as intermediates in the preparation of nitramines, in particular RDX and HMX. The results of our efforts are reported in the following sections.

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SUMMARY OF RESULTS

At the inception of this project, the two areas of specialization were separated into two tasks: Task 1, Amine Catalysis Chemistry, and Task 2, Organometallic Explosives. The following discussions maintain this convention to provide continuity with our previous reports.

Task 1. Amine Catalysis Chemistry

Our original strategy for preparing polymethyleneimine compounds that could be used as intermediates in the synthesis of RDX and HMX was based on our discovery that we could catalyze the transalkylation reaction, as illustrated by reaction (1).

$$Et_3N + Pr_3N \xrightarrow{\text{catalyst}} Et_2NPr + Pr_2NEt \qquad (1)$$

Catalyst = $Ru_3(CO)_{12}$, $Os_3(CO)_{12}$, $Rh_6(CO)_{16}$, $Ir_4(CO)_{12}$, Pd black

This strategy involved the idea that diamine compounds could be used, as in reaction (1), to provide polyamine compounds, as shown in reaction (2):

$$xR_2N(CH_2)_yNR_2 \xrightarrow{\text{catalyst}} \begin{array}{c} xR_3N + R-[N(R)(CH_2)_y]_x-NR_2 \\ \\ (R)N[(CH_2)_yNR]_x \end{array} \qquad (2)$$
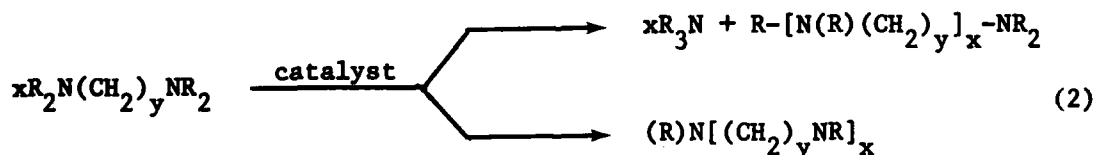
We anticipated that, with the proper choice of starting diamines, the reactions would produce the desired polymethylene amine compounds. Therefore, we investigated two approaches to preparing HMX precursors via reaction (2).

The ease of hydrolyzing a trimethylsilyl amine prompted us to examine this functional group as a potential HMX precursor, as in

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compound $\underline{1}$;

$$(Me_3Si)_2NCH_2N(SiMe_3)_2 \xrightarrow{\text{catalyst}} \overset{\displaystyle SiR_3 \quad SiR_3}{\underset{\displaystyle \underline{1}}{\boxed{CH_2-[N-CH_2]_x N}}} \qquad (3)$$
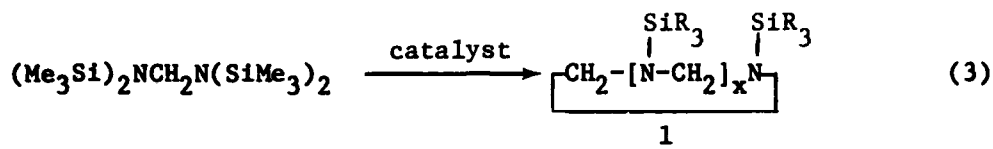
removed via hydrolysis with water, reaction (4):

$$\boxed{CH_2-[N-CH_2]_x \overset{SiR_3 \quad SiR_3}{N}} + H_2O \longrightarrow (Me_3Si)_2O + \boxed{[CH_2-N]_x^{H}} \qquad (4)$$

Thus, in one approach, the catalysis chemistry of silicon "protected" diamines was investigated. The most important results of this work are described in Appendix A. One important finding was the discovery that the catalyst was capable of activating Si-N bonds at a much faster rate than C-N bonds. Consequently, the approach exemplified by reaction (3) was not feasible. However, the activation of Si-N bonds opened up an entirely new set of routes to HMX intermediates based on Si-N bond chemistry, which were described in 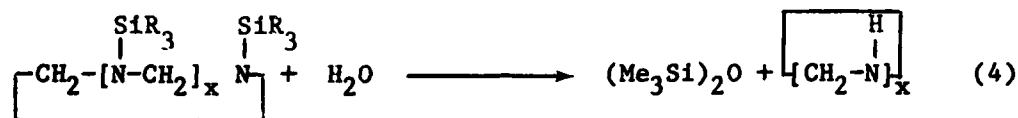the last progess report and will not be detailed here. Furthermore, as noted in Appendix A, our discovery of the catalytic activation of Si-N bonds has provided a novel means to make Si-N polymers, which have exceptional potential as precursors to silicon-carbide-nitride fibers, space-age ceramic fibers with very high-strength/low-weight properties.

Our second approach consisted of conducting kinetic studies on catalysis of reaction (1) in order to develop a complete kinetic and mechanistic understanding of how the reaction proceeds and how it might be best applied to effecting reaction (2). This work, which is detailed in Appendix B, has been exceptionally rewarding. Briefly, we studied the homogeneous ruthemium-catalyzed transalkylation of tertiary amines and derived a kinetic expression for transalkylation catalysis based on initial reaction rates.

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The pertinent discoveries made in the work described in Appendix B are as follows:

- Alcohol solvents maintain the stability of the ruthenium catalyst system when the reaction is run under slight pressures of CO.

- Mixtures of iron and ruthenium carbonyl catalysts give significantly higher transalkylation catalyst activities than the ruthenium system alone even though iron carbonyl by itself is inactive.

- We can successfully oligomerize N,N,N',N'-tetraethyl-ethylenediamine without loss of catalyst activity and we can successfully cyclize the tetramethyl derivative to give six-membered rings in high yield.

In addition, a remarkable reaction was discovered that oligomerizes the ethyl groups in Et_3N. Unfortunately, this work is not complete and cannot be discussed here.

We presently plan to apply for patents based on the silicon work and on the new mixed-metal catalyst systems.

We developed a comprehensive mechanistic picture for heterogeneous catalysis leading to hydrodenitrogenation. (HDN is the process by which nitrogen is removed (as NH_3) from crude oil, coal, oil shale, or tar sands during the refining process.) Appendix C is one of the three papers currently in press.

The kinetic and mechanistic studies provided us with an explanation for how C-N bond cleavage occurs during HDN. With this explanation we were also able to explain several of the heretofore inexplicable anomalies of HDN. For example, we were able to clarify why the normal catalyst poison, H_2S, has such a positive effect on HDN catalysis.
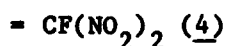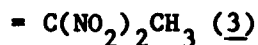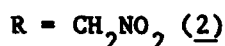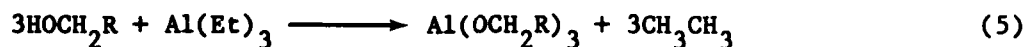
We also became involved in trying to understand transalkylation catalysis by palladium black, a heterogeneous catalyst. We have previously proved that its catalytic actions are much like those of ruthenium. We have been able to show that palladium black catalysts rapidly lose their catalytic activity via an extremely unusual low temperature sintering process, as described in Appendix D.

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In addition, we synthesized a nickel trinitromethide compound and examined the bonding in the methide anion, (see Appendix E.) We found that the anion has a beta-diketonate structure rather than a completely symmetrical structure, as previously reported. This suggests that with the proper choice of metals the trinitro-methide could be used to synthesize organometallic explosives, the subject of Task 2.

Task 2. Organometallic explosives

Nitroalkoxy Aluminates

We attempted the syntheses of nitroalkoxy aluminates following the procedures for known compounds to determine what interaction may occur between the covalently bonded aluminum atoms and nitro substituents. Three previously unreported nitroalkoxy aluminates were prepared as shown in reaction (5):

$$3HOCH_2R + Al(Et)_3 \longrightarrow Al(OCH_2R)_3 + 3CH_3CH_3 \qquad (5)$$

$$R = CH_2NO_2 \quad (\underline{2})$$

$$= C(NO_2)_2CH_3 \quad (\underline{3})$$

$$= CF(NO_2)_2 \quad (\underline{4})$$

No aluminum-nitro group interactions were indicated by the infrared spectra of these products. The nitroalkoxyaluminates $\underline{3}$ and $\underline{4}$ detonated with moderate hammer blows. Decomposition on exposure to air decreased with increasing substitution, with compound $\underline{2}$ being the most sensitive and compound $\underline{4}$ the least sensitive; these compounds also survived several hours of exposure at ambient environment. This trend suggests that air-stable nitroalkyl and nitroalkoxy aluminates are possible.

Further evidence of stable alanes was found in the literature, where preparation of the following air-stable aluminum compounds is described:

5

```
            Ph                                    tBu
      Ph     |    Ph                               |
        \    C    /                   iBu     0        iBu
Me        \ / \ /      Me                \   /  \   /
    \     Al   Al    /          iBu        Al      Al        iBu
Me  /     / \ / \     \  Me       \       /  \   /  \       /
          C                       iBu     0        iBu
      Ph  |   Ph                          |
          Ph                             tBu
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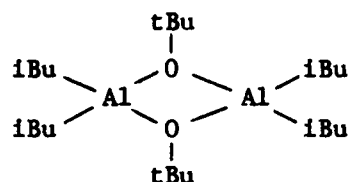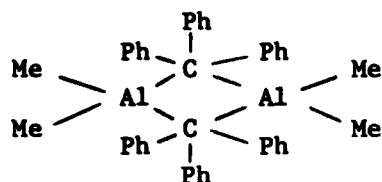
Nuclear magnetic resonance spectra of alkoxides 2 through 4 su ᵧ. they
exist in monomeric form even in nonpolar solvents, unlike similar
aluminum alkyls and alkoxides. Compounds 2 through 4 form 1:1 complexes
with xanthone. The carbonyl adsorptions (IR) provide further evidence
that the inductive effect of nitro substituents is comparable to that of
halo substituents. The results of this work are described in more
detail in Appendix F.

The stability toward hydrolysis of a polymeric aluminum nitro-
alkoxide was examined briefly with preparation of an aluminum,
2,2-dinitro-1,3-propanediol condensation polymer. The polymer, isolated
as a white powder, was impact sensitive and qualitatively, was less
sensitive to hydrolysis than tris(2,2-dinitropropoxy)aluminum.

Several different routes to nitroalkylaluminates were explored.
First we tried to use the previously prepared nitroalkoxy aluminates by
inserting a methylene group between the central aluminum atom and alkoxy
group oxygen, as shown in reaction (6).

$$Al(OR_{NO_2})_3 + 3CH_2N_2 \longrightarrow Al(CH_2OR_{NO_2})_3 + 3N_2 \qquad (6)$$
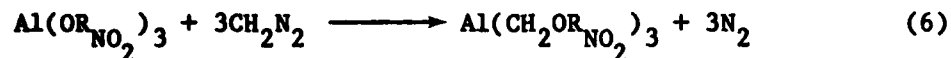
This insertion reaction was found to occur in the alkyl and haloalkoxy
aluminates, but not in the aluminum alkoxides. Mixtures of diazomethane
and nitroalkoxyaluminates failed to react. Because the electronic
environment at the reaction site should parallel that in the haloalkoxy-
aluminates and because the difference in steric hindrance between the

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halo and nitroalkoxyaluminates is probably not appreciable, continued attempts under a wide range of conditions may well prove successful.

The second route explored involved the well known addition of an aluminum alkyl to a double bond, as shown in reactions (7) and (8). Our

$$Al(iBu)_3 + CH_2=CHCH_2CH_3 \longrightarrow (iBu)_2Al(CH_2)_3CH_3$$
$$+ \qquad\qquad (7)$$
$$CH_2=C \underset{CH_3}{\overset{CH_3}{\diagup}}$$

$$(iBu)_2AlH + CH_2=CHCH_2CH_3 \longrightarrow (iBu)AlCH_2CH_2CH_2CH_3 \qquad (8)$$
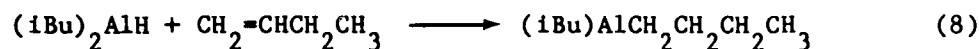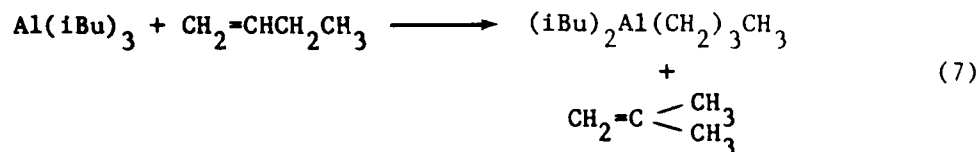
attempts to add diisobutylaluminumhydride and triisobutylaluminum to 4-nitro-1-butene resulted in no reaction. Although it is tempting to attribute failure of this reaction to the effect of an electronegative substituent and the double bond, this hypothesis should be tested, under more vigorous conditions.

The final route explored was the reaction between elemental aluminum and nitroalkylhalides, as shown in reaction (9).

$$Al^\circ + 3BrCH_2CH_2NO_2 \longrightarrow AlBr_3 + Al(CH_2CH_2NO_2)_3 \qquad (9)$$
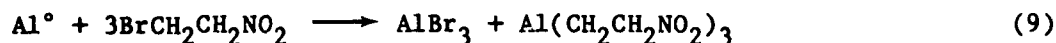
When simple alkylhalides are used, the reaction is normally vigorous, but sometimes difficult to start.

Energetic Chelates

In a separate approach our purpose was to demonstrate the feasibility of synthesizing new organometallic materials with an emphasis on developing general synthesis routes to high energy organometallics, and on determining correlations between chemical and physical properties. An exhaustive literature study of reactions useful in the synthesis of energetic organometallics offered little new information. Based on what literature was available, three research

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topics were explored:

- Complexation of energetic malonate ligands with various transition metals.

- Design and synthesis of energetic ligands for subsequent complexation based on the acetylacetone (AcAc) backbone.

- Stabilization of the aluminum-carbon (Al-C) bonds through intramolecular or intermolecular coordination.

Several research groups have investigated the coordination of beta-diketones and beta-keto esters as oxygen-donor chelating ligands.[1-9] These complexes are generally prepared as mixed ligand complexes of Co(II), Cu(II), Zn(II), and Ni(II) ions with malonic esters and nitrogen donor alkyl, aryl, or heterocyclic amines. We attempted to expand the scope of this reaction to energetic malonate ligands, such as $CH_2[CO_2CH_2CF(NO_2)_2]_2$ and $CH_3[CO_2CH_2C(NO_2)_3]_2$, which were readily available via existing synthesis routes.[10,11] Unfortunately, all attempts to coordinate the energetic malonates with either Ni(II) or Co(II) failed. The free malonates were generally recovered, or, if stringent conditions and protic solvents were used, hydrolysis or transesterification of the malonates was observed. Work on this still attractive concept was halted, however, in favor of the work on the synthesis and reactions of energetic acetylacetone ligands.

The design of energetic ligands for metal complexation centered on the acetylacetone (AcAc) backbone because of the wealth of literature concerning synthesis, complexation, and reactions of these systems.[12-15] We developed a synthesis route to the bis-ketal of 1,5-diazido-2,4-pentanedione (5), as shown in Scheme I

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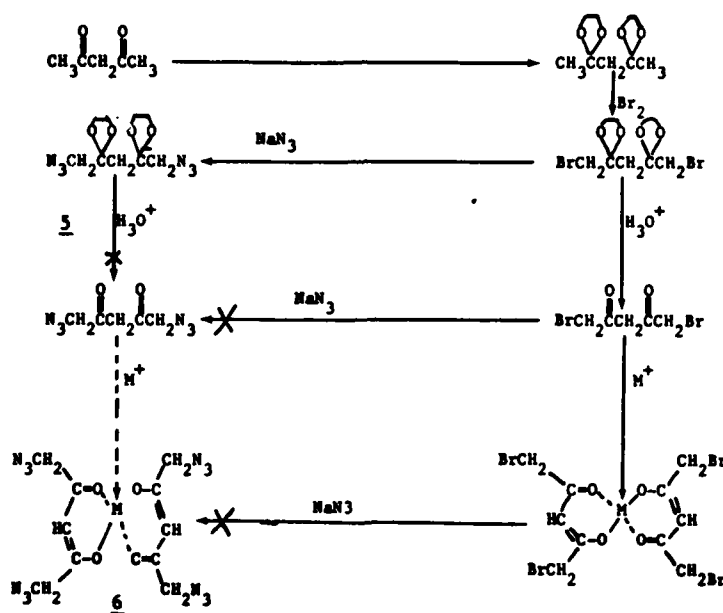
SCHEME I

All the routes to the desired complex 5 were stymied by the failure of
key reactions as shown in the scheme. A similar series of reactions was
used in an attempt to prepare the analogous 2,6-dibromo-3,5-heptanedione
or the corresponding bis-ketal. Unfortunately, the bromination that
liberates HBr as a by-product yielded numerous decomposition products.
Further transformation of the crude reaction mixture and attempted
purification proved fruitless. Although the dibromo bis-ketals under-
went rapid acid hydrolysis, the corresponding azido compounds were
resistant to acid-catalyzed hydrolysis. This failure to obtain the free
diketones, coupled with the three-week reaction time required to
complete azido displacement of bromine forced us to consider alternative
research directions.

9

LIST OF PUBLICATIONS AND TECHNICAL REPORTS PUBLISHED

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7. "The Transalkylation Reaction. Homogeneous Catalytic Formation of C-N Bonds. 3," R. M. Laine and R. B. Wilson, Jr., submitted to J. Am. Chem. Soc.

8. "Tris(bipyridyl)nickel Bis(trinitromethanide)," R. M. Laine, M. F. Fredrich, R. B. Wilson, Jr., A. S. Hirschon, R. Malhotra, submitted to Inorg. Chem.

9. "Homogeneous Catalytic Disproportionation of Triethylamine," R. B. Wilson, Jr., and R. M. Laine, manuscript in preparation.

10. "Preparation and Properties of Aluminum Nitroalkoxides," D. A. Levins, manuscript in preparation.

SCIENTIFIC PERSONNEL SUPPORTED BY THIS PROJECT

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Appendix A

HOMOGENEOUS CATALYTIC FORMATION OF CARBON-NITROGEN
BONDS.   2.   CATALYTIC ACTIVATION OF THE SILICON-
NITROGEN BOND

Homogeneous Catalytic Formation of Carbon–Nitrogen Bonds. 2. Catalytic Activation of the Silicon–Nitrogen Bond[†]

M. T. Zoeckler and R. M. Laine*

Physical Organic Chemistry Department, SRI International, Menlo Park, California 94025

The catalytic formation of new carbon–nitrogen single bonds can be promoted via catalytic activation of silicon–nitrogen bonds. Silazanes, compounds containing Si–N bonds, will react, in the presence of a catalyst, with compounds containing carbon–oxygen double bonds to form new C–N and Si–O bonds concurrently. Thus, CO_2 and phenyl isocyanate can be reacted with a number of silazane compounds to give urethane and urea derivatives in 60–90% yields. In the absence of catalysts, the identical reactions either do not proceed or go to less than 20% conversion. Aldehydes and ketones also react in a similar manner to give imines and enamines, respectively. A variety of group 8 metals have been found to activate the Si–N bond in the catalytic formation of PhCH=NPh from PhNHSiMe₃ and PhCHO. Iron and rhodium catalysts were found to be the most active for this reaction. The catalytic activation of Si–N bonds was also found useful in the ring-opening oligomerization of $\overline{-[(CH_3)_2SiNH]_4-}$ in the presence of $(Me_3Si)_2NH$.

The chemistry that is the subject of this preliminary report arises as a result of our continuing interest in developing new catalytic methods for the formation of C–N bonds. A second directive for pursuing the following studies was the knowledge that silicon compounds are

excellent oxygenophiles, and, as such, the formation of Si–O bonds could be the driving force that promotes catalytic reactions. Consequently, our initial goal was to develop simple catalytic reactions in which C–N and Si–O bonds are formed simultaneously.

One logical approach was envisioned in which compounds containing Si–N bonds (silazanes) were reacted with compounds containing C–O multiple bonds via cat-

[†] Previous paper in this series: Laine, R. M.; Cho, B. R.; Wilson, R. B., Jr. *J. C, Mol. Chem.*, in press.

Chart I

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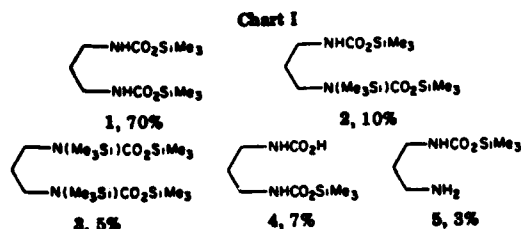
alytic activation of the Si–N bond. Although $\mathcal{c}$. reactions are known to occur in some instances in the absence of catalysts,[1,2] a search of the literature did not reveal any examples of catalytic activation of the Si–N bond, despite the fact that silicon compounds have been shown to participate in a wide variety of catalytic reactions. A review by Curtis[3] indicates that one can catalytically cleave and reform (redistribute) silicon–oxygen, silicon–halogen, silicon–hydrogen, silicon–carbon, and even silicon–silicon bonds.[3] Thus, it seemed reasonable to expect that Si–N bonds could also be catalytically activated.

In a recent paper, Süss-Fink[4] reported that the ruthenium-catalyzed hydrosilylation of carbon dioxide, CO_2, gave good yields of silyl formates (eq 1). These results

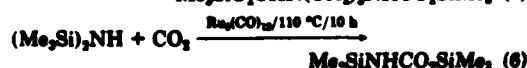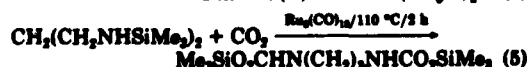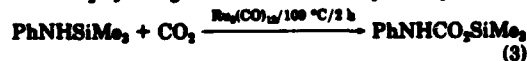$$Et_3SiH + CO_2 \longrightarrow HC(O)OSiEt_3 \qquad (1)$$

suggested that it might be possible to catalyze a similar reaction by substituting silazanes for silanes to form silylurethanes (eq 2). Such a reaction would result in the

$$(R_3Si)_2NH + CO_2 \longrightarrow R_2NHC(O)OSiR_3 \qquad (2)$$

simultaneous formation of C–N and Si–O bonds and serve as a test case for our two directives.

Results and Discussion

We report here reactions, which are the first examples of transition-metal-promoted catalytic activation of the Si–N bond, that may be of use to the synthesis chemist. We also describe several previously unknown reactions that may be of exceptional promise to the polymer chemist. As indicated in reactions 3–6, it is possible to catalytically promote the formation of C–N bonds by reacting silazanes with CO_2 by using a ruthenium carbonyl catalyst.

$$PhNHSiMe_3 + CO_3 \xrightarrow{Ru_3(CO)_{12}/100\ ^\circ C/2\ h} PhNHCO_2SiMe_3 \qquad (3)$$

$$PhNHSiMe_3 + CO_2 \xrightarrow[THF]{Ru_3(CO)_{12}/110\ ^\circ C/10\ h} PhNHC(O)NHPh + (Me_3Si)_2O \qquad (4)$$

$$CH_2(CH_2NHSiMe_3)_2 + CO_2 \xrightarrow{Ru_3(CO)_{12}/110\ ^\circ C/2\ h} Me_3SiO_2CHN(CH_2)_3NHCO_2SiMe_3 \qquad (5)$$

$$(Me_3Si)_2NH + CO_2 \xrightarrow{Ru_3(CO)_{12}/110\ ^\circ C/10\ h} Me_3SiNHCO_2SiMe_3 \qquad (6)$$

Rhodium [as $Rh_6(CO)_{16}$] can also be used in reactions 3–6. The crude yields for these reactions are 60–90%, with the isolated yields being somewhat less. Blank reactions run in the absence of catalyst gave less than 20% conversion and in the case of eq 4 gave only small amounts of the urethane observed in eq 3.
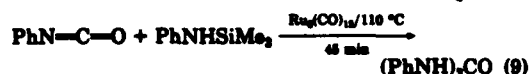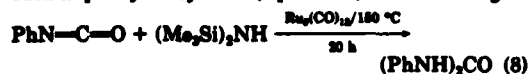
A more in-depth analysis of reaction 5 provides some interesting observations. For example, GC/MS analysis of the products gives the product distribution shown in Chart I.

The starting material $[CH_2(CH_2NHSiMe_3)_2]$ is pure according to GC/MS analysis; therefore, the origin of compounds 2–5 must result from exchange of Me_3Si groups as exemplified by reaction 7.

$$2CH_2(CH_2NHCO_2SiMe_3) \longrightarrow$$

$$\qquad + \qquad (7)$$
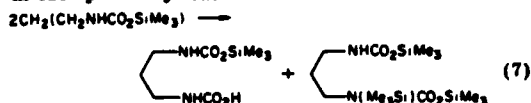
This observation is surprising in view of the fact that silicon–oxygen bonds (bond dissociation energy = 128 kcal/mol) are substantially stronger than silicon–nitrogen bonds (bond dissociation energy = 100 kcal/mol).[5] It seems reasonable to assume that carboxyl substitution on the nitrogen atoms in 1 enhances the electronegativity of the nitrogen sufficiently to promote formation of an unusually strong silicon–nitrogen bond, which accounts for formation of 2–5.[6]
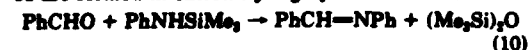
The next step in our study was to use a CO_2 analogue such as phenyl isocyanate (eq 8 and 9). Reaction 8 goes

$$PhN{=}C{=}O + (Me_3Si)_2NH \xrightarrow[20\ h]{Ru_3(CO)_{12}/130\ ^\circ C} (PhNH)_2CO \qquad (8)$$

$$PhN{=}C{=}O + PhNHSiMe_3 \xrightarrow[45\ min]{Ru_3(CO)_{12}/110\ ^\circ C} (PhNH)_2CO \qquad (9)$$

to completion in 45 min, whereas the blank reaction (without catalyst) gives no product under the same conditions after 2 days.

The mechanism by which diphenylurea forms in eq 8 or 9 is unclear at present. It is disconcerting that the product is always diphenylurea because one would expect to obtain at least a silylated analogue of diphenylurea in reaction 9.[2] However, the expected intermediate, PhN(Me₃Si)C(O)NHPh, is known to silylate such weakly acidic hydrogens as those in malonate ester.[5c] Moreover, given our observations on reaction 5, it is likely that the intermediate silylates the remaining $PhNHSiMe_3$ to produce $PhN(Me_3Si)_2$. Furthermore, as noted in the Experimental Section, we isolate, in low yield, a compound whose spectral characteristics suggest that it is the compound PhN[C(O)NHPh]₂. This compound would result from reaction of the proposed intermediate PhN(Me₃Si)C(O)NHPh with a second PhN=C=O followed by Me₃Si for H exchange.

With simpler, but perhaps more useful reactants, considerable rate enhancements were observed in the ruthenium-catalyzed reactions relative to the uncatalyzed reactions. Thus, the imine in eq 10 and the enamine in eq 11 are formed in extremely high yield under conditions

$$PhCHO + PhNHSiMe_3 \rightarrow PhCH{=}NPh + (Me_3Si)_2O \qquad (10)$$

$$CH_3C(O)CH_2CH_3 + PhNHSiMe_3 \xrightarrow[20\ h]{Ru_3(CO)_{12}/100\ ^\circ C} CH_3C(NHPh){=}CHCH_3 + (Me_3Si)_2O \qquad (11)$$

(1) (a) Comi, R.; Franck, R. W.; Reitano, M.; Weinreb, S. M. *Tetrahedron Lett.* 1973, 33, 3107–9. (b) Selin, T. G. U.S. Patent *Chem. Abstr.* 1972, 76, 46258e.

(2) Morton, D. W.; Neilson, R. H. *Organometallics* 1982, 1, 289–96.

(3) Curtis, M. D.; Epstein, P. S. *Adv. Organomet. Chem.* 1981, 19, 213–56.

(4) Süss-Fink, G.; Reiner, J. *J. Organomet. Chem.* 1981, 221, C36–8.

(5) (a) Walsh, R. *Acc. Chem. Res.* 1981, 14, 246–52. (b) Rochow, E. G. *Pure Appl. Chem.* 1966, 13, 247–62. (c) "Silicon Compounds Register and Review"; Petrarch Systems, Inc.: Bristol, PA, 1982.

(6) One set of products that we have considered that contain the N=C(OSiMe₃)₂ moiety rather than the N(Me₃Si)CO₂SiMe₃ moiety appear to be prescribed by the ¹H NMR data and the evidence (M. T. Zoeckler, unpublished work) that these compounds can readily lose CO_2. CO_2 loss would not be expected from N=C(OSiMe₃)₂. However, a tautomeric mixture of the two species cannot be ruled out at present.

Catalytic Formation of Carbon–Nitrogen Bonds

Table I. Comparison of the Catalytic Activities of Various Group 8 Metals When Used as Catalysts for Reaction 10[a]

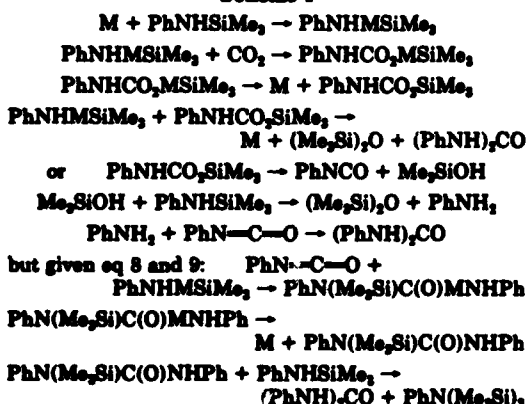| catalyst precursor	% conversion[b]	turnover frequency[c]
Fe(CO)$_5$	95	134
Fe$_3$(CO)$_{12}$	90	121
Ru$_3$(CO)$_{12}$	24	34
NaHRu$_3$(CO)$_{11}$	<3	
Os$_3$(CO)$_{12}$	4	4
Co$_2$(CO)$_8$	85	117
Rh$_6$(CO)$_{16}$	87	120
Ir$_4$(CO)$_{12}$	7	5
(Ph$_3$P)$_4$Pd	5	6
H$_2$(Ph$_3$P)$_3$Ru(CO)	1	
d	1	

[a] Reactions were run in sealed-glass reactors in which were mixed 0.05 mmol of catalyst precursor, 14 mmol of PhNH SiMe$_3$, 14 mmol of PhCHO, 2.8 mmol of PhOPh as an internal standard, and 2.0 mL of THF. Reactions were heated at 100 °C for 2 h and analyzed by gas chromatography. [b] Values are percent conversion of reactants to products. [c] Turnover frequency = moles product/moles catalyst precursor/hour. [d] Blank reaction; no catalyst added.

where the starting compounds are essentially unreactive in the absence of catalyst. Of importance here is that reactions 3–11 are all conducted under essentially neutral conditions, making them quite useful when the reactant molecule has acid- or base-sensitive functional groups. (See ref 7 for alternate methods of synthesizing enamines.)

With regard to catalysts, the results shown in Table I indicate that several of the group 8 metals are active catalysts for reaction 10. To date, of those catalysts examined, Fe(CO)$_5$ provides the highest catalytic activity.

While the exact reaction mechanism(s) must await further study, a logical sequence of events for the CO$_2$ insertion reactions, based on the work of Suss-Fink and of Curtis, is shown in Scheme I. It could be argued that

Scheme I

M + PhNHSiMe$_3$ → PhNHMSiMe$_3$

PhNHMSiMe$_3$ + CO$_2$ → PhNHCO$_2$MSiMe$_3$

PhNHCO$_2$MSiMe$_3$ → M + PhNHCO$_2$SiMe$_3$

PhNHMSiMe$_3$ + PhNHCO$_2$SiMe$_3$ →
M + (Me$_3$Si)$_2$O + (PhNH)$_2$CO

or PhNHCO$_2$SiMe$_3$ → PhNCO + Me$_3$SiOH

Me$_3$SiOH + PhNHSiMe$_3$ → (Me$_3$Si)$_2$O + PhNH$_2$

PhNH$_2$ + PhN=C=O → (PhNH)$_2$CO

but given eq 8 and 9: PhN=C=O +
PhNHMSiMe$_3$ → PhN(Me$_3$Si)C(O)MNHPh

PhN(Me$_3$Si)C(O)MNHPh →
M + PhN(Me$_3$Si)C(O)NHPh

PhN(Me$_3$Si)C(O)NHPh + PhNHSiMe$_3$ →
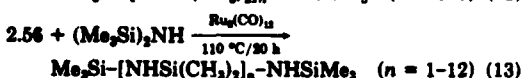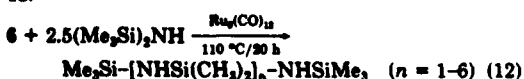(PhNH)$_2$CO + PhN(Me$_3$Si)$_2$

in actuality the catalytic reactions 3–11 do not involve the catalytic activation of the Si–N bond but rather involve catalytic activation of the other reactants. One additional set of reactions that was run based on the following rationale indicates otherwise.

If Si–N bonds are being catalytically activated in the above reactions, then there appears to be an application to polymer chemistry that could have far-reaching effects

(7) Cook, A. G., Ed. "Enamines, Synthesis, Structure and Reactions"; Marcel Dekker: New York, 1969.
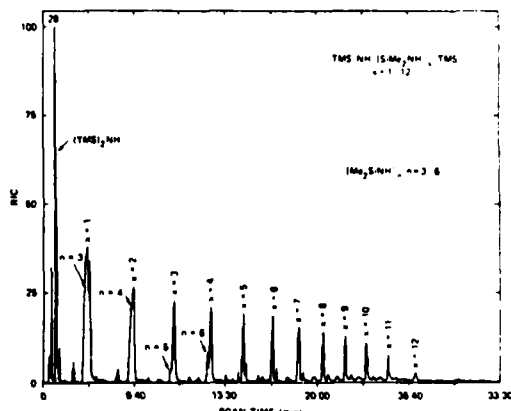
Figure 1. Ruthenium-catalyzed formation of oligomers from [Me$_2$SiNH]$_n$ and (Me$_3$Si)$_2$NH.

in the area of polysilazane chemistry.

Consider the catalytic ring opening of octamethyl-tetrasilazane (6, –[(CH$_3$)$_2$SiNH]$_4$–). With the proper catalyst, it might be possible to catalytically open the ring in 6 and couple one ring-opened intermediate with another to obtain chain growth. If a compound is added that reacts to give chain termination [e.g., (Me$_3$Si)$_2$NH], it should be possible to produce long-chain polymers with the repeating unit –(CH$_3$)$_2$SiNH–. These products would be polysilazane analogues (silazones) of polysiloxanes (silicones). Depending on the concentration of the chain-terminating compound relative to the chain-propagating ring compound, one should be able to control the polymer chain length. We tested these ideas by running reactions 12 and 13.

$$6 + 2.5(Me_3Si)_2NH \xrightarrow[110\ °C/20\ h]{Ru_3(CO)_{12}}$$
$$Me_3Si-[NHSi(CH_3)_2]_n-NHSiMe_3 \quad (n = 1\text{-}6) \quad (12)$$

$$2.56 + (Me_3Si)_2NH \xrightarrow[110\ °C/20\ h]{Ru_3(CO)_{12}}$$
$$Me_3Si-[NHSi(CH_3)_2]_n-NHSiMe_3 \quad (n = 1\text{-}12) \quad (13)$$

As shown by the GC/MS results in Figure 1 for reaction 13, we succeeded in opening the rings and producing long-chain oligomers. In addition, by controlling the concentration of 6 relative to (Me$_3$Si)$_2$NH (ratio of 1:2.5 in reaction 12 and 2.5:1 in reaction 13), we were able to control the average molecular weight distribution of the oligomers.

Previously, oligomers such as those prepared in eq 13 could only be prepared in low yield (~10%) after 10 days of reaction time under more severe conditions according to reaction 14.[8]

$$6 + NH_3 \text{ (10 atm)} \rightarrow$$
$$NH_2-[NHSi(CH_3)_2]_n-(CH_3)_2SiNH_2 \quad (14)$$

It is somewhat early to speculate on the mechanism of Si–N bond activation. However, in view of the mechanisms proposed by Curtis for transition-metal-catalyzed siloxane redistribution reactions, we can present the tentative general mechanisms for reactions 11 and 13 shown in Scheme II.

In analogy to the Curtis work, the intermediacy of a metal-complexed silicon–nitrogen double bond seems reasonable in view of the formation of Me$_3$SiNH–

(8) Redl, G.; Rochow, E. G. *Angew. Chem.* 1964, 76, 650-2.

Scheme II
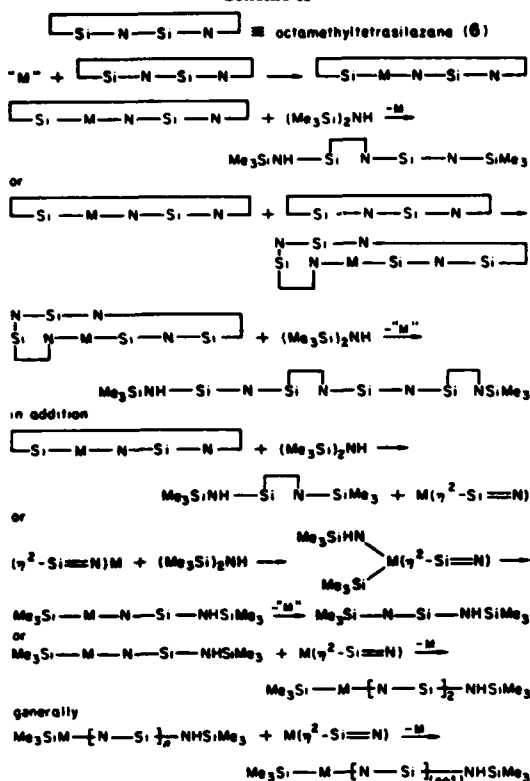
[(CH$_3$)$_2$SiNH]$_n$-SiMe$_3$, where $n = 1$, although repeated "clipping" of the longer chains to give $n = 1$ is still possible.

Summary

We have demonstrated that catalytic formation of new C–N bonds can be promoted by the catalytic activation of Si–N bonds. Thus, a variety of silazanes will react in the presence of several group 8 metal catalysts with compounds containing carbon–oxygen double bonds to form C–N and Si–O bonds concurrently. In our preliminary investigations, we have established that CO$_2$ and phenyl isocyanate can be reacted with several silazanes to form urethane and urea derivatives in 60–95% yield. In the absence of catalyst, these reactions give at most a 20% yield of the same products under comparable conditions. Aldehydes and ketones react with silazanes to give imines and enamines. Furthermore, we have been able to use the catalytic activation of Si–N bond as a means of producing high molecular weight oligomers containing the –(CH$_3$)$_2$SiNH– unit. This observation suggests that it may eventually be possible to synthesize silazane analogues of silicones.

Considerable work remains to develop the best catalysts for the above-described reactions and to fully explore the generality of these reactions.

Experimental Details

General Procedures. Solvents were purified via distillation from suitable drying agents under a nitrogen atmosphere. Benzaldehyde, phenyl isocyanate, and N-(trimethylsilyl)aniline were distilled under N$_2$ and stored under N$_2$ prior to use. NaHRu$_3$(CO)$_{11}$ was prepared by the method of Shore.[9] All silazanes, with

the exception of 1,3-bis[(trimethylsilyl)amino]propane, were purchased from Petrarch, distilled under N$_2$, and stored under N$_2$ before use.

Analyses for the studies shown in Table I were performed on a Hewlett-Packard 5711 gas chromatograph equipped with a 1.5 m × 0.325 cm column packed with 5% Carbowax 20M on acid-washed Chromosorb W and with FID. Infrared spectra were obtained by using a Perkin-Elmer 281 IR spectrophotometer. NMR spectra were taken on a Varian EM-360. GC/MS analyses were performed by using an LKB-9000 mass spectrometer or a Ribermag R 10-10C.

1,3-Bis[(trimethylsilyl)amino]propane. The title compound was prepared by the method of Birkhoffer[10] and characterized by mass spectroscopy (electron impact): m/e (relative intensity) 218 (2), 203 (12), 129 (90), 114 (61), 102 (35), 100 (60), 88 (37), 73 (100), 59 (22), 45 (15); ^{1}H NMR [pyridine, (CH$_3$)$_4$Si] δ 2.70 (CH$_2$CH$_2$NH), 1.40 (quintet, CH$_2$CH$_2$CH$_2$), 0.75 (br s, NH?), 0.08 (Me$_3$Si); pure by GC/MS.

PhNHCO$_2$SiMe$_3$. In an oven-dried, general-purpose, quartz-lined, Parr bomb reactor (34 mL volume) with a magnetic stir bar were placed 1.84 mL (10.5 mmol) of N-(trimethylsilyl)-aniline and 48 mg (0.075 mmol) of Ru$_3$(CO)$_{12}$. The bomb was flushed three times with nitrogen and twice with CO$_2$ and pressurized with 300 psi of CO$_2$. After 20 h at 100 °C, the bomb was cooled to room temperature, depressurized, and opened. The product was 1.66 g (76% yield) of an orange solid. Recrystallization from hexane/THF removed most of the catalyst, leaving a gray powder, mp 125–130 °C. Sublimation under reduced pressure gave fine white needles: mp 134 °C; mass spectrum, m/e (relative intensity) 209 (M$^+$, 30), 194 (13), 165 (18), 150 (100), 129 (8), 75 (42), 73 (56); IR (KBr) 3300 (s), 3030 (w), 2950 (w), 2320 (m), 1660 (s), 1590 (m), 1520 (s), 1440 (m), 1310 (m), 1270 (m), 1250 (m), 1180 (w), 1045 (w), 1020 (w), 850 (s), 745 (m), 715 (w), 690 (w) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.25 (m, 5 H), 0.28 (s, 9 H).

(PhNH)$_2$CO from PhNHSiMe$_3$ and CO$_2$. The same procedure as described above was followed except that the bomb was pressurized with 200 psi of CO$_2$, and the reaction was conducted at 150 °C for 20 h. The product mixture, crystals mixed with a red-brown gum, was rinsed from the reactor with acetone, and the crystals (0.36 g) were isolated by suction filtration. A second crop (0.17 g) was obtained by chilling the filtrate in ice, giving a combined yield of 48%: mp 248 °C; mass spectrum, m/e (relative intensity) 212 (M$^+$, 17), 93 (100); IR (KBr) identical with the Aldrich spectrum of diphenylurea. Note that the reaction run with 2.0 mL of THF solvent at 110 °C gives the same or better yields after 20 h of reaction time.

(PhNH)$_2$CO from PhN=C=O. In a 34-mL quartz-lined bomb reactor were mixed 1.0 mL (9.2 mmol) of phenyl isocyanate, 1.0 mL (5.7 mmol) of N-(trimethylsilyl)aniline, and 48 mg (0.075 mmol) of Ru$_3$(CO)$_{12}$. The bomb was flushed twice with nitrogen, pressurized with 300 psi of nitrogen, and then stirred at 100 °C for 20 h. The product, a semisolid material, was rinsed from the reactor with ether. Three crops of crystals were collected: 0.17 g, mp 145 °C; 0.64 g, mp 245 °C dec; 0.51 g, mp 245 °C dec. The second and third crops were diphenylurea (95% yield, based on PhNHSiMe$_3$), as shown by IR. The first crop was a mixture of diphenylurea and a compound with the following spectral characteristics: mass spectrum, m/e (relative intensity) 331 (M$^+$, 7), 212 (34), 119 (28), 93 (100); IR (KBr) 3300 (m), 3170 (m), 3060 (m), 1695 (s), 1665 (s), 1590 (s), 1520 (br), 1490 (s), 1430 (s), 1310 (s), 1260 (s), 1175 (s), 1095 (w), 1070 (w), 1025 (w), 895 (w), 860 (w), 830 (w), 750 (m), 685 (m) cm^{-1}. The reactants, the mass spectrum, and the IR spectrum suggest that this product is PhN[C(O)NHPh]$_2$.

Reaction of CH$_2$(CH$_2$NHSiMe$_3$)$_2$ with CO$_2$. In a quartz-lined bomb reactor were mixed 2.0 mL of THF, 2.56 g (11.7 mmol) of 1,3-[(trimethylsilyl)amino]propane, and 32 mg (0.05 mmol) of Ru$_3$(CO)$_{12}$. The reactor was sealed, degassed as described above with CO$_2$, charged to 750 psi of CO$_2$, and heated to 110 °C for 1 h, at which time 1.9 equiv of CO$_2$ were taken up, and no further reaction was observed.

(9) Bricker, J. C.; Nagel, C. C.; Shore, S. G. J. Am. Chem. Soc. 1982, 104, 1444–5.

(10) Birkhoffer, L.; Kuhlthau, H. P.; Ritter, A. Chem. Ber. 1963, 93, 2810–3.

A white, highly crystalline solid was filtered off and identified as $CH_2(CH_2NHCO_2SiMe_3)_2$, GC/MS analysis revealed the presence and allowed the identification of compounds 2–5. GC/MS characterization for these compounds gives the following results for compound 1: electron-impact (EI) mass spectrum, m/e (relative intensity) 172 (4), 157 (52), 100 (12), 75 (100), 73 (23), 45 (22), 44 (22); chemical ionization (CI, NH_3) mass spectrum, m/e (relative intensity) 307 (56), 217 (20), 191 (21), 173 (45), 101 (100), 75 (35); negative chemical ionization (NCI, with NH_3) mass spectrum, m/e (relative intensity) 241 (18), 171 (100), 99 (30), 89 (42). For compound 2: EI mass spectrum, m/e (relative intensity) 273 (4), 157 (40), 147 (67), 100 (12), 75 (100), 73 (59), 59 (18), 45 (27); CI (NH_3) mass spectrum, m/e (relative intensity) 379 (5), 289 (19), 173 (31), 101 (100), 90 (16), 75 (17); NCI mass spectrum, m/e (relative intensity) 245 (5), 171 (100), 99 (22), 89 (40). Compound 3 gave the following spectra: EI mass spectrum, m/e (relative intensity) 450 (3), 435 (29), 246 (27), 232 (55), 218 (43), 147 (32), 73 (100); CI (NH_3) mass spectrum, m/e (relative intensity) 451 (100), 361 (10), 289 (27), 173 (13); NCI mass spectrum, m/e (relative intensity) 243 (4), 171 (100), 89 (6). Compound 4 was determined by difference, as it decomposes on GC/MS analysis to give spectra as found for compound 5. 4 gave the following: EI mass spectrum, m/e (relative intensity) 100 (17), 75 (100), 56 (9), 47 (13), 45 (18); CI mass spectrum, m/e (relative intensity) 191 (100), 101 (96), 75 (93); NCI mass spectrum, m/e (relative intensity) 117 (17), 99 (53), 89 (100). Compound 5 has the identical pattern but can be differentiated from 4 by further silylating the reaction solution with $CF_3SO_3SiMe_3$ and running the GC/MS to determine the amounts of 4 that have been doubly and triply silylated [e.g., $(Me_3Si)_2N(CH_2)_3-N(Me_3Si)CO_2SiMe_3$, m/e 406]. This procedure allows the determination of amounts of 4 present as well.

The yields of these compounds as determined by GC were ca. 70% for 1, 10% for 2, 5% for 3, and 10% for 4 and 5 combined. Compound 1 was further characterized as follows: ^1H NMR (Me_2SO-d_6) δ 5.40 (t, NH?); 3.42 (q, CH_2NH), 1.80 (quintet, CH_2CH_2N), 0.26 (s, $OSiMe_3$); ^1H NMR (pyridine) δ 3.35 (q), 1.78 (quintet), 0.28 ($OSiMe_3$); IR (KBr) 3340 (br s), 2960 (s), 2880 (br s), 1670 (s), 1575 (br s), 1490 (br s), 1390 (ms), 1325 (br s), 1280 (ms), 1253 (ms), 1155 (m), 1135 (mw), 1060 (m), 1020 (w), 840 (s), 765 (mw); mp 85–87.

Compounds 2 and 3 were also characterized by ^1H NMR. Clean NMR samples were prepared by treating 1 with $CF_3SO_3SiM_3$ in pyridine. For compound 2: ^1H NMR (pyridine) δ 3.30 (quintet, CH_2CH_2N), 1.78 (quintet?, $CH_2CH_2CH_2$) 0.26 (s), 0.34 (s, Me_3Si). Compound 3 has essentially the same spectrum, however, the integrations for the silyl groups are different but as expected (see ref 6).

Reaction of $(Me_3Si)_2NH$ with CO_2. In a magnetically stirred, quartz-lined bomb reactor of 34-mL volume were mixed 32 mg (0.05 mmol) of $Ru_6(CO)_{18}$ and 2.0 mL of $(Me_3Si)_2NH$. The reactor was sealed, pressurized to 300 psi with CO_2, and heated at 100 °C for 12 h. When the reactor cooled, no liquid remained, and the product, $Me_3SiNHC(O)OSiMe_3$, was sublimed prior to analysis: IR (KBr) 3230 (s), 2960 (s), 2895 (mw), 2790 (w), 1675 (br s), 1400 (m, sh), 1330 (s), 1245 (s), 1050 (s), 880 (m, sh), 850 (br s), 810 (m, sh), 745 (m), 723 (m), 642 (w) cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.5 (br s, NH), 0.30 (s, 9 H, Me_3SiN), 0.21 (s, 9 H, Me_3SiO); NCI mass spectrum, m/e (relative intensity) 206 (100). A blank reaction (without catalyst) gave 10–15% conversion.

Reaction of $PhNHSiMe_3$ with $PhCHO$. In a magnetically stirred, sealed, glass reactor of 30-mL volume were mixed 0.05 mmol of catalyst precursor (see Table I). 14 mmol of $PhNHSiMe_3$,

14 mmol of PhCHO, 2.8 mmol of PhOPh as an internal standard, and 2.0 mL of THF. The reactor was heated at 100 °C for 2 h, and the product was analyzed by GC. The product yields for the various catalysts and the catalytic activities for these catalysts are listed in Table I.

Authentic PhCH=NPh was prepared by reaction of PhCHO and $PhNH_2$ and used for the GC standards. The product isolated from the reactions was found to be identical, spectrally, with the authentic PhCH=NPh. Blank reactions gave essentially no product.

Reaction of $PhNHSiMe_3$ with 2-Pentanone. In a magnetically stirred glass reactor were mixed 2.5 mL (14 mmol) of $PhNHSiMe_3$, 1.5 mL of 2-pentanone, and 32 mg (0.05 mmol) of $Ru_3(CO)_{12}$. The reactor was sealed under N_2 and heated at 100 °C for 20 h. GC analysis indicated 70% conversion to enamine as identified by mass spectroscopy; EI mass spectrum, m/e (relative intensity) 161 (20), 146 (25), 118 (57), 77 (100), 51 (63), CI (NH_3) mass spectrum, m/e (relative intensity) 162 (100), 146 (12), 133 (12), 118 (22); NCI (NH_3) mass spectrum, m/e (relative intensity) 160 (100); ^1H NMR ($CDCl_3$) δ 6.88 (br m, 6 H, ArH, =CH), 3.55 (br s, ~1 H, NH), 2.15 (q, CH_2CH_3), 1.57 (s, CH_3C=CH), 0.88 (t, CH_2CH_3). A blank reaction run concurrently gave 10% conversion.

Silazones. In a glass reactor were mixed 4.0 mL (19 mmol) of $(Me_3Si)_2NH$ and 2.1 g (7 mmol) of octamethyltetrasilazane for reaction 12, or 1.0 mL (4.2 mmol) and 3.0 g (10 mmol), respectively, for reaction 13, and 32 mg (0.05 mmol) of $Ru_3(CO)_{12}$. The reactor was sealed and heated at 110 °C for 14 h; the product was then analyzed via a combination of EI, CI, and NCI GC/MS. For reaction 12 the products were solely the silazanes $Me_3SiNH-[(CH_3)_2SiNH]_n-SiMe_3$, where $n = 1-7$, in a normal Schulz–Flory distribution. The analysis for reaction 13 was somewhat more complex and is shown in Figure 1. Similar silazones were also prepared using $Rh_6(CO)_{16}$ as catalyst, and in this case the reaction was complete in 10 h with much the same analysis as that shown in Figure 1.

Typically, the NCI mass spectral fragmentation pattern for $Me_3SiNH-[(CH_3)_2SiNH]_n-SiMe_3$ is M – H, M – 18, and M – 32; for the higher molecular weights, M – H is not found. For the cyclic compounds $[(CH_3)_2SiNH]_n$, the NCI mass spectral fragmentation is generally only M – H. The fragmentation patterns for EI, CI, and NCI corroborated the structures of the various oligomeric products.

Appendix B

THE TRANSALKYLATION REACTION. HOMOGENEOUS
CATALYTIC FORMATION OF C-N BONDS 3.

THE TRANSALKYLATION REACTION
HOMOGENEOUS CATALYTIC FORMATION OF C-N BONDS. 3.

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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 trans-alkylation catalysis based on initial reaction rates. We find that transalkylation proceeds most efficiently in alcoholic solvents (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 two or three atoms binds the amine through insertion into an α C-H bond to give a metalloazocyclopropane 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 trans-alkylation products. The catalyst system has been tested as a synthetic tool for the oligomerization and cyclization of tertiary diamines. These preliminary studies have proved to be quite successful. Thus, N,N'-tetramethylethylene diamine can be transformed into Me_3N, N,N'-dimethylpiperazine, and N-methyl, N'-(dimethylaminoethyl)piperazine with good conversion and high selectivity. N,N'-tetraethylethylene diamine can be transformed into Et_3N and the perethyl linear ethylene diamine dimer, trimer, tetramer, and pentamer with excellent conversion.

Introduction

The catalytic formation and cleavage of carbon-nitrogen (C-N) single bonds is of considerable importance to numerous diverse areas of chemistry because of the ubiquitous presence of nitrogen-containing compounds in nature.[1-3] For example, the catalytic formation of C-N bonds plays a significant role in the synthesis of biologically active molecules.[3] 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.[4-6] Catalytic C-N bond formation and cleavage are both essential to the functioning of life-controlling processes.[7]

In general, research on the catalysis chemistry of C-N bonds has focussed on the formation of C-N bonds with very little attention paid to the cleavage of the C-N bond, especially in tertiary amines. At the time we first 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 several thousand psi of H_2).[5,6,8] In fact, the only evidence of catalysis of C-N bond scission at lower temperatures was obtained by Murahashi and coworkers with palladium black catalysts at 200°C.[9-11] They reported that they could efficiently catalyze the exchange of alkyl groups between tertiary amines as shown in reaction (1).[9]

$$R_3N + R'_3N \xrightarrow{\text{Pd Black}} R_2NR' + R'_2NR \qquad (1)$$
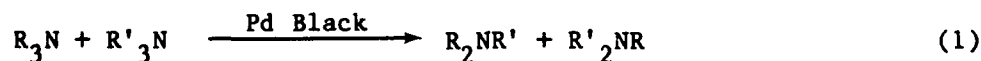
The discovery by Murahashi of catalysts that cleave and reform C-N single bonds in tertiary amines at 200°C was in itself a considerable feat given that an average C-N bond dissociation energy is ~ 75 kcal/mol for tertiary amines.[12]

Because of the similarity between Murahashi's work on deuterium exchange reactions of tertiary amines catalyzed by Pd black and our own studies of similar reactions catalyzed by homogeneous catalysts,[13] we attempted to catalyze reaction (1) using homogeneous catalysts. In 1980, we published a preliminary report describing the first examples of homogeneous transition metal catalyzed alkyl exchange between tertiary amines, reaction (2).[14]

$$Et_3N + Pr_3N \xrightleftharpoons{catalyst} Et_2NPr + Pr_2NEt \qquad (2)$$
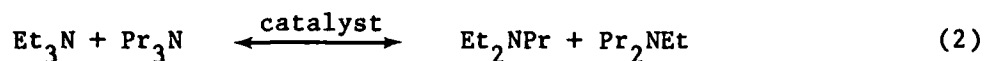
$$Catalyst = Ru_3(CO)_{12}, Os_3(CO)_{12}, Rh_6(CO)_{16}, Ir_4(CO)_{12}$$

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 were able to demonstrate that the homogeneous catalysts are far more active for (2) than the heterogeneous Pd black catalyst. This higher activity allowed us to reduce "transalkylation reaction" 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 the purposes of 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 industrially important areas including biocides, phase-transfer catalysts, surfactants, and polymerization catalysts. Moreover, if the transalkylation reaction can be applied to diamines as shown in (3) for N,N,N',N' tetraalkylethylene diamines, then

$$xR_2NCH_2CH_2NR_2 \xrightarrow{catalyst} \begin{cases} xR_3N + R-[N(R)CH_2CH_2]-_xNR_2 \\ xR_3N + RN[CH_2CH_2NR]-_x \end{cases} \qquad (3)$$

B-4
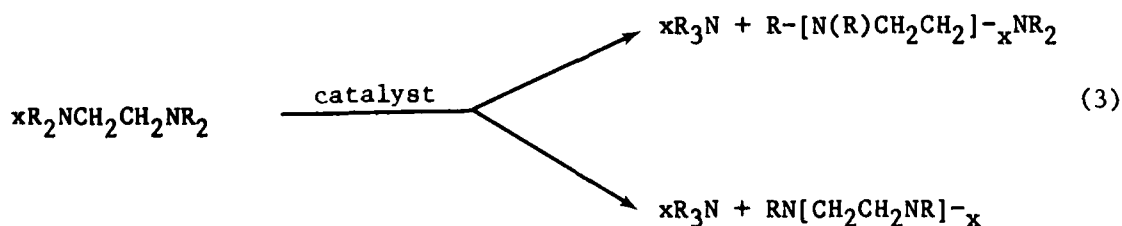
transalkylation holds considerable potential for the preparation of tertiary and quaternary amine polymers and unusual amine macrocycles. These amine macrocycles might include analogs of crown ethers, cryptands, and cryptates. Amine macrocycles continue to play an important role in the development of models of various bioinorganic processes such as oxygen transport,[19] oxidation catalysis,[20] and various electron transfer processes.[21]

In this context, we have undertaken kinetic and mechanistic studies of the transalkylation reaction in an effort to understand the catalys:s chemistry involved; improve the stability, selectivity, and activity of the catalysts; and explore the scope of the reaction as it applies to organic synthesis. We describe here our efforts to develop a kinetic and mechanistic understanding of ruthenium- catalyzed transalkylation and our preliminary studies on its use as a synthetic tool. During the preparation of this manuscript, Murahashi et al. published an excellent paper describing the use of palladium black to catalyze transalkylations of primary and secondary amines for synthetic purposes.[22] The similarities and differences between Murahashi's work and the work reported here are also discussed.

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. Tetrahydrofuran (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. Pr_2NEt was prepared by reaction of Pr_2NH with EtBr followed by neutrallization and distillation (b.p. 125-127°C).

Analytical Procedures

Product analyses for all the kinetic studies were performed on a Hewlett-Packard 5880A reporting gas chromatograph (GC) equipped with FID using a 2.5 m by 0.325 cm column packed with 60/80 Carbopack/4% carbowax 20M/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 using a Perkin-Elmer 281 IR spectrophotometer. Nuclear magnetic resonance (NMR) spectra were taken on a JEOL FX 90-MHz instrument. Gas chromatograph/mass spectrometer (GC-MS) analyses were performed 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 3.35 M in both Et_3N and Pr_3N unless indicated otherwise, were stored under argon at 0°C and analyzed before use. Magnetically stirred, 34-mL quartz-lined bomb reactors were dried by heating at 120°C, then cooled and stored in a desiccator until used.

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 psi of N_2 or CO and then pressurized to the desired pressure with N_2 or CO (normally 100 psi) 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 the reactorsand removing a 0.1-mL sample. The reaction was then restarted following the above procedure.

<u>Procedure B.</u> A second set of kinetic studies was conducted
following the procedures described above but with slight modifica-
tions. 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 psi 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 1 h thereafter until the mole percentage of mixed alkyl amines
approached 70 or until the mole percentage of mixed alkyl amines failed
to change significantly, indicating catalyst degradation.

CO Pressure Studies

These reactions were run following procedure A with the amine
concentration for Et_3N and Pr_3N set at 0.74 M and with methanol as the
only solvent. The CO pressure was varied from 0 to 400 psig at ambient
temperature.

Catalyst Concentration Studies

The catalyst concentration reactions were run following procedure
A. Experiments were conducted in methanol under 100 psig of CO at
160°C. The total amine concentration was 4.36 M with a 1:1 ratio of Et_3N
to Pr_3N. $Ru_3(CO)_{12}$ concentrations were varied between 5.0×10^{-3} M and
4.0×10^{-2} M.

Amine Concentration Studies

The amine concentration reactions were run as in the CO pressure
studies except that the CO pressure was held constant at 100 psig. The
overall amine concentration was varied from 0.7 M to 3.7 M. In the
first series of experiments the ratio of Et_3N to Pr_3N was maintained at
1:1. Later the ratio of Et_3N to Pr_3N was varied while the total amine
concentration was held constant.

Temperature Studies

These reactions were run as in the CO pressure studies except that the CO pressure was held constant at 100 psig CO and the temperature was varied between 130°C and 160°C.

Reaction of N, N, N', N' tetramethylethylene Diamine

In a magnetically stirred, 34-mL quartz-lined bomb reactor were 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 μL of $Fe(CO)_5$ (0.3 mmol), and 2.0 mL (13.2 mmol) of N,N,N',N-tetramethyl ethylene diamine. 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. Then the reactor was cooled, and depressurized. The GC analysis of the contents showed small amounts of Me_3N. After 120 h of reaction approximately 7 mmol of Me_3N were formed along with 3 mmol of N,N'-dimethylpiperazine, 0.5 mmol of N-ethyl, N,N',N' trimethylethylene diamine, 0.5 mmol of N,N,N',N'',N''-pentamethyldiethylene triamine [$Me_2NCH_2CH_2N(Me)CH_2CH_2NMe_2$], and 1.5 mmol of N-methyl, N'-(2-dimethylaminoethyl)piperazine.

Reaction of N,N,N',N- tetraethylethylenediamine

The same procedure used for the tetramethyl derivative was used for tetraethylethylene diamine (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''-pentaethyldiethylene triamine, [$Et_2NCH_2CH_2N(Et)CH_2CH_2NEt_2$], 0.8 mmol of N,N,N'',N''',N'''',N''''-heptaethyltriethylene tetramine, [$Et_2N-[CH_2CH_2N(Et)]_2-CH_2CH_2NEt_2$], 0.1 mmol of the per-ethyltetraethylene pentaamine, traces of the pentaethylene hexamine, traces of the N,N'-diethylpiperazine and the N,N',N''-triethyl-1,4,7-triazacyclononane. We also observed the formation of 0.1 mmol of N,n-butyl,N,N',N'-triethyl-ethylenediamine.

Reaction of N,N,N',N'-tetramethylhexamethylene Diamine

The same procedure used for the tetramethylethylene diamine
derivative was used for tetramethylhexamethylene diamine (2.0 mL = 9.4
mmol). After 16 h reaction time, GC analysis showed production of small
amounts of Me_3N. After an additional 96 h of reaction time GC/MS
analysis revealed that 25% of the amine reacted to give, very
selectively, 2.1 mmol of the open-chain dimer, N,N,N',N'',N''-
pentamethyl-1,7,15-triazapentadecane and a trace (0.2 mmol) of the
N-ethyl, N,N',N'-trimethylethylene diamine.

Results

A rational approach to exploring the synthetic utility of a new
reaction is to develop a kinetic and mechanistic understanding of the
reaction, to fully appreciate the reaction's potential. Our preliminary
studies of the transalkylation reaction[14] were run in neat amine at 125–
150°C. Use of neat reactant as solvent is not an appropriate approach
to undertaking kinetic studies, consequently, our first objective was to
find a useful solvent system. For this reason, we conducted a
systematic solvent survey.

Solvent Survey:

In our original studies with neat amines[14] [reaction (2)], we
consistently obtained 50–58 mol% mixed-alkyl amines. Although these
yields were always less than those obtained by Murahashi with palladium
black at 200°C (60–65 mol% mixed-alkyl amines), 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 (see
Table I), using $Ru_3(CO)_{12}$ as the catalyst precursor, in that these
experiments resulted in much the same final distribution of amines.
Moreover, the initial rates in all cases were comparable (see Table
I). However, on testing alcohol solvents it became evident that a rapid
degradation of the catalyst was occurring.

In an attempt to prevent catalyst degradation in the alcohol studies, we performed the reactions 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-alkyl amines 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 does not enhance transalkylation catalysis. Although slight amounts of transalkylation products do form in ether solvents under low CO pressures (50-100 psig), in general most of the starting $Ru_3(CO)_{12}$ is recovered.

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

CO Pressure Studies

After discovering that added CO facilitated 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. The initial rate appears to increase as the CO pressure increases to approximately 100 psi, after which increasing the CO pressure causes a rapid decline in catalyst activity.

Catalyst Concentration Studies

We have previously shown[23] that valuable information on catalyst nuclearity can be obtained by studying the effects of catalyst concentration on relative catalyst activity. Therefore, we conducted experiments in which the catalyst concentration was varied from 0.002 to 0.4 M. The results are shown in Figure 2.

The data plotted in Figure 2 indicate that the product yield is not linearly dependent on catalyst concentration; otherwise, a straight line would be obtained. These results are indicative of a cluster-
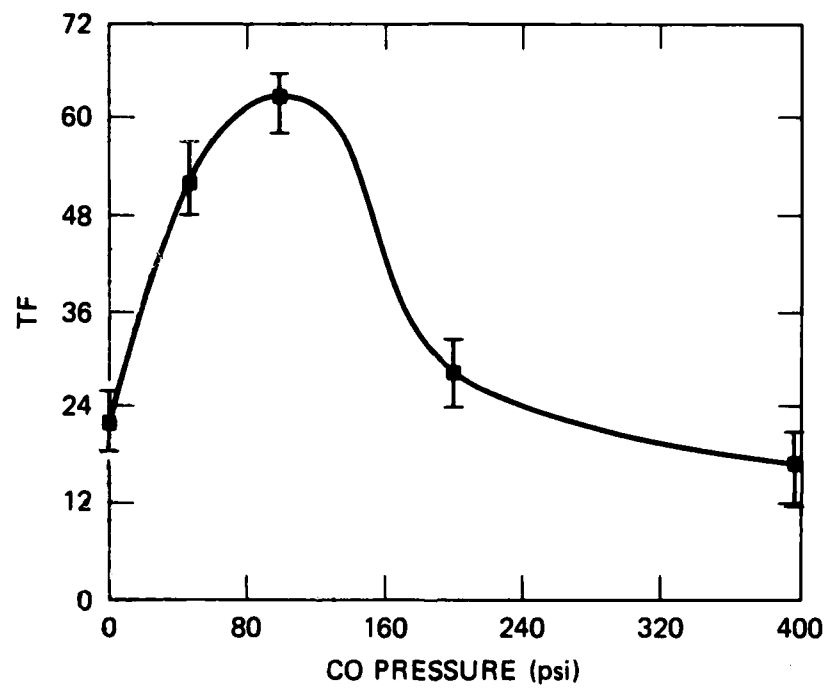
FIGURE 1   CO PRESSURE VERSUS INITIAL RATE

B-11
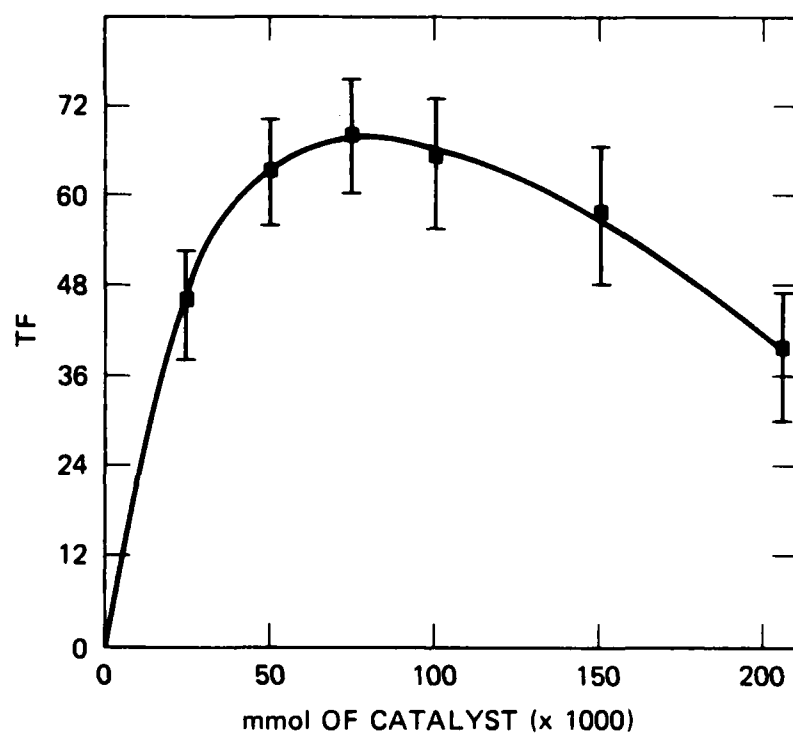
JA-327583-81

FIGURE 2   INITIAL RATES AS A FUNCTION OF mmol OF ADDED
CATALYST

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

Solvent[a,b]	THF	Diglyme	Diethyl-ether	Methanol	Ethanol
Initial Rates no CO[c]	80	45	19	22	18
Initial Rates 100 psi CO	2.4	4.3	7	63(160°C) (130°C)	28, 46[d]
Final mol% Mixed-Alkyl Amines[e]	48	40	47	63, 71	61, 64[d]
(final time in h)	(3)	(7)	(4)	(4), (16)	(6), (4.5)

---

[a]For diethyl ether and methanol, the reactions were run as described in procedure A (see the Experimental Section); for THF, diglyme, and ethanol procedure B was followed. Reaction solutions in diethyl ether and methanol were 0.9 M in each amine and 0.86 M for the other solvents.

[b]Initial rates are defined as turnover frequency (TF); where TF is defined as moles of Et_2NPr/moles of catalyst precursor-hour. Determined by the turnover frequency after 0.5 h of reaction.

[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]Mixed-metal catalyst [0.15 mmol of $Fe(CO)_5$] added to the standard reaction.

[e]Values recorded are based on CO-promoted reactions in the alcoholic systems and represent the results obtained in the absence of CO in the absence of CO in the ether solvents.

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

Amine Concentration Studies

The effects of amine concentration were studied in two ways. In one set of experiments, initial rates were measured as a function of the total amine concentration (Et_3N and Pr_3N) while the other variables were held constant. The results of these studies are shown in Figure 3.

In the second set of experiments, initial rates were measured as a function of changes in the ratios of the two amines where total amine concentration was kept constant. These results are presented in Figure 4.

Temperature Studies

Reaction rate data were obtained for reaction (2) run in methanol at 130°C and 160°C, as recorded in Table 1. These data allow us to calculate the enthalpy of activation, $\Delta H = 27$ kcal/mol, and the entropy of activation, $\Delta S = -11.21$ cal/mol, for reaction (2).

Mixed-Metal Catalysts

We previously reported the synergistic effects obtainable by adding iron carbonyl to ruthenium-cluster-catalyzed reactions such as the water-gas shift reaction,[24] hydroformylation,[25] and amino-methylation.[26] Without any understanding of the processes involved, we attempted to obtain similar rate enhancements in transalkylation catalysis by using iron carbonyls. As the results in Table I show, we observe rate enhancements when iron carbonyl is added, despite the fact that iron carbonyl by itself is not catalytically active.

From Figure 3, it is evident that the reaction is first order in total amine concentration. From Figure 4, it is evident that the reaction is independently first order both in Et_3N concentration and Pr_3N concentration. Consequently, the slow step must involve binding of an amine , either Et_3N or Pr_3N, to the catalyst (see discussion section).
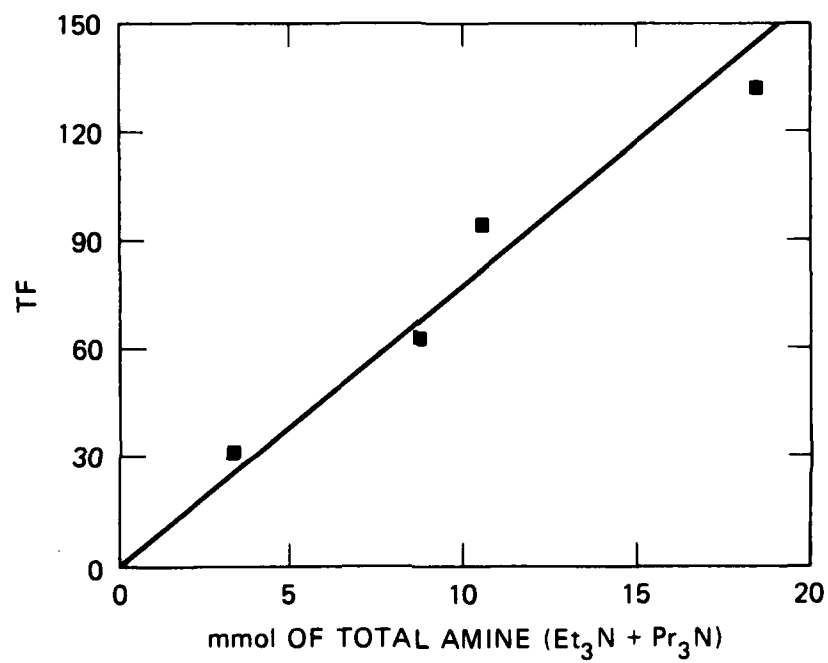
FIGURE 3   PLOT OF INITIAL RATES AS A FUNCTION OF TOTAL
mmol AMINE PRESENT

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B-15
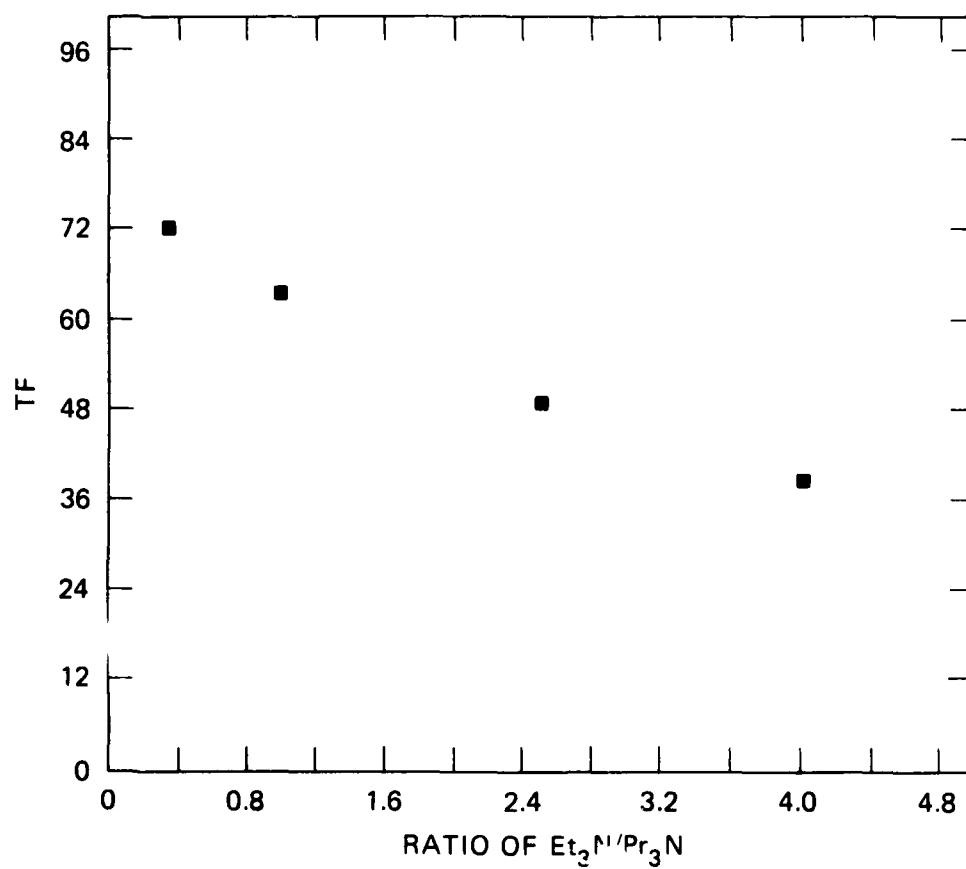
FIGURE 4   AMINE RATIO VERSUS INITIAL RATE

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Other Products

In addition to the transalkylation reaction, we observed another reaction that consumes Et_3N irreversibly. The remarkable reaction, (4), which we will discuss elsewhere,

$$Et_3N \xrightarrow{\text{catalyst}} Et_2NH + Et_2N(\text{n-butyl}) \text{ and } Et_2N(\text{n-hexyl}) \quad (4)$$
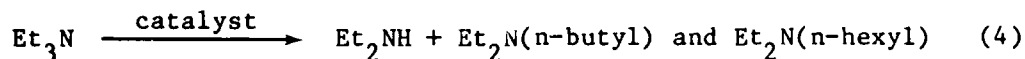
proceeds very slowly under the conditions employed in the kinetic studies (except at high catalyst concentration). It appears likely that a study of (4) will help elucidate the mechanistic pathways for transalkylation as discussed below.

Discussion

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 a kinetic expression that conforms to the experimental observations.

Kinetic Studies

To develop a useful kinetic expression for catalysis of the transalkylation reaction in the Et_3N/Pr_3N model system, we must first consider the results of the amine concentration studies. The data in Figure 3 show that the rate of production of mixed-alkyl amines exhibits first-order dependence on total amine concentration. Thus, either Et_3N or Pr_3N is involved in the catalytic steps preceding or including the rate-determining step, but not together in the same sequence of events. If we choose to ignore the influence of catalyst concentration and CO pressure on the rate by assuming they are constants, then based on initial rates, an expression can be written for the disappearence of Pr_3N as shown in (5):

$$-d[Pr_3N]/dt = k_1[Et_3N] + k_2[Pr_3N] \quad (5)$$

The reverse reaction would then be as in (6), assuming that binding of

$$d[Pr_3N]/dt = k_3[Et_2NPr] + k_4[Pr_2NEt] \tag{6}$$

either Et_2NPr or Pr_2NEt to the catalyst is also the slow step in the reverse reaction. At equilibrium, (5) and (6) are equal, and we can write:

$$k_1[Et_3N] + k_2[Pr_3N] = k_3[Et_2NPr] + k_4[Pr_2NEt] \tag{7}$$

From the rate data plotted in Figures 3 and 4, we can extract k_1 and k_2. Thus, at a constant catalyst concentration of .01 M [defined as added $Ru_3(CO)_{12}$], $k_1 = 3.89$ h^{-1} and $k_2 = 8.72$ h^{-1}. Because the transalkylation approaches statistical distribution, the equilibrium constant must be K = 7.54, assuming that at equilibrium the mole percent of mixed-alkyl amines is 73.3.

We are in the process of determining k_4 from initial rates of transalkylation of Pr_2NEt and will be able to deduce k_3 via equation (6).

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 and catalyst concentration on reaction rates are especially valuable in interpreting the mechanism(s) of transalkylation.

The Catalytic Cycle

Any discussion of the catalytic mechanisms of transalkylation must take into account our previous observations concerning catalytic deuteration of tertiary amines.[13,15,16] Deuteration occurs as a

consequence of C-H activation, a necessary step in transalkylation
catalysis (see below). Scheme 1 illustrates the proposed mechanism for
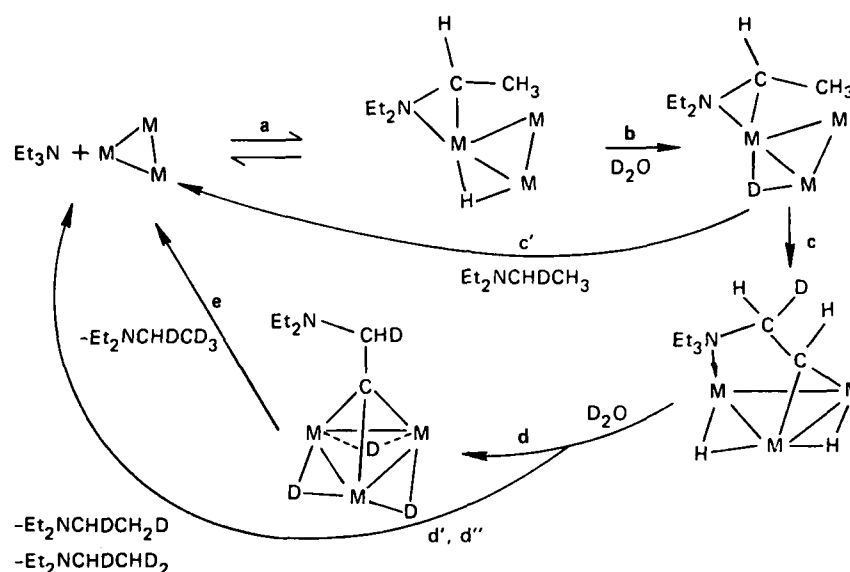
SCHEME 1

Et$_3$N deuteration as catalyzed by ruthenium and osmium. A similar scheme
has been used to illustrate rhodium-catalyzed deuteration of Et$_3$N. The
major products in ruthenium-catalyzed or osmium-catalyzed deuteration of
Et$_3$N and Pr$_3$N are as follows:

Et$_2$NCHDCD$_3$ > Et$_2$NCHDCHD$_2$ > Et$_2$NCHDCH$_2$D > Et$_2$NCHDCH$_3$

Pr$_2$NCHDCH$_2$CH$_3$ > Pr$_2$NCHDCHDCH$_3$ > Pr$_2$NCHDCD$_2$CH$_3$
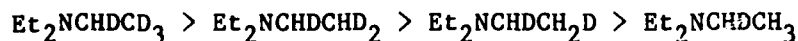
The key point related to the current work is that deuteration of
Pr$_3$N proceeds via pathway a more often than by pathway b or c, whereas,
the reverse is true for Et$_3$N.

CO Pressure Studies

Initiation of the catalytic cycle must begin with the creation of
at least one site of unsaturation on the catalyst precursor. Two

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potential pathways to coordinative unsaturation can be proposed based on the results of the CO pressure studies shown in Figure 1. These results show that at low CO pressures the rate of transalkylation increases with increasing CO pressure and then at about 100 psig CO, begins to decrease with further increases in pressure. We can suggest two possible explanations for this behavior. First, if catalysis is promoted by mononuclear species, these results are consistent with the first step being CO-promoted cluster fragmentation to mononuclear species. This would account for the rate increases at low CO pressure, reaction (8).

$$Ru_3(CO)_{12} + 3CO \longleftrightarrow 3Ru(CO)_5 \tag{8}$$

$$Ru(CO)_5 \longleftrightarrow CO + Ru(CO)_4 \tag{9}$$

$$Ru(CO)_4 + R_3N \longleftrightarrow Ru(CO)_4NR_3 \tag{10}$$
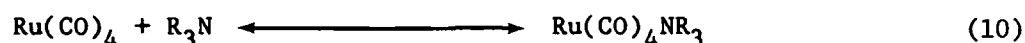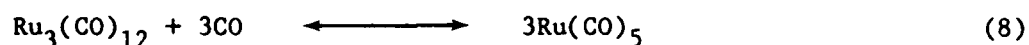
The mononuclear species then loses CO to become coordinatively unsaturated, reaction (9), and catalytically active, reaction (10). Reaction (10) would be susceptible to CO inhibition and would account for the rate decreases observed at higher CO pressure.

A second explanation is that the catalyst decomposes in the absence of CO, and the presence of free CO prevents catalyst decomposition. However, because CO will compete with amine for the same sites of coordinative unsaturation, one would expect CO pressure to probably contribute to a delicate balance between maintaining catalyst stability and reducing catalyst activity. Thus, the initial rise in catalyst activity with increasing CO pressure is primarily a function of catalyst stability, and the decrease in activity with further increases in CO pressure occurs as a consequence of competition for sites of unsaturation between CO and amine.

Catalyst Studies

The second explanation seems most likely on the basis that the
catalyst does, in fact, decompose in all solvents in the absence of CO
and only maintains its stability under CO pressure. Furthermore, the
catalyst concentration studies will, as we have discussed at length
elsewhere,[23] provide an indication of equilibria occurring between
clusters and fragments. The catalyst concentration studies do indicate
fragmentation equilibria. They show that the relative rate of catalysis
increases with increasing amounts of added $Ru_3(CO)_{12}$ up to a
concentration of approximately 0.015 M and then begins to decline. If
the reaction was in fact catalyzed by a mononuclear complex, then the
relative activity would be highest at the lowest catalyst concentrations
and diminish as the concentration increased. Because this was not
observed, the active catalyst complex is most likely 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 ruthenium-catalyzed hydroformylation
under water-gas shift conditions where equilibrium (8) is coupled to
reactions (11) and (12).[27] In this case, work by Suss-Fink and Reiner[28]

$$Ru_3(CO)_{12} + OH^- \longrightarrow HRu_3(CO)_{11}^- + CO_2 \qquad (11)$$

$$HRu_3(CO)_{11}^- + H_2 \longleftrightarrow H_3Ru_4(CO)_{11}^- + CO \qquad (12)$$

shows that the $HRu_3(CO)_{11}^-$ species is the active catalyst and not the
tetranuclear species. In keeping with these observations, in reaction
(2) we observe the formation, in high yield, of $Ru_6C(CO)_{17}^{2-}$ which is
not catalytically active after extended reaction periods.[28] This
observation proves that higher cluster species do form in the reaction
solution. The question of nuclearity is discussed in greater detail
below.

C-H Bond Activation and Alkyl Transfer

Once a site of coordinative unsaturation forms, it becomes possible for an amine to bind at that site. We previously studied the catalytic exchange of deuterium for hydrogen on tertiary amines using homogeneous group 8 metal catalysts or the heterogeneous catalysts, palladium black or reduced cobalt-molybdenum oxides on gamma alumina.[15,16] These experiments indicate that following coordination of the amine nitrogen electron pair, reaction (10), the metal can insert into an α C-H bond as shown in (13):

$$\text{Et}_3\text{N} + \text{M} \longrightarrow \overset{R}{\underset{R}{\diagdown}} \overset{+}{\text{N}} - \overset{\overset{H}{|}}{\underset{\underset{H^-}{M}}{C}} - R' \qquad\qquad R_2N^+ = CHR \atop \downarrow \atop MH^- \qquad (13)$$
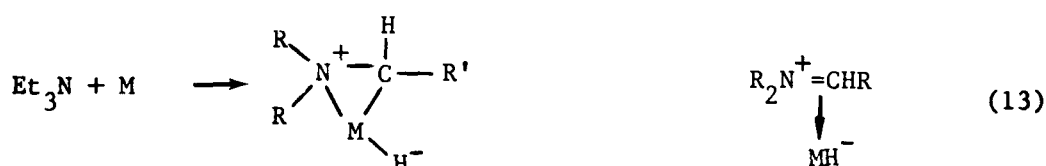
We have previously argued[17,18] that one cannot distinguish between the formation of a metalloazocyclopropane, 1, and an iminium ion complex, 2. Both types of complexes are known to form in reactions of amines with transition metals. Kaesz et al.,[30] have reported the formation of metalloazacyclopropane 3 from reactions of dimethylferrocenyl amine with MeMn(CO)$_5$, and Shapely et al, have reported the formation of the iminium osmium complex, 4, from the reaction of Et$_3$N with Os$_3$(CO)$_{12}$.[31]

3   4
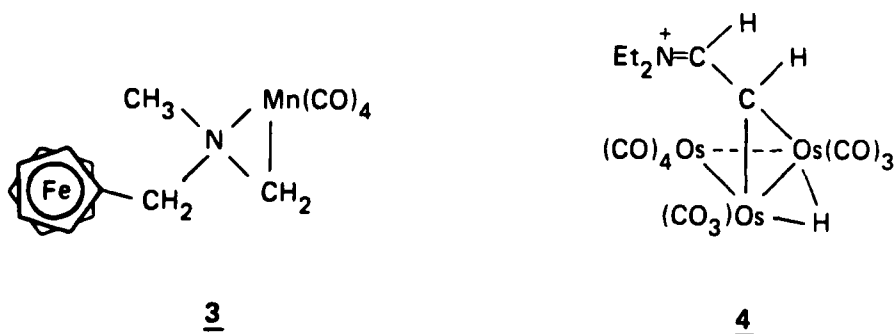
Two divergent steps could follow the insertion reaction. The simplest step mechanistically would be to follow C-H insertion with

nucleophilic attack of free amine at the electron deficient carbon in either $\underline{1}$ or $\underline{2}$, reaction (14):
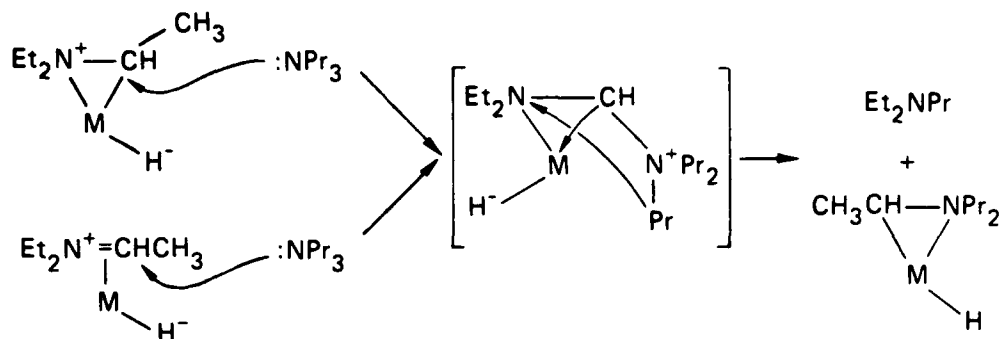
Both reactions are possible because aziridinium compounds will undergo ring opening via attack of nucleophiles as weak as chloride ion[32] [reaction (15)], and even imines, normally less electrophilic than

$$(15)$$
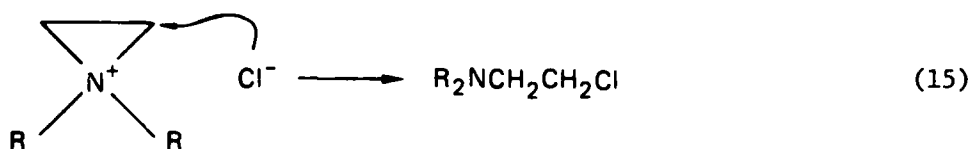
iminium species, are readily susceptible to attack by amine nucleophiles [reaction (16)], as evidenced by the work of Garrou,[33] Nicoletti,[34] Porzi,[35] and Murahashi.[22]

$$R-CH=N-R' + R''NH_2 \longrightarrow \left[R-CH \begin{matrix} NHR'' \\ NHR' \end{matrix} \right] \longrightarrow RCH=NR'' + R'NH_2 \quad (16)$$
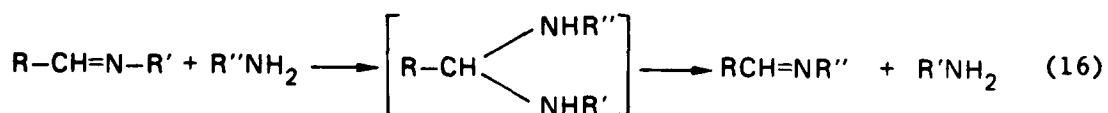
The following observation suggests an alternative mechanism. When transalkylation, reaction (2), occurs in the presence of D_2O, every alkyl group that is transferred is extensively and selectively deuterated. The products are always $Et_2NCHDCD_2CH_3$ and $Pr_2NCHDCD_3$. This result would occur if the species undergoing nucleophilic attack were $\underline{4}$

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rather than <u>1</u> or <u>2</u>, as shown in reaction (17). The general mechanism for transalkylation via an intermediate such as <u>4</u> would then be as shown in (17).

$$Et_2N^+=C-H \quad :NPr_3 \quad \longrightarrow \quad Et_2N-CH \quad \overset{Pr \quad Pr}{N^+-Pr} \quad \longrightarrow \quad Et_2NPr + \quad HC=N^+Pr_2 \quad (17)$$
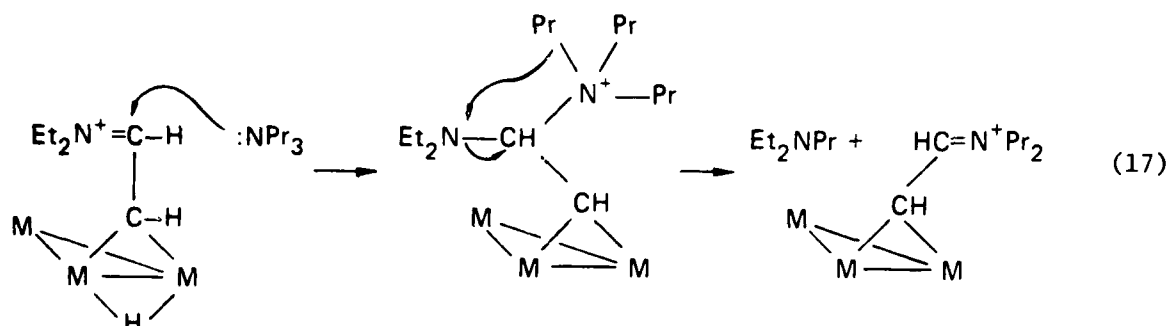
From our deuterium exchange studies,[13,15,16] we know that it is possible to catalyze deuteration without promoting transalkylation. This indicates that deuterium for hydrogen exchange occurs much faster than transalkylation. If such is the case, then the fact that all transferred alkyl groups are extensively deuterated is simply a consequence of rate differences between deuteration and transalkylation. However, it is important to note that the exchanged ethyl group always contains four deuterium atoms and the exchanged propyl group always contains three deuterium atoms. In each case, one α hydrogen does not exchange. For this to occur, <u>deuteration and then transalkylation must happen while the amine remains bound to the catalyst species.</u>[36]

The fact that transalkylation is faster when Pr_3N binds to the active catalyst rather than when Et_3N binds to the catalyst can be viewed in two ways. One viewpoint would be that Et_3N makes a better, less sterically encumbered nucleophile than Pr_3N does. The other is that the metalloazocyclopropane intermediate formed when Pr_3N binds to the catalyst is energetically more favorable than its Et_3N counterpart complex, especially regarding the formation of the bridging carbene that results in complete deuteration, e.g., <u>4</u>. This assumes that the metalloazocyclopropane intermediate is the intermediate that leads to alkyl transfer. If the lifetime (relative concentration) of the metalloazocyclopropane is greater for the Pr_3N complex than it is for

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the Et_3N complex, then alkyl transfer will proceed at a greater rate via the Pr_3N complex. The fact that the major deuteration product for Pr_3N is $Pr_2NCHDEt$ supports the idea that the propylamine metalloazocyclopropane complex is the preferred complex for interactions of Pr_3N with the ruthenium catalyst. Because transalkylation with complexed Pr_3N is faster than with complexed Et_3N, the deuteration results support the idea that the metalloazocyclopropane intermediate is the reactive intermediate that leads to transalkylation.

A discussion of the nuclearity of the active catalyst complex further illustrates these last two points.

Catalyst Nuclearity

We previously demonstrated[15] 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; therefore, Murahashi's mechanistic arguments concerning transalkylation catalysis 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 and that catalytic deuteration of tertiary amines involves reversible isomerization of the initially formed palladium-iminium complex with a palladium-enamine complex, as shown in Scheme 2.

Scheme 2
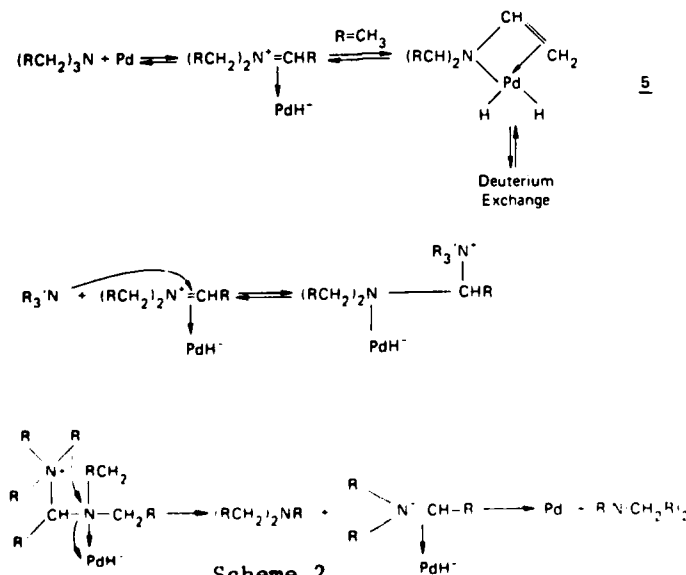
There appear to be two difficulties with this conceptualization. First, it is reasonable to envision the formation of 5 in the context of a normal organometallic complex of palladium because it would be an 18-electron species. However, 5 presumably depicts the reaction of a palladium atom at a metal surface with an enamine and two hydrides. As shown, the palladium would not be capable of binding to other palladium atoms in the surface. This rationale alone suggests that at least two palladium atoms are involved and, likewise, that at least two ruthenium atoms are involved in the homogeneous system.

The second problem is, as mentioned above, the fact that both palladium black and ruthenium catalyze deuteration of only four of the five exchangeable hydrogens in the ethyl group undergoing transalkylation, and only three of the four α and β hydrogens on the propyl groups. Furthermore, the first hydrogen exchanged is always the α hydrogen. For this to occur, either the α carbon stays bound to the catalyst throughout the reaction sequence (deuterium exchange and then possibly transalkylation) or is held away from the catalyst complex as in 4. Alternatively, the selectivity could derive from a two- or three-metal-atom intermediate similar to 5 that undergoes repeated β C–H insertion, deuterium exchange, and reductive elimination. In any case, the selective exchange of only one α hydrogen argues in favor of a catalytic site of two or three metal atoms. One can also argue that because deuteration always precedes or occurs concurrently with transalkylation (see Scheme 2) and always to the same extent, the same site promotes both deuteration and alkylation, although both reactions need not obtain from the same reaction sequence.

A three-metal-atom site for transition-metal-catalyzed deuteration and transalkylation catalysis seems most favorable based on our studies described above and the literature. The most compelling evidence comes from structural characterizations described by Deeming and Yin,[38] and by Shapely et al.[31] such as that for 4, which shows that an iminium species based on Et_3N can be obtained under mild conditions through

reaction with $Os_3(CO)_{12}$. If $\underline{4}$ were deuterated so as to regenerate Et_3N-d_3, the product would be $Et_2NCHDCHD_2$, which is the only d_3 product observed in osmium-catalyzed deuteration and transalkylation. Furthermore, bridging carbenes, such as those depicted in Schemes 1 and 2, are commonly found to form from the reactions of $Os_3(CO)_{12}$ with amines, without cluster fragmentation, as evidenced by the work of Deeming, who was able to prepare and characterize compounds $\underline{6}$, $\underline{7}$, and $\underline{8}$ from the reactions of dimethylbenzyl amine with $Os_3(CO)_{12}$.
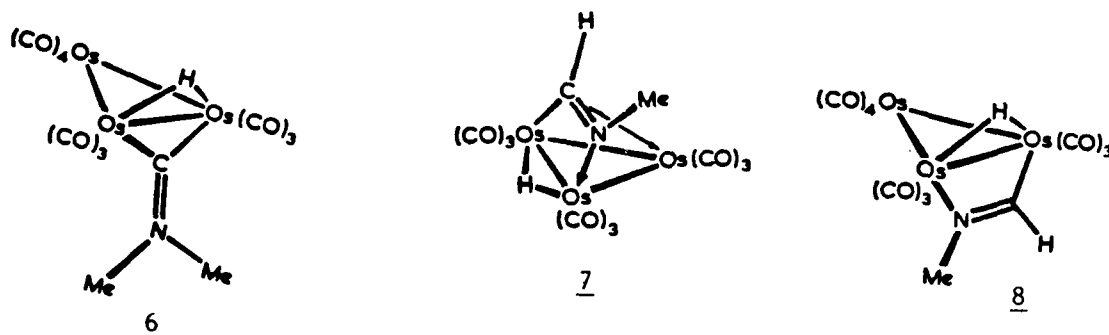
The osmium compounds are generally more robust than their ruthenium counterparts, which may explain why there are few examples of carbenes bridging ruthenium. However, because osmium is, under some conditions, a better transalkylation catalyst than ruthenium, it is likely that the same catalyst intermediates are involved for both metals. Thus, ruthenium analogies to $\underline{4}$ and $\underline{6-8}$ may be available via reaction of ruthenium carbonyl with the same substrates, but may not be readily isolable.

Recently, Jensen and Kaesz have reported[39] the preparation and characterization of a bridging amine-carbene, $\underline{9}$, under extremely mild
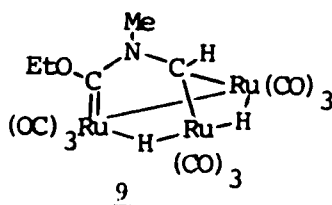
conditions, which provides further support for the existence of species analogous to $\underline{4}$ in ruthenium-catalyzed transalkylation.[40] Yet, until we have isolated ruthenium species from reaction (2) that can be demonstrated to participate in the transalkylation reaction, the exact nature and nuclearity of the transalkylation catalyst must remain in doubt. We are currently studying this problem.

Mixed-Metal Studies

We have previously surmised that the catalysis rate enhancements we observe when iron carbonyls are mixed with ruthenium carbonyls arise due to the formation of mixed-metal cluster complexes that bind less strongly to the reactants and/or products than ruthenium alone. The rate enhancement observed with the addition of iron carbonyl would then be further support for a cluster-catalyzed reaction, as mentioned above in the Catalyst Concentrations Studies Section. An alternative explanation could be that the iron species accelerate the reaction through electron transfer processes. At present both possibilities require further investigation.

Applications to Synthesis

Our initial objectives for the synthetic studies were to develop transalkylation routes to nitrogen macrocycles because this area appears to have the most potential for immediate reward. Our approach has been to establish the reactivity patterns of various tetra-substituted diamines with the premier catalyst system developed in the first part of the studies, the mixed-metal iron/ruthenium catalyst system. Our goal is to develop an understanding of the factors that affect polyamine oligomerization and cyclization. At present, our results are only preliminary; however, they are promising, especially when considered in light of Murahashi's recent work.[22]

The results of the first series of reactions studied, (18) and (19), qualitatively indicate that dimethylamino groups undergo

$$\text{Me}_2\text{NCH}_2\text{CH}_2\text{NMe}_2 \xrightarrow[\text{122 h/145\% conversion}]{\text{Ru}_3(\text{CO})_{12}/160^0\text{C}} \text{N,N-dimethylpiperazine} \quad (18)$$

$$\text{Et}_2\text{NCH}_2\text{CH}_2\text{Net}_2 \xrightarrow[\text{72 h/50\% conversion}]{\text{Ru}_3(\text{CO})_{12}/160^0\text{C}} \text{Et}\left[\text{N(Et)CH}_2\text{CH}_2\right]_x\text{NEt}_2 \quad (19)$$
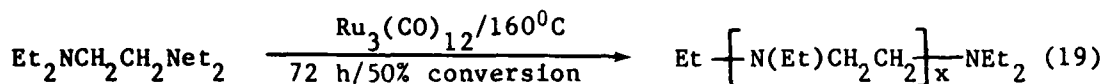
$x = 2-5$

transalkylation at a significantly slower rate than do diethylamino groups. This result is reasonable considering that the C-N bond dissociation energy of methyl amines (75 kcal) is 3 kcal higher than that of the ethyl amines (72 kcal).[12] Another difference between the methyl amine reactions and those of the ethyl amines is that the methyl-substituted ethylenediamine gives cyclized products almost exclusively, whereas the ethyl-substituted diamine gives staight chain oligomers almost exclusively.

It is of interest to note that the dimethylpiperazine produced in reaction (13) must derive from two tetramethylethylene diamines; yet, only trace quantities of the intermediate pentamethyldiethylene triamine are found in the reaction solution. This suggests that either the reactivity of the triamine with the catalyst is much higher than that of the diamine or, more likely, that once the intermediate triamine is formed, it remains bound to the catalyst species and preferentially cyclizes rather than becoming displaced by another amine ligand.

It is still too early to determine whether or not these differences in reactivity and selectivity are a consequence of steric or electronic effects. The important points are as follows: it is possible to efficiently oligomerize tertiary diamines, and it is possible to cyclize these same types of amines. In fact, in reaction (20), because considerable amounts of Et_3N are produced, it is likely that the Et_3N successfully competes with the oligomeric amines for catalyst, and thus the reaction has reached equilibrium. Therefore, reaction (14) could be considerably improved by continually distilling the Et_3N. All these

possibilities are currently being pursued in this laboratory.

At this point, it is not possible to compare the results of our synthetic studies with those of Murahashi[22] because we have not as yet explored the synthetic utility of our catalyst systems in-depth. However, our own studies with palladium black catalysts in many forms reveal that these catalysts rapidly lose activity when heated with tertiary amines at moderate temperatures (125-150°C).[41] Garrou et al.[33] report the same findings when palladium black is reacted with primary or secondary amines. Thus, it appears that palladium black is not the catalyst of choice for transalkylation reactions.

Garrou et al. also find that ruthenium chloride and tributyl phosphine react in the presence of primary and secondary amines to give transalkylation catalysts that are quite active. These catalysts appear to be better than either the Murahashi palladium black catalyst or the ruthenium chloride triphenylphosphine catalyst system used by Porzi et al.[35] to catalyze the transalkylation of primary and secondary amines. Finally, the rates at which our ruthenium carbonyl catalyst systems function are comparable to those reported by Garrou and by Murahashi even though our substrates are tertiary amines. This suggests that our systems are potentially useful catalysts for primary and secondary amine transalkylation.

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36. A third mechanism for transalkylation is also possible. In this mechanism the metalloazocyclopropane intermediate, 1, opens up to give a metal-bound amide and a carbene, $Et_2N-M_x=CHCH_3$ that subsequently undergoes attack by Pr_3N to give $Et_2N-M_x=CHCH_2CH_3$ and Pr_2NEt. Work by Motschi and Angelici (Ref. 37) on reactions of metal carbene complexes with nucleophiles suggests that such a mechanism is possible; however, we have at present no evidence for this type of mechanism.

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40. Because of the lack of literature precedent, we have neglected a two-atom mechanism although there is no valid argument against the possibility.

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CAPTIONS FOR FIGURES

Figure 1   A Plot of the Initial Rates of Transalkylation as a Function
of CO Pressure

(a)   Initial rates are defined as the turnover frequency
(TF) = no. of mol of Et_2NPr produced/mol of $Ru_3(CO)_{12}$-
hour.

(b)   Reactions were run in methanol under 100 psig CO, at
160° C; total volume was maintained at 5.0 mL; 3.71
mmol of Et_3N and Pr_3N were used in a 1:1 ratio.

Figure 2   A Plot of the Initial Rates of Transalkylation as a Function
of Catalyst Concentration

(a)   Initial rates are defined as the turnover frequency
(TF) = no. of mol of Et_2NPr produced/mol of $Ru_3(CO)_{12}$-
hour.

(b)   Reactions were run in methanol under 100 psig CO, at
160° C; total volume was maintained at 5.0 mL; 3.71
mmol of Et_3N and Pr_3N were used in a 1:1 ratio.

Figure 3   Initial Rates of Catalysis as a Function of Changes in the
Total Amine Concentration

(a)   Initial rates are defined as the turnover frequency
(TF) = no. of mol of Et_2NPr produced/mol of $Ru_3(CO)_{12}$-
hour.

(b)   Reactions were run in methanol with 0.05 mmol
$Ru_3(CO)_{12}$, under 100 psig CO, at 160°C; total volume
was maintained at 5.0 mL.

Figure 4   Initial Catalytic Rates as a Function of the Ratio of Et_3N to
Pr_3N

(a)   Initial rates are defined as the turnover frequency
(TF) = no. of mol of Et_2NPr produced/mol of $Ru_3(CO)_{12}$-
hour.

(b)   Reactions were run in methanol with 0.05 mmol
$Ru_3(CO)_{12}$, under 100 psig CO, at 160°C; volume was 5.0
mL; total amine was maintained at 8.72 mmol.

Appendix C

COMMENTS ON THE MECHANISMS OF HETEROGENEOUS
CATALYSIS OF THE HYDRODENITROGENATION REACTION

COMMENTS ON THE MECHANISMS OF HETEROGENEOUS
CATALYSIS OF THE HYDRODENITROGENATION REACTION

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Abstract:

We have recently demonstrated that it is possible to model the catalytic reactions of tertiary amines with heterogeneous catalysts by studying the reactivity patterns of tertiary amines with homogeneous group 8 transition metal catalysts. In one study we modeled the catalytic reactions of the industrial hydrodenitrogenation (HDN) catalyst cobalt-molybdenum (CoMo) using a homogeneous rhodium catalyst. This study included modeling the catalytic cleavage of saturated carbon-nitrogen bonds.

Based on our modeling studies and on literature evidence we can, for the first time, propose mechanisms that describe how HDN catalysts remove nitrogen as NH_3 from the nitrogenous materials found in crude oil, other potential hydrocarbon/fuel sources, or model compounds. Moreover, our proposed mechanisms can also account for the anomalous behavior exhibited by HDN catalysts in the presence of normal catalyst poisons such as H_2S or H_2O that enhance HDN catalysis. We propose that H_2S, H_2O, or related compounds enhance catalysis by promoting heterocyclic ring opening via nucleophilic attack on the metal-complexed heterocycle. We predict that NH_3 should also enhance HDN catalysis.

INTRODUCTION

The purpose of this commentary is to draw from recent observations in these laboratories and from literature examples to propose logical mechanisms that describe the catalytic pathways by which heterogeneous catalysts catalyze hydrodenitrogenation.

The objective is to provide researchers in the area with a comprehensive hypothesis of the mechanisms operative in catalytic hydrodenitrogenation that can be tested experimentally and that has the potential to result in the development of better catalysts.

Hydrodenitrogenation (HDN) is the catalytic process by which nitrogen is removed as NH_3 when petroleum is refined to fuel or petrochemical feedstocks. HDN is also an important step in converting coal, oil shale, or tar sands to synthetic fuels. If nitrogen is not removed from these hydrocarbon sources, products with undesirable characteristics form during refining. More important, the basic nature of the nitrogen-containing species effectively poisons the acidic hydrocracking and reforming catalysts used in the refining process. Thus, HDN is necessary and vital in producing high-quality, low-cost fuels and feedstocks.

At the industrial level, HDN catalysis is performed using hetero-geneous catalysts consisting of either cobalt and molybdenum oxides (CoMo) or nickel and molybdenum oxides (NiMo) supported on alumina. HDN is normally performed at 350-500°C and at up to several thousand psi of hydrogen.[1-5]

Because it is difficult, if not impossible, to study CoMo- or NiMo-catalyzed HDN of crude oil, studies are often conducted using model compounds such as pyridine,[1] indole,[6] or quinoline.[2,7,8] It is thought that these compounds most closely resemble the nitrogen-containing compounds found in crude oil, coal, oil shale, or tar sands. Studies performed with NiMo catalysts and a quinoline substrate have resulted in the HDN reaction network shown in Scheme 1.

QUINOLINE HDN REACTION NETWORK

Scheme 1

C-3
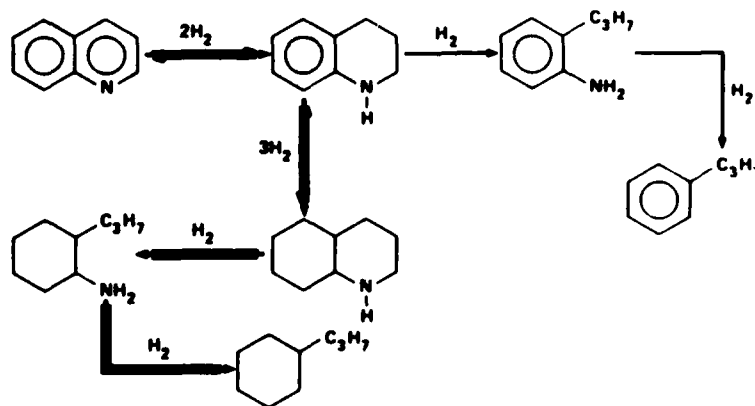
Most of the quinoline undergoes HDN by the heavily lined pathway that produces propylcyclohexane. This pathway uses almost twice as much hydrogen as the pathway that produces the more desirable (higher octane) propylbenzene. A considerable savings in hydrogen and a better hydrocarbon product would be obtained if NiMo or CoMo catalytic activity for C-N bond cleavage could be enhanced relative to their activities for hydrogenating the hydrocarbon aromatic ring or if new HDN catalysts could be developed with improved relative C-N bond-breaking efficiencies. The end result would be cheaper fuels.

If it is possible to understand the mechanisms for C-N bond cleavage in NiMo- or CoMo-catalyzed HDN, it should be possible to improve the NiMo or CoMo catalysis of HDN or to develop better catalyst. To date, modeling studies of NiMo- or CoMo-catalyzed HDN have resulted in the determination of rate constants and thermodynamic equilibria for the formation and disappearance of all the species shown in Scheme 1.[7,8] No one has attempted to describe mechanisms for C-N bond cleavage as it occurs in HDN. Nelson and Levy[9] have suggested that most C-N bond cleavage arises from Hofmann degradation. In contrast, the results we reported[10a,b] indicate that no organic chemistry (C-N bond cleavage) occurs even at 260°C, at least with tertiary amines. C-N bond cleavage is observed only in the presence of a metal catalyst. These observations are confirmed by the work of Bhindo et al.[10c]

We have recently demonstrated the homogeneous catalytic cleavage of C-N single bonds[11] and we have successfully demonstrated that the catalytic interactions of several homogeneous group 8 metal catalysts with tertiary amines closely mimic the catalytic interactions of several heterogeneous catalysts with these amines.[10,12] One of these heterogeneous catalysts was CoMo.

On the basis of these results and the inferences drawn from the literature, as described below, we believe that the stoichiometric and homogeneous catalytic reactions of transition metal complexes with amines can be used to explain the mechanisms of heterogeneous catalysis of HDN, in particular, the specific reactions by which C-N bonds are broken in saturated nitrogen heterocycles.

BACKGROUND

We have recently observed the catalytic cleavage of saturated C-N bonds in the transalkylation reaction (1)[11] at 125°C.

$$R_3N + R_3'N \xrightarrow[M = Ru,Os]{M_3(CO)_{12}/125°C} R_2NR' + R'_2NR \qquad (1)$$
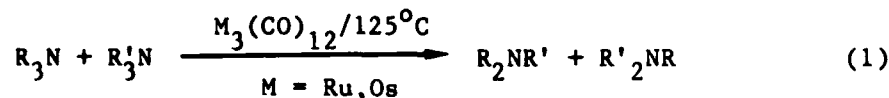
We have also found it possible to homogeneously catalyze the exchange of deuterium for hydrogen on several tertiary amines[12] using a variety of group 8 metal complexes:[10]

$$Et_3N + D_2O \xrightarrow[\text{CO/125}^\circ\text{C}]{Rh_6(CO)_{16}} Et_2NCHDCD_3 \text{ (major product)} \qquad (2)$$
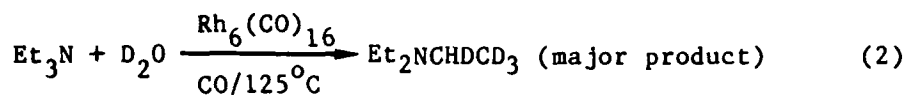
From studies of the homogeneous catalysis of reactions (1) and (2), we can conclude the following concerning the mechanisms of C-H and C-N bond activation.

The deuterium for hydrogen exchange studies with homogeneous ruthenium catalysts or palladium black[12] indicate a mechanism for C-H activation as shown in Scheme 2.
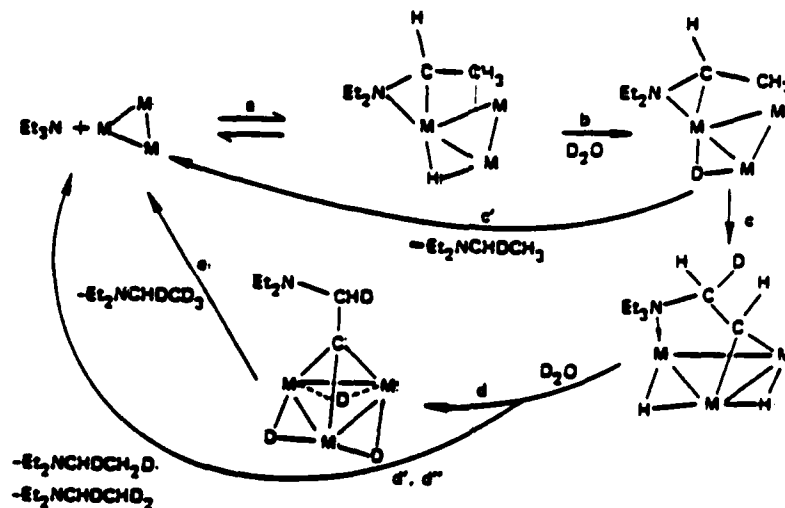
Scheme 2

For the rhodium cluster or CoMo catalyzed exchange reaction,[10] a mechanism for C-H exchange as depicted in Scheme 3 can be proposed.

SCHEME 3

C-5
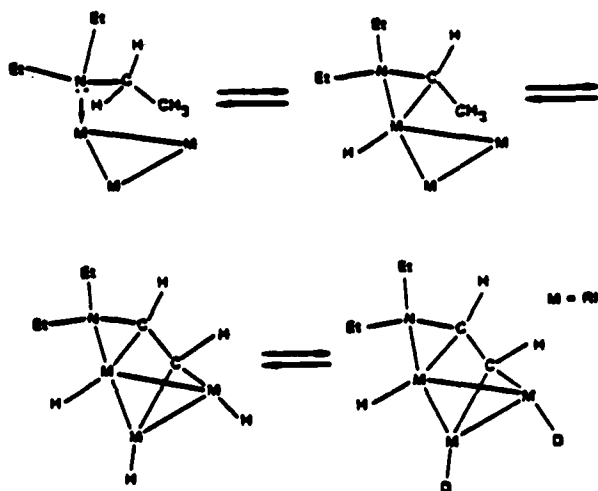
In each case, the reaction begins with the formation of a metalloaza-cyclopropane, $\underline{1}$, which is an extreme form of an iminium ion complex, $\underline{2}$.

$$\underline{1} \qquad\qquad \underline{2}$$
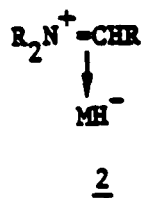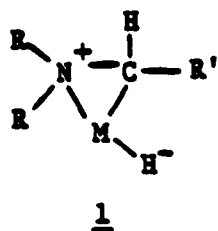
When D_2O was added to reaction (1), the mixed alkyl amine products were found to have the transferred alkyl group deuterated exactly as it is when reaction (2) is the only reaction allowed to occur. Thus, C-N bond activation is initiated by C-H bond activation. Moreover, it is reasonable to conclude that complexes such as $\underline{1}$ or $\underline{2}$ are intermediates in the transalkylation reaction.

In fact, Murahashi proposes the mechanism shown in Scheme 4 to account for palladium black catalysis of reaction (1).[12b]
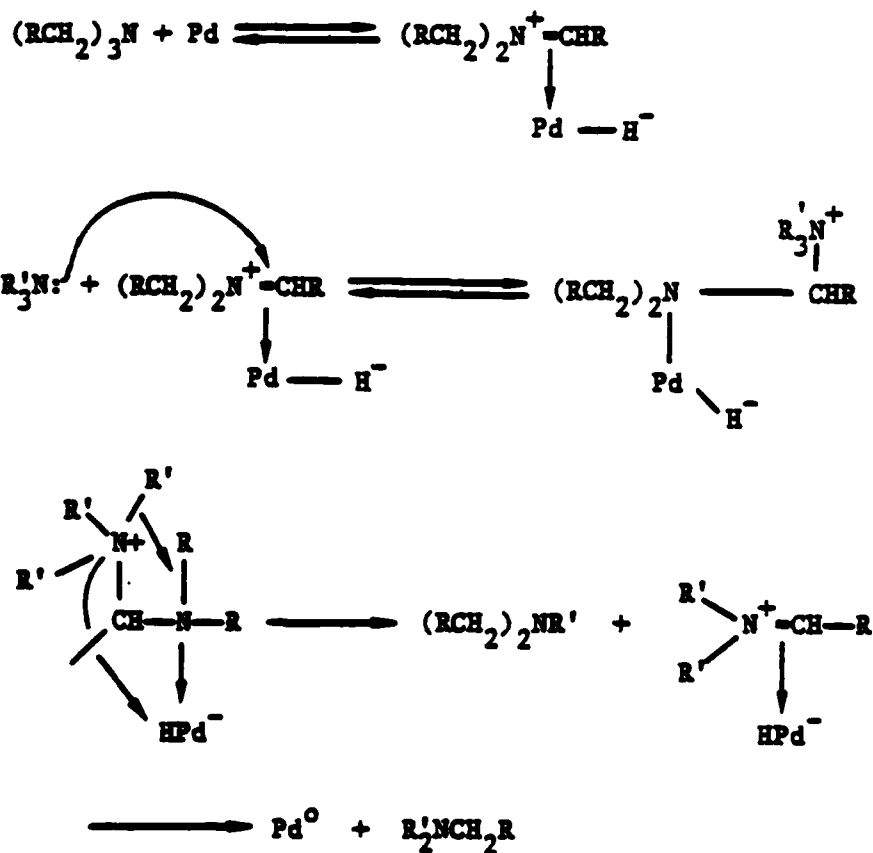
While Murahashi's mechanism proceeds through an iminium complex such as 2, an intermediate metalloazacyclopropane (e.g., 1) is not unreasonable in view of the literature[13] and the ease with which cationic azacyclopropane rings (aziridinium rings) undergo nucleophile promoted ring openings.[13b]

These precedents become invaluable towards developing a complete mechanistic understanding of HDN when coupled with the fact that the reactivity patterns of tertiary amines with the homogeneous ruthenium or rhodium catalysts correlate extremely well with the reactivity patterns of these same amines with the respective heterogeneous catalysts palladium black and CoMo.[12,13]

On the basis of these results and observations, it now appears possible to propose reasonable mechanisms for C–N bond cleavage as it occurs in HDN of model compounds or crude oil. Furthermore, it is even possible to propose novel mechanisms that explain the anomalous behavior of HDN catalysts in the presence of sulfur (as H_2S) or H_2O and predict their behavior in the presence of excess NH_3.

Most catalytic reactions are poisoned if the feedstocks contain H_2S, H_2O, or NH_3.[3,14,15] In contrast, CoMo or NiMo catalysis of HDN experiences significant rate enhancement[2] if the feedstock contains H_2S and some rate enhancement if H_2O[15] is present. We predict that NH_3 will also enhance the rate even though it is a product and its presence would normally disadvantageously shift the equilibrium (Scheme 1).

The current point of view, at least in the case of sulfur, is that sulfiding slowly transforms the molybdenum oxides in the CoMo catalyst into MoS_2, which is a better catalyst because of its different physical properties.[16*] While this is at least partially true,[16] there are several attractive alternative explanations in which H_2S, NH_3, and H_2O act as nucleophiles to facilitate ring opening, as illustrated below.

In the following discussion of CoMo- or NiMo-catalyzed C–N bond scission, it is assumed that piperidine is representative of the saturated heteroaromatic rings that undergo C–N bond cleavage as part of the HDN process. Furthermore, our discussions are devoted only to developing mechanistic explanations of how the ring opens, and not HDN of primary amines, based on the following information.

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*Note that Bhinde et al.[10c] point out that C–N bond cleavage is enhanced by H_2S in the gas phase and not by sulfided CoMo, thus casting doubt on this explanation.

Thermodynamic calculations predict that the formation of ethylamine is favored at low temperatures:[17]

$$NH_3 + CH_2=CH_2 \longrightarrow EtNH_2 \qquad \Delta G_{298°C} = -3.5 \text{ kcal/mole} \qquad (3)$$
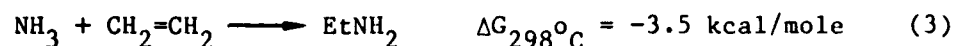
At slightly higher reaction temperatures the reaction becomes thermo-neutral, and finally at temperatures near 450°C, the reverse reaction is favored. Primary amines are readily cracked to alkenes and NH_3 in the presence of alumina.[18,19] Consequently, the difficult step in HDN is heterocyclic C–N bond scission to ring-opened products. Any primary amines formed will rapidly give NH_3 and alkene. The alkene will then be hydrogenated to alkane. Therefore, in the following sections, we propose a set of mechanisms for ring opening via catalytic C–N bond cleavage based on the mechanisms we and others have previously proposed for the trans-alkylation reaction, reaction (1).[10-12]

Mechanisms of C–N Bond Cleavage in Heterocycles

For simple, unassisted ring opening, at least two pathways are possible. One requires a metal alkyl intermediate (Scheme 5) and the other a metal alkylidene intermediate (Scheme 6).*

Scheme 5

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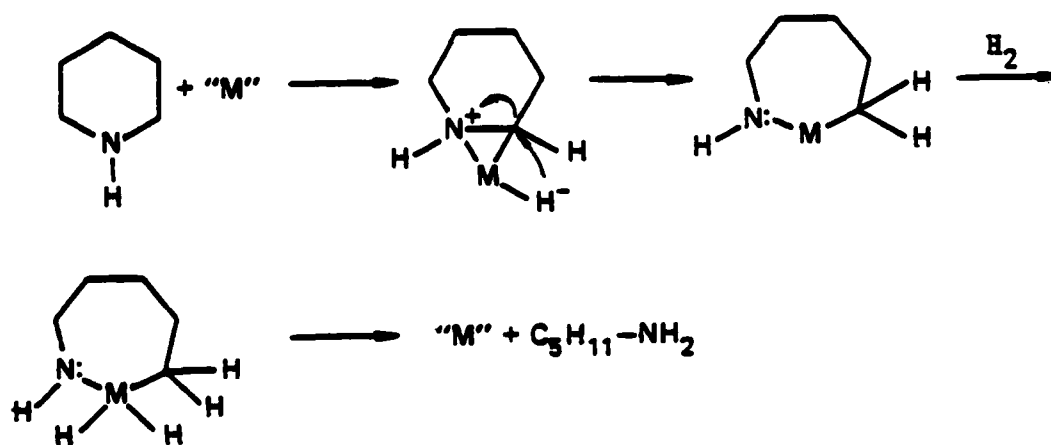
*Although in Scheme 5 and in the following schemes we have illustrated the propose mechanisms using only one metal atom, it is likely; considering the number of coordination sites necessary for catalysis, that more than one metal atom is required especially heterogeneously, to promote catalysis.

C-8

Scheme 6
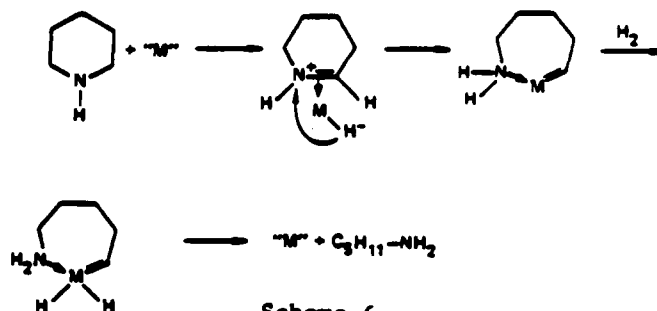
We have chosen to obtain a ring-opened metal alkyl intermediate via a metalloazocyclopropane and a metal carbene intermediate via an iminium complex intermediate to illustrate the various choices of pathways. These proposed mechanisms should not be construed as limiting: there are undoubtedly other choices. Our intent here, as well as with the mechanisms described below, is to provide logical mechanistic pathways to explain our results and literature observations. More important, the proposed mechanisms can serve as initial guidelines for future kinetic and mechanistic studies.

A true test of a proposed mechanism's viability is that it must explain the characteristic anomalies of the reaction. As noted above, CoMo catalysis of HDN is enhanced by the presence of H_2S and H_2O, which are normally catalyst poisons. Of key importance is the observation by Satterfield that the rate enhancement occurs in the C-N bond breaking/ ring-opening step of the saturated ring and not in the hydrogenation step.[2,15] In the following schemes, we propose reaction mechanisms for HDN that account for the anomalous increases in catalytic activity that occur when HDN is performed in the presence of H_2S or H_2O and what might be expected in the presence of NH_3. In all cases, we believe that enhanced HDN catalysis occurs because ring opening is promoted through nucleophilic attack by H_2S, H_2O and NH_3 on the metal-complexed ring.

The first mechanism considers HDN catalysis as passing through an iminium complex intermediate where, in the presence of H_2S, ring opening proceeds via nucleophilic attack to form the thiohemiaminal.

Scheme 7

C-9
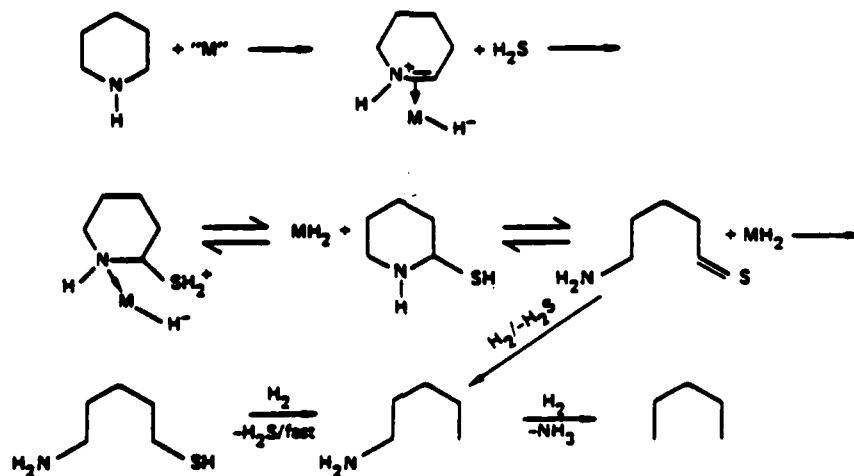
A similar scheme can be written using H_2O as the nucleophile.

If the reaction proceeds via a metalloazocyclopropane in the presence of NH_3, an alternative but equivalent mechanism can be proposed based on nucleophilic attack by NH_3.
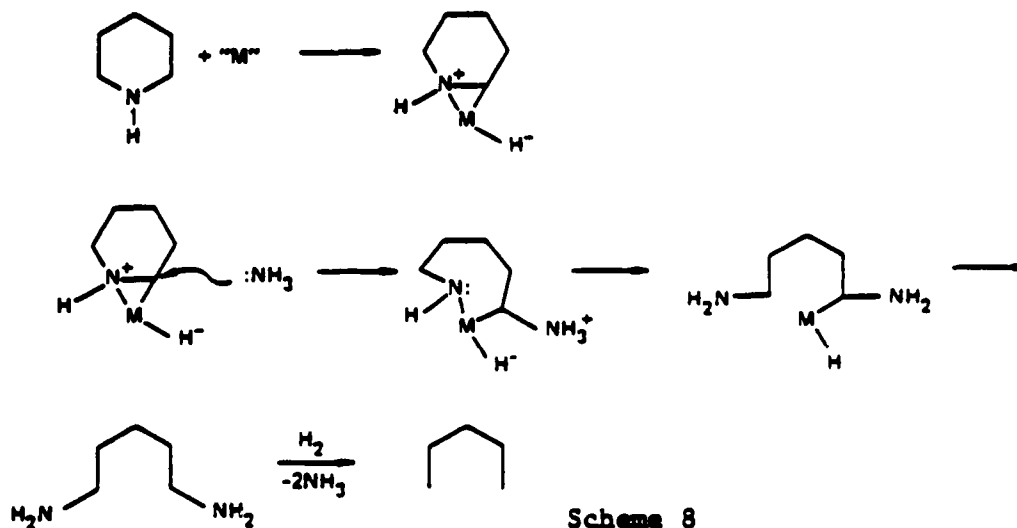
Scheme 8

An analogous reaction pathway can be written for H_2S or H_2O.

Alternatively, secondary amines are known to form Schiff's base complexes with metals.[20,21] Thus we obtain a mechanism based on nucleophilic attack as in Scheme 9.[17]
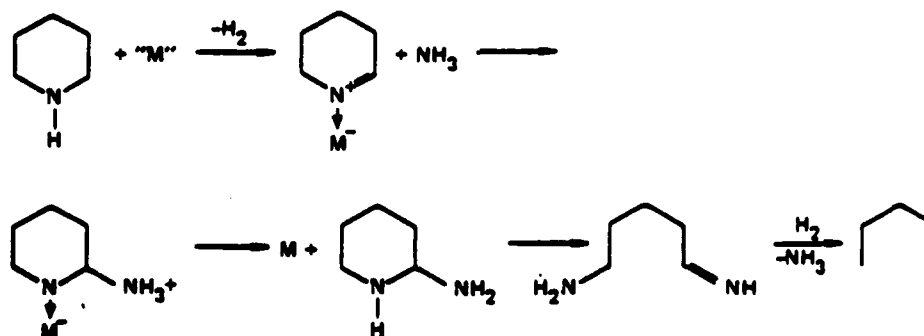
Scheme 9

Reactions such as those depicted in Scheme 9 have been proposed for a number of heterogeneously catalyzed transalkylation reactions, reaction (4)[21-23] and one homogeneously catalyzed reaction, reaction (5).[24]

$$2RCH_2NH_2 \xrightarrow[\text{or CuO}]{\text{Raney Ni or Pd black}} (RCH_2)_2NH + NH_3 \qquad (4)$$

$$2(RCH)_2NH \xrightarrow{\text{RuCl}_2[\text{P(PH)}_3]_3} (RCH_2)_3 + RCH_2NH_2 \qquad (5)$$
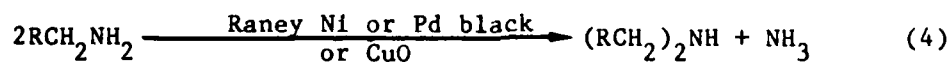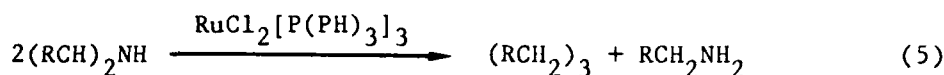
Similar mechanisms have been suggested for homogeneously catalyzed amination reactions (6)[25] and (7).[26]

$$R_2NH + CH_3CN \xrightarrow{\text{La}^{3+}} \qquad (6)$$

$$CH_2=CH(CH_2)_nNHR \xrightarrow[n=3]{\text{PtCl}_4^{2-}/\text{H}^+} \qquad (7)$$
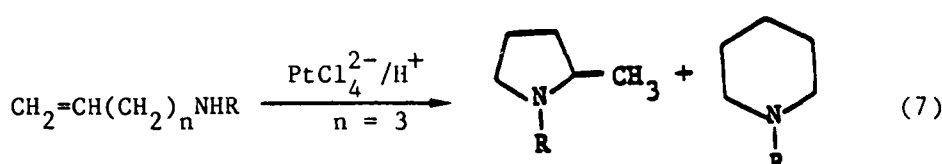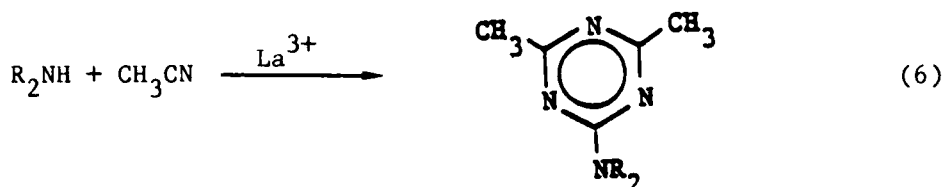
In addition, related stoichiometric reactions involving amine additions to complexed alkynes, reaction (8),[27] and those with alkenes are also known.[28-30]

$$(8)$$
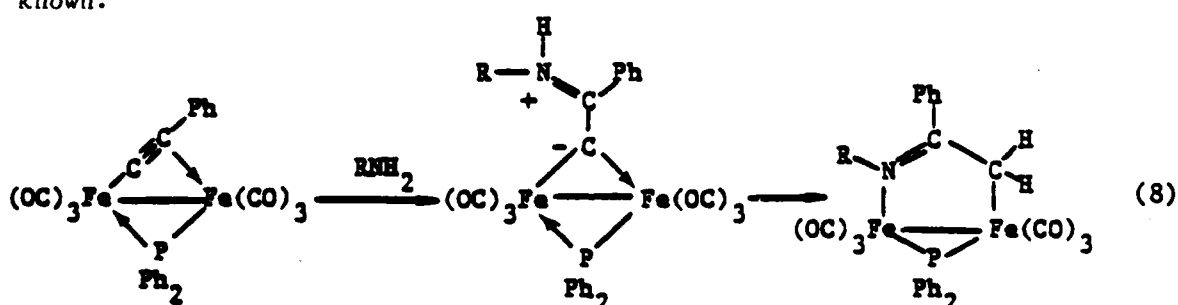
A key observation that supports our contention that H_2S enhancement of HDN catalysis occurs via nucleophilic attack assisted ring opening is the observation by Klemm et al. that the standard HDN catalyst $CoMo$ can catalyze the formation of sulfur-carbon bonds under HDN conditions:[31]

$$(9)$$

C-11
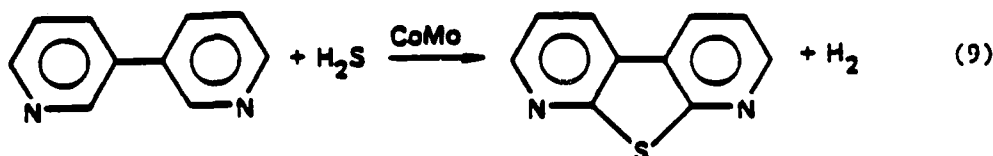
In fact, the preferred position of sulfur insertion is on the carbon α to the nitrogen. In separate work, Sharpless et al. have shown that molybdenum oxyimido species can add in a stoichiometric fashion to carbon-carbon double bonds to give various types of diamines and hydroxyamines, thus supporting the H_2O and proposed NH_3-related mechanisms of ring opening.[32,33]

The formation of the aminal intermediates and their ring opening to give imines, 3, thialdehydes, 4, and aldehydes 5, have been known for decades and are most commonly found in sugar chemistry.
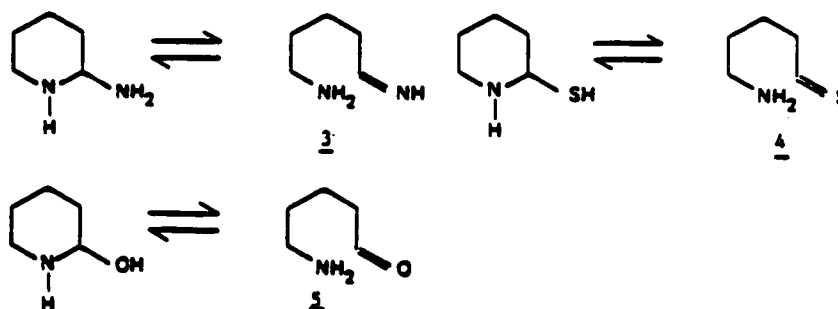
The deamination of the imine species, 3, probably occurs by hydrogenation to the diamine, which is subsequently cracked as described above. Thialdehyde (e.g. 4) desulfurization can occur at 0°C on supported molybdenum catalysts.[34] Only hydrodeoxygenation of aldehydes such as 5, or the related hydrogenation product the primary alcohol, have not been demonstrated for heterogeneous catalysts, although we have shown that our homogeneous rhodium cluster catalysts can hydrodeoxygenate amino alcohols to amines.[35]

If in Scheme 9, piperidine were substituted for NH_3 in either of the mechanisms, the end product would not be pentane but n-pentylpiperidine (see Scheme 10) because the tertiary amine formed following ring opening would not be as susceptible to HDN as the primary amines.

Scheme 10

C-12
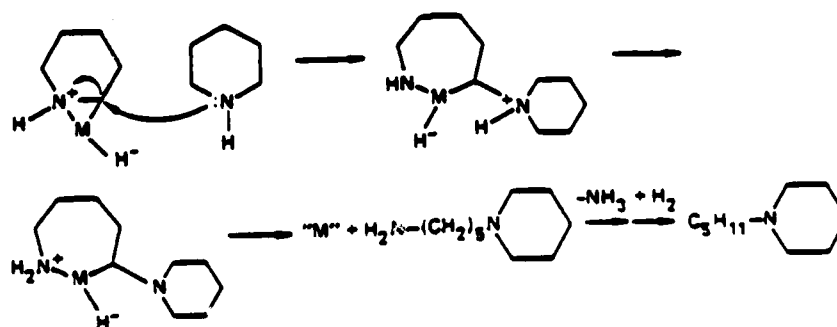
In fact, Sonnemans et al. see n-pentylpiperidine as the major intermediate in the CoMo-catalyzed HDN of either pyridine or piperidine.[1]

In our modeling studies using rhodium cluster catalysts to hydrogenate pyridine we observed hydrodenitrogenation of pyridine [as shown in reaction (10)] to give 1,5-bis(piperidino)pentane in better than 60% yield:[35]*

$$\text{(10)}$$
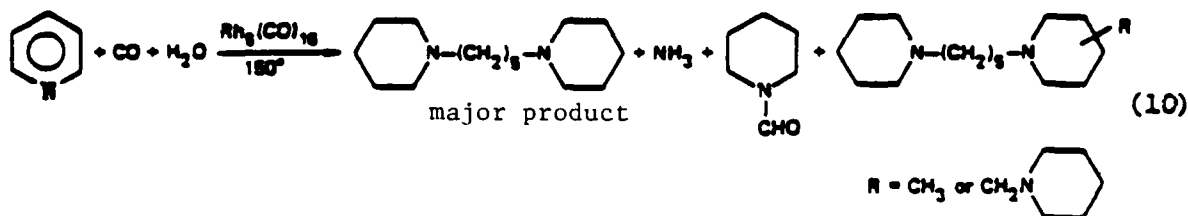
Most recently, in unpublished work, we have observed that substitution of quinoline for pyridine in (10) gave good yields of ring-opened dimers of tetrahydroquinoline and ring closed dimers. In other studies, we have found that substitution of H_2/CO mixtures for H_2O/CO in (10) gave essentially the same products though with slightly lower yields. This result negates our original conjecture[35] that water was <u>necessary</u> for ring opening in reaction (10) and further supports our current concept that nucleophilic attack promotes ring opening.

Finally, the most convincing support for enhanced catalytic cleavage of C-N bonds via nucleophilic attack of sulfur, nitrogen, or oxygen species comes from the rates one would expect based on the relative nucleophilicities of the attacking species. Qualitatively, in the following series of compounds $RSe^- > RS^- > R_2NH > NH_3 > H_2O$, selenium is the most nucleophilic and H_2O is the least nucleophilic. Thus, if nucleophilic attack of these types of species were responsible for C-N bond cleavage of complexed piperidine, then RSe^- should be most active and H_2O should be least active.

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*Cracking of primary amines is not expected to occur at 150°C. The resulting bispiperidinopentane probably results from attack of a second piperidine on a complex formed from the amino group of 1-piperidino-5-aminopentane.

Goudriaan[36] reported that CoMo-catalyzed HDN of piperidine gave n-pentylpiperidine exclusively if the CoMo was reduced in the absence of sulfur compounds. This would be expected if piperidine acts coincidently as substrate and nucleophile, because it is a better nucleophile than NH_3.

Goudriaan also found that in the presence of H_2S the amount of n-pentylpiperidine formed is greatly reduced in favor of n-pentylamine as would be predicted given the greater nucleophilicity of sulfur compared with piperidine or NH_3 and given the proposed mechanism shown in Scheme 7. This assumes that the rate of hydrodesulfurization is greater than HDN for the thioaldehyde-amine intermediate.

If this rationale for nucleophilic attack is reasonable, then selenide compounds, which are more nucleophilic than sulfur compounds, should facilitate ring opening at an even faster rate than sulfur.

Murahasi and Yano have shown that phenyl selenide can be used for ring opening as shown in reaction (11).[37]

$$\text{(pyrrolidine)} + \text{PhSeLi} \xrightarrow[\text{Ru metal}]{80°} \xrightarrow{H_2O} \text{PhSe(CH}_2\text{)}_4\text{NH}_2 \qquad (11)$$
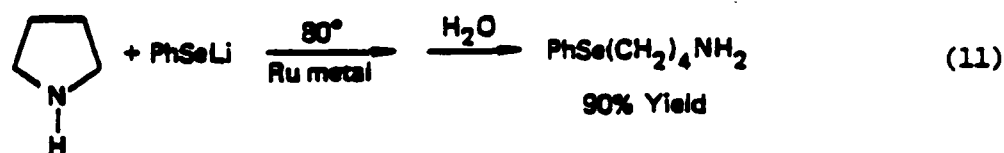
90% Yield

The 90% yield at 80°C for reaction (11) is consistent with what would be expected for ring opening involving nucleophilic attack. In addition, Murahashi and Yano find ring opening with phenyl sulfide to occur at one fourth the rate found with phenyl selenide as predicted by differences in nucleophilicity.

Finally, reaction (11) further supports our proposed mechanism of sulfur-assisted ring opening because hydro-deselenation does not occur; thus the carbon-selenium bond is preserved and provides an analogy to the species proposed in Scheme 7.

Post Script

In the foregoing discussions, we have attempted to develop a comprehensive mechanistic picture of the catalytic pathways by which heterogeneous catalytic HDN proceeds. The various mechanisms that have been proposed account for in detail, all of the observations made in these laboratories and the majority of those reported in the

literature. It is our hope that these proposed mechanisms will prove valuable in the development of improved HDN catalysts or in the development of the next generation of HDN catalysts.

Acknowledgements

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Appendix D

METALLIC PALLADIUM, THE ACTUAL CATALYST
IN LINDAR AND ROSENMUN REDUCTIONS?

METALLIC PALLADIUM, THE ACTUAL CATALYST IN
LINDLAR AND ROSENMUND REDUCTIONS?

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SUMMARY: We provide evidence that the poisons used in the preparation of LINDLAR and ROSENMUND catalysts do not block active sites but act to rearrange the surface structure of the catalyst.

The hydrogenation of alkynes to cis–alkenes (LINDLAR reduction) and the catalytic hydrogenolysis of acid chlorides to aldehydes (ROSENMUND reduction) are well known text book examples of reactions with 'selectively poisoned' catalysts.[1]

scheme 1

The partial hydrogenation of alkynes to give cis-alkenes, an important reaction in natural product synthesis, is usually achieved by heterogeneous hydrogenation with 'poisoned' LINDLAR catalysts. There has been considerable effort in the past to replace this 'mythical' catalyst by homogeneous methods. Thus, Li in THF,[2] Na with BF_3 in diglyme,[3] diisobutyl aluminum hydride and methyl lithium,[4] chloroborane in ether,[5] $PdCl_2$ and H_2 in DMF,[6] $LiAlH_4$ and $TiCl_4$,[7] $Rh(NBD)(PPhMe_2)_3$,[8] and CuI[9] can be used to hydrogenate alkynes to give cis-alkenes. None of these methods, however, has replaced the LINDLAR catalyst, which is used in the total synthesis of Leukotrienes,[10] prostaglandines,[11] carbohydrates,[12] and various other natural products[13].

The LINDLAR catalyst and its modifications generally consist of deactivated palladium supported on $BaCO_3$ or $CaCO_3$ although Pd/C has also been used.[14] Historically, LINDLAR catalysts are poisoned by lead acetate, with quinoline as additional catalyst poison.[15] Successful reactions with untreated catalysts have

also been reported.[16] In a very recent paper Dev describes the effects of using various transition metal chlorides to modify LINDLAR catalysts. Dev finds that the $MnCl_2$ modified catalyst is the most selective for alkyne hydrogenation to alkenes;[17] however, no data concerning the stereoselectivity (cis/trans ratio) of the $MnCl_2$ poisoned catalyst were reported.

The ROSENMUND reduction[18] catalyst is palladium supported on barium sulfate poisoned by sodium acetate,[19] N,N-dimethylaniline,[20] thiourea,[21] thiophene,[21] dibenzothiophene,[21] ethyldiisopropyl amine,[22] or, most commonly, quinoline (with and without sulfur)[23]. While the ROSENMUND reduction has long been replaced by more practical homogeneous procedures with metal hydrides, the secret of the selective catalyst deactivation has never been uncovered. The very similar preparation procedures suggest that the ROSENMUND catalysts are related to LINDLAR catalysts; although, the literature surprisingly, does not draw any comparison.

The broad range of poisons used to cause identical or similar modifications of the catalytic activity of supported palladium to give either LINDLAR or ROSENMUND catalysts is suggestive that the poisons are not involved in the catalytic process but rather change the surface of the catalyst. The generally accepted rationale for the effect of catalyst poisoning suggests that the 'poison' blocks the most active catalyst sites and thus prevents undesired further reactions. However, as described below, we find that the poisons do not block certain active sites but rather act to rearrange the palladium structure in a very drastic way.

RESULTS AND DISCUSSION

We find that untreated, commercial palladium foil catalyzes the hydrogenation of alkynes to cis-alkenes with high selectivity. The following test reactions were carried out in the presence of 6 cm² of palladium foil (see table 1). 5-decyne is converted to cis-5-decene with no trans by-product detectable. Diphenylacetylene as well gives pure cis-stilbene. Even dimethyl acetylene dicarboxylate, hydrogenated at 100 °C for 160 hrs, resulted in dimethylmaleate (cis/trans ratio 30:1).

table 1

Our results are especially remarkable for two reasons:

1. Conventional LINDLAR hydrogenations use supported catalysts with surface areas much larger than 100 m²/g, whereas our palladium foil has only a surface area of only 6 cm². The conversion achieved (turnover frequency = 4 (molecules/surface

atom x second)) is even more surprising, when we consider that such turnover frequencies larger 1 have only been observed under ultrahigh vacuum conditions with extremely clean surfaces.[24].

2. Lindlar reductions are very rarely completely selective. The observed cis/trans ratio commonly varies between 10-30 and often the reaction must be carefully monitored and stopped in order to achieve the desired cis excess. The high selectivity achieved with the foil is therefore very unusual and certainly worth further study to pursue other practical applications. The palladium foil is not as readily deactivated as are supported catalysts and may be used indefinitely. We are presently engaged in the development of a more practical modification of this foil method in order to provide a reliable synthetic method for cis hydrogenation of alkynes.

Our results suggest that the actual catalytic species in the LINDLAR catalysts is the metallic palladium and the poison serves only to modify the surface structure of the catalyst. In fact, the above described studies evolved as a consequence of the following experiments that justify the concept of surface re-ordering.

During a hydrodenitrogenation study[25] we observe that a palladium on silica catalyst loses all its hydrogenolysis activity after contact with indole (which is structurally related to the ROSENMUND and LINDLAR poison quinoline). During this treatment the surface area of the deactivated catalyst reduces from 395 m^2/g to 195 m^2/g (N_2-BET method). Considering the high surface area of the pure support (235 m^2/g) these data indicate that the catalyst has lost almost all of its palladium surface. Combustion analysis of the deactivated catalyst[26] does not reveal significant presence of carbon, and the traces of nitrogen detected are not consistent with adsorbed indole.[27] This deactivated catalyst did, however, produce cis-5-decene from 5-decyne and propanal from propionyl chloride, thus acting as both a 'LINDLAR' and a 'ROSENMUND' catalyst.

We also find that palladium black, after contact with triethylamine and D_2O at 150 °C for 20 hrs in a batch reactor, is completely rearranged to metallic palladium.[28] The following scanning electron micrographs[29] demonstrate the observed change. Picture 1 shows the untreated palladium black[30] at 2K and 100 k magnification. Picture 2 shows the same palladium after contact with the amine. Clearly the metal has completely changed its structure and is converted to metallic particles of low surface area.

Picture 1: Palladium black at magnification 2,000 and 100,000.[29]

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<u>Picture 2:</u> Palladium black after contact with triethylamine at 150 °C, magnification 2,000 and 100,000.[29]

In addition to these observations, we have recently presented evidence that amines (e.g., quinoline) react with palladium black to form labile palladium-hydride species.[28] Moreover, it is well known that high surface area palladium reversibly 'dissolves' large quantities of hydrogen with great facility, through formation of labile palladium hydrides.[31] It is our contention that these hydrides in decomposing change the metal crystallite morphology to reduce surface area.

These observations strongly support our hypothesis that the poisons used to deactivate palladium catalysts do not block active sites, but act to rearrange the surface structure of the palladium.

That the catalyst poisons are not involved in the actual reductions is also supported by the observed transformation of benzoyl chloride (429 mg) to benzaldehyde with ultrapure palladium powder[32] (29 mg) at 0 °C (7% conversion after 16 hrs). The same, untreated palladium powder also catalyses the transformation of 5-decyne (10 ml) to <u>cis</u>-5-decene (after 22 hrs complete conversion to 70% <u>cis-</u>, 8% <u>trans</u>-5-decene, 12% decane and 10% unidentified isomers was obtained).

However, the 'LINDLAR'-active palladium foil showed no activity for the conversion of benzoyl chloride to benzaldehyde under various conditions. This experiment demonstrates, that despite similar catalyst preparation procedures, the two reactions are catalysed by different active sites; the active site for semihydrogenation being the 'metallic' palladium, the nature of the active site for acid chloride hydrogenolysis is not identified yet. A detailed investigation with defined palladium surfaces is actively being pursued.[33]

Appendix E

SYNTHESIS AND CRYSTAL STRUCTURE OF
TRIS(BIPYRIDYL)NICKEL BIS(TRINITROMETHIDE)

SYNTHESIS AND CRYSTAL STRUCTURE OF
TRIS(BIPYRIDYL)NICKEL BIS(TRINITROMETHIDE)

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Abstract: We have synthesized and characterized tris(bipyridyl)nickel bis(trinitromethide) to study the use of trinitromethane anion (trinitromethide) as a novel ligand, to understand the nature of the bonding in trinitromethide, to improve our understanding of how nitrogen heteroaromatic compounds bind to metals, and to determine if metal binding affects the rates of catalytic hydrogenation of nitrogen heteroaromatic species. We report the results of a crystallographic study on the nickel complex and some related experimental findings. Two independent trinitromethides in the unit cell each contain two nitro groups that are planar, including the carbon atom, whereas the third nitro group oxygens are roughly perpendicular to the plane of the other two nitro groups. Thus, the three-fold symmetry expected for a fully delocalized trinitromethane anion is not observed. Moreover, the third nitro group nitrogen has a considerably longer C-N bond [1.46(2) Å] than the other two [1.37(3) Å]. In fact, trinitromethide appears to be delocalized in analogy to a beta-diketonate ligand. This observation suggests that trinitromethide could act as a novel ligand. The tris(bipyridyl)Ni cation is normal and structurally identical with previous structural characterizations of this cation.

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Introduction

Initially, we undertook the work described below for three reasons: to study the use of the trinitromethane anion (trinitromethide) as a novel ligand, to improve our understanding ⋯ aromatic compounds complex to metals, ⋯ complexation improves the rates ⋯ heteroaromatic species.

We recently became intrigued ⋯ as a ligand for the formation ⋯ metal complexes, especially ⋯ complexes that can function ⋯ specifically attempted to prepare methide because we anticipated ⋯ susceptible to oxygenation ⋯ Furthermore, we were curious ⋯ because it has resonance forms ⋯ diketonate ligands and consequently ⋯

1   2   3
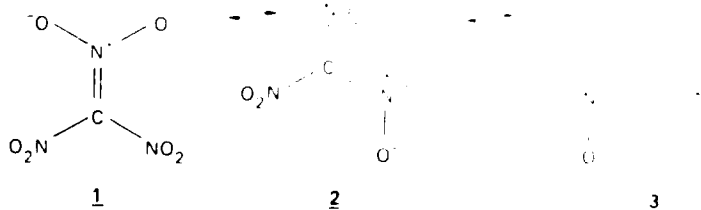
We are also currently exploring the use of homogeneous catalysts as models of heterogeneous catalytic hydrodenitrogenation (HDN).[3] HDN is the process by which nitrogen is removed (as NH_3) from crude oil, coal, oil shale, or tar sands during the refining process. Nitrogen is commonly present in the form of nitrogen heteroaromatics in these substances. In HDN catalysis, the heteroaromatic rings are first hydrogenated; then, by some as yet poorly understood process, the C—N bonds in the resultant heterocycle are cleaved and NH_3 is formed.[4]

Industrial HDN catalysts are usually mixtures of nickel or cobalt and molybdenum oxides, supported on alumina, that have been activated by reduction under flowing hydrogen at high temperatures.[5]

Nickel has frequently been implicated as the catalyst in the heteroaromatic hydrogenation step.[4,5] In addition to acting as the hydrogenation catalyst, nickel(II), when coordinated to the electron pair on the pyridine nitrogen, will under some conditions promote hydrogenation of the ring.[6] This result prompted us to consider what effects nickel(II) might have on the ring that would make it more susceptible to hydrogenation.

There are two possible explanations for this effect. One explanation is that simple binding of the electron pair on the nitrogen introduces a positive charge on the nitrogen, which in turn reduces the electron density in the adjacent C-N double bond and makes it more susceptible to hydrogenation via nucleophilic attack of hydride. If this is the case, then simple protonation, or alkylation of the nitrogen in the ring, should also improve hydrogenation rates.

Alternatively, backbonding of the ring through the nitrogen to the nickel could reduce the overall aromatic character of the ring, thus facilitating hydrogenation. Despite the fact that the tri(bipyridyl)-nickel cation has previously been the subject of a structural analysis,[7] we have undertaken a low temperature X-ray diffraction study of tris(bipyridyl)nickel bis(trinitromethide) $[(bipy)_3Ni][C(NO_2)_3]_2$ to set the stage for our future work in this area and to see if through low temperature studies it is possible to obtain more exact information on the structural changes that occur from complexation of the nitrogen heteroaromatic than is currently available.

Experimental Section

General Methods

X-ray Crystallography: Crystals of $[(bipy)_3Ni[C(NO_2)_3]_2]$ suitable for crystallographic studies were grown via vapor diffusion of diethyl ether into a solution of the compound in acetone. Intensity data were obtained on a Nicolet R_3M/E Autodiffractometer at -110°C, using Wyckoff

scanning techniques with a scan rate of 8.0 degrees/min over a 0.8 degree scan range. Monochromatic Mo Kα radiation was used throughout the study. Examination of the systematic absences observed with the diffractometer provided the space group assignment noted in Table 1. Unit cell parameters were obtained by least-squares refinement of 25 centered reflections. The cell parameters and other pertinent data are also listed in Table 1.

The structure of tris(bipyridyl)nickel bis(trinitromethide) was solved with SHELXTL Revision 4.0 using direct methods and a Patterson transformation. The position of the nickel atom and most of the carbon, nitrogen; and oxygen atoms were located by direct methods; the remaining atoms, including hydrogen atoms, were located using difference Fourier techniques. Cascading diagonal least-squares refinement with anisotropic nonhydrogen atoms and anisotropic hydrogen atoms converged to R = 0.054 and Rw = 0.0481.

Specific Compounds

$[(bipy)_3Ni[C(NO_2)_3]_2]$: Bis(2,2'-bipyridyl) nickel(II) chloride dihydrate (1 g, 21 mmol) was stirred with 5 mL of water. An aqueous solution of nitroform, (2 mL, 2.1 M) was slowly added to the stirred mixture to give a yellow solid. The solid was washed with water and dried under vacuum at RT. The yield was 91.6% of theoretical (1.06 g, 1.3 mmol).

Anal. Calcd. for $NiC_{32}H_{24}N_{12}O_{12}$: C, 46.46; H, 2.92; N, 20.31. Found: C, 46.41; H, 2.90; N, 20.26.

$[(Bipy)Ni(NO_3)_2 \cdot 3H_2O]$: Bipyridine (1.6 g, 10.2 mmol) was added to an aqueous solution of nickel nitrate hexahydrate (1.0 g, 3.4 mmol). The solution was stirred for 24 h, and the water was removed under reduced pressure. The product was recrystallized from ethanol and ethyl ether to give a blue solid in 91% yield (1.2 g, 3.1 mmol).

Anal. Calcd. for $NiC_{10}H_{14}N_{24}O_3$: C, 30.56; H, 3.59; N, 14.25. Found: C, 30.52; H, 3.46; N, 14.50.

$[(Bipy)_2Pd\ C(NO_2\ _2]$: Bipyridine (140 mg, 0.9 mmol) was added to a solution of 200 mg (0.30 mmol) of palladium(II) acetate in ethanol. An

aqueous solution of nitroform was added to the solution until no more yellow precipitate formed. The product was washed with ethanol to give the yellow product in 90% yield (167 mg, 0.27 mmol).

Anal. Calcd. for $PdC_{22}H_{16}N_8O_8$: C, 42.16; H, 2.57; N, 17.87. Found: C, 42.13; H, 2.74; N, 17.31.

$[(Bipy)_2NiCl_2 \cdot 2H_2O]$: Bipyridine (2.0 g, 12.8 mmol) was added to an ethanolic solution of nickel chloride hexahydrate (1.0 g, 4.2 mmol). The solution was stirred for 24 h to give a precipitate. The crude product was recrystallized from ethanol and ethyl ether to give a pink product in 86% yield (1.75 g, 3.6 mmol).

Anal. Calcd. for $NiC_{20}H_{20}N_2O_2Cl_2$: C, 49.42; H, 4.15; N, 11.52. Found: C, 50.17; H, 4.49; N, 11.77.

Results and Discussion

In our original efforts to synthesize a nickel complex containing the trinitromethide anion, we attempted to synthesize a $(bipy)_2Ni$ trinitromethide complex as shown in reaction (1). Unexpectedly, we

$$(bipy)_2NiCl_2 + HC(NO_2)_3 \longrightarrow [(bipy)_2Ni-\eta^2-C(NO_2)_3][C(NO_2)_3] \qquad (1)$$
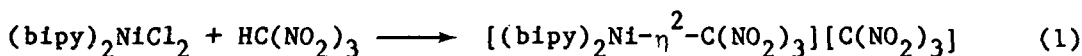
were able to isolate only the disproportionated trisbipy product:

$$(bipy)_2NiCl_2 + HC(NO_2)_3 \longrightarrow [(bipy)_3Ni][C(NO_2)_3]_2 + HCl \qquad (2)$$
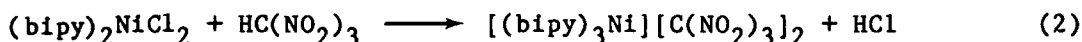
Even when using a monobipy nickel complex, $(bipy)Ni(NO_3)_2$, we were able to isolate only the trisbipy complex, although there was some evidence (color changes) that there were other intermediate products that perhaps were the desired complexes. In an effort to overcome the undesirable disproportionation effects, we substituted palladium for nickel in the hopes that reaction (3) would obtain.

$$Pd(OAc)_2 + HC(NO_2)_3 + bipy \longrightarrow (bipy)Pd[\eta^2-2-C(NO_2)_3] + HOAc \qquad (3)$$
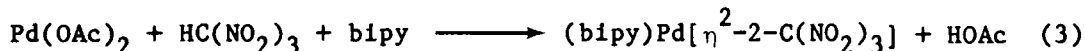
In this reaction, we observed the formation of a $(bipy)_2Pd$ complex, reaction (4), but we were able to coordinate the trinitromethide.

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$$Pd(OAc)_2 + HC(NO_2)_3 \longrightarrow [(bipy)_2Pd][C(NO_2)_3] + HOAc \qquad (4)$$
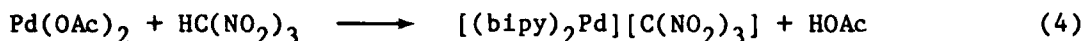
Because we were still interested in the bonding of the trinitromethide, we decided to proceed with a low temperature structural determination of the product from reaction (2). The results of this determination are described as follows.

$C(NO_2)_3$ Anion:

In 1967, Dickens[8] reported the crystal structure of the trinitromethane anion at $-160°C$ with monoprotonated hydrazine as the counterion. The results of that study and particularly the conclusions do not correlate well with our results. Dickens observed two forms of the methide anion: one in which the average C-N bond length was 1.40-1.42 Å and one that was of the same form we observe in these studies as seen in Table 2 and Figure 1, wherein there are two short C-N bond distances of 1.37(2) Å [we find 1.386(15) Å, averaged for both anions] and one longer C-N bond of 1.46(2) Å [1.459(11) Å avg. see Table 2]. Futhermore, Dickens finds the dihedral angle between the unique nitrogroups (defined as longest C-N bond) to be either 41 degrees or 74 degrees. We observe in our studies (see Table 3) that one anion has a dihedral angle of 90.1(5) degrees. The other anion is less symmetrical and has a dihedral angle of >63.1(6)°. From the torsion angle data in Table 3, it is evident that in one anion, two nitro groups (including all the oxygens and the carbon atom) are essentially planar. The oxygens of the third nitro group are nearly perpendicular to the plane as seen clearly in Figure 1. The second anion deviates from this configuration to some degree, especially in that the unique nitro group is not perpendicular to the other two nitro groups nor is the planarity well defined; however, the key feature of one long and two short C-N bonds is maintained.

Dickens argues that the crystallographic differences between the two anions that he observes are a consequence of his counter-ion (hydrazine) hydrogen bonding to the methide and a result of crystal packing forces. In the present case, there are no hydrogen bonding forces to contend with, but it is possible that crystal packing forces

contribute significantly to the distortion in bonding in the one somewhat irregular anion.

The most important point, which Dickens fails to mention, is that there is a unique nitro group which because of its long C-N bond length and its significant lack of planarity with respect to the other two nitro groups (see Figure 1), is unable to participate in delocalization of the anionic charge, despite the great probability for this occurrence. That is, on the basis of resonance structures 1-3, equivalent delocalization of the charge is expected to occur across all the possible resonance structures. The fact that this does not occur, as illustrated by Figure 1, points to the likelihood that from a molecular orbital standpoint, complete delocalization is not attainable.

In view of our original objectives, this observation strongly supports our contention that the trinitromethane anion can function as a stable bidentate ligand. The next step will be to search for an appropriate metal to bind this new ligand.

(Bipy)$_3$Ni Cation

The bond lengths and bond angles listed in Tables 2 and 3 do not present any significant departure from the structural features reported by other workers for the (bipy)$_3$Ni cation (see Figure 2), with the exception that the average value for the Ni-N bonds [2.102(4) Å] reported here is somewhat longer than the value of 2.089(4) Å reported by Wada et al.[7] in 1976 for [(bipy)$_3$Ni]SO$_4$·7.5H$_2$O. The average C-N bond length is considerably longer than that of 2.062 Å reported by Tedenac and Phillippot[9] for the (bipy)Ni(H$_2$O)$_2$, 4. Here we see some indication that electronic effects can influence metal-heteroaromatic binding. In compound 4, only one bipy group can act as both a σ donor and π acceptor ligand. In [(bipy)$_3$Ni[C(NO$_2$)$_3$] there are three such groups, and these groups compete for the available electron density at the Ni center. Consequently, the bonds between the Ni and the bipy groups in this compound will be weaker than those in compound 4, as evidenced by the longer Ni-N bond lengths.

The changes in electron density in the ring are more difficult to evaluate based on the C-N and C-C bond lengths because these values do

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not seem to change significantly on bonding. Therefore, we have tried an alternative analytical approach to measuring the effects of complexation on electron density in the heteroaromatic ring. This approach consists of determining the changes in electron density at the ring carbons as a function of perturbations of the electron pair on the ring nitrogen. Perturbations can be made via protonation, alkylation, and complexation to various metals in a number of oxidation states and with a variety of ligands. We are currently pursuing this possibility in-depth and will report the results later when we will also report the results of our hydrogenation studies.

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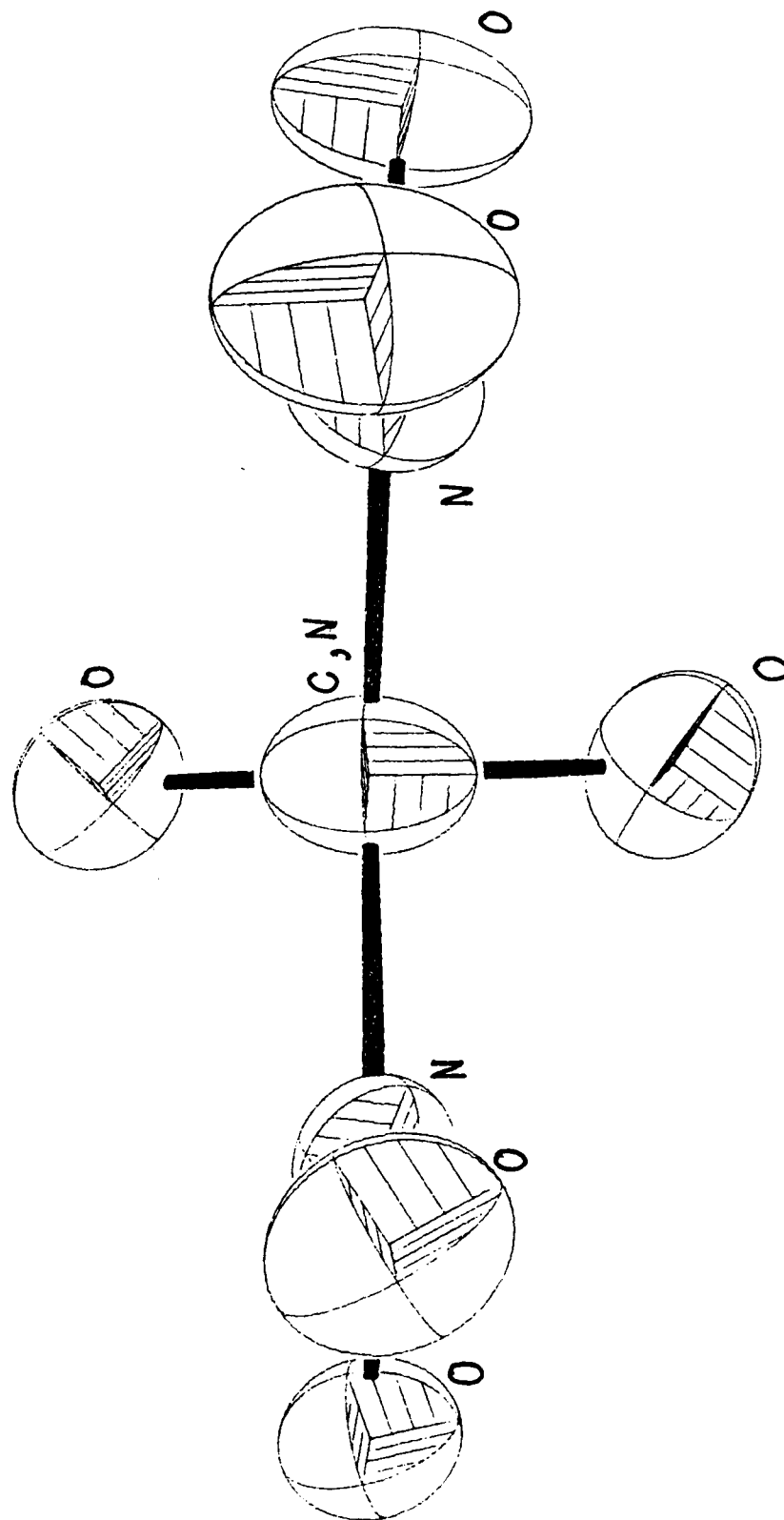
Figure 1   Trinitromethane Anion

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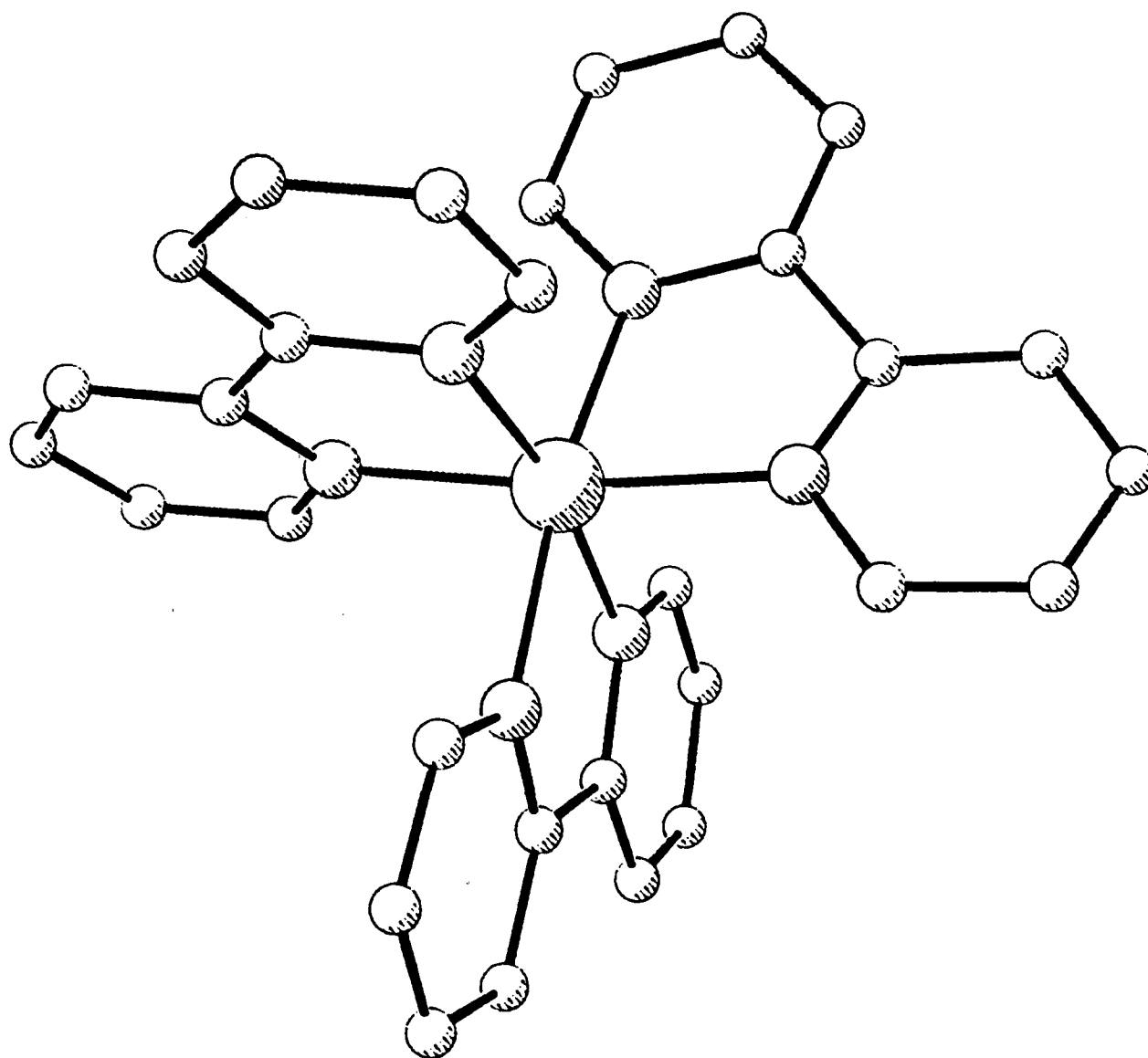
Figure 2   Tris(bipyridyl)Nickel Dication.

Table 1

Crystallographic Parameters for $(bipy)_3Ni[C(NO_2)_3]_2$
Crystal Data

Mr (amu)	827.37	Space Group	$P\bar{1}$
a (Å)	9.811(1)	α(deg)	87.75(8)
b (Å)	10.754(5)	β(deg)	88.72
c (Å)	18.349(4)	γ(deg)	66.19(2)
vol ($Å^3$)	1769.9(5)	F(000)	591.8(4)
dcalcd(g/cm^3)	0.93	Z	2
Radiation	Mo, Kα	cryst size,mm	irreg. cube-0.3

Experimental Data

2θ range (deg)	3.0-48.3 deg
bkgd meas.	bkgd/scan: 1.0; 1.0 deg offset
freq of std meas.	every 100 reflections
no. of reflections measd.	5658
obsvd $[Fo_2 > 3\ \sigma(Fo_2)]$	4390
final residuals, R = 0.054	Rw = 0.0481.

Table 2

Selected Bond Distances (Å)

bipy 1		bipy 2		bipy 3	
$Ni-N_1$	2.108(3)	$Ni-N_3$	2.091(3)	$Ni-N_5$	2.107(3)
$Ni-N_2$	2.098(3)	$Ni-N_4$	2.088(3)	$Ni-N_6$	2.122(3)

Bipy (Average of the Three)

N_1-C_1	1.357(7)	C_1-C_2	1.395(5)
N_1-C_5	1.359(4)	C_2-C_3	1.392(8)
		C_3-C_4	1.396(4)
		C_4-C_5	1.392(5)
		C_5-C_6	1.501(6)
N_2-C_6	1.358(5)	C_6-C_7	1.397(5)
N_2-C_{10}	1.353(6)	C_7-C_8	1.390(7)
		C_8-C_9	1.387(6)
		C_9-C_{10}	1.399(5)

$\underline{1} = C(NO_2)_3$				$\underline{2}\ C(NO_2)_3$			
$C_{31}-N_7$	1.381(7)	N_7-O_1	1.257(4)	$C_{32}-N_{12}$	1.374(6)	$N_{12}-O_{11}$	1.270(4)
		N_7-O_2	1.246(5)			$N_{12}-O_{12}$	1.244(4)
$C_{31}-N_8$	1.400(5)	N_8-O_3	1.237(6)	$C_{32}-N_{10}$	1.389(6)	$N_{10}-O_7$	1.253(5)
		N_8-O_4	1.256(7)			$N_{10}-O_8$	1.250(5)
$C_{31}-N_9$	1.448(6)	N_9-O_5	1.237(6)	$C_{32}-N_{11}$	1.470(5)	$N_{11}-O_9$	1.236(6)
		N_9-O_6	1.226(6)			$N_{11}-O_{10}$	1.236(5)

Table 3

Selected Angles (deg) for $(\text{bipy})_3\text{Ni}[C(NO_2)_3]^{2-}$

bipy (Average of the three):

N_1-Ni-N_2 78.8(3)	$Ni-N_1-C_1$	126.1(2)	$Ni-N_2-C_6$ 115.8(3)
	$Ni-N_1-C_5$	115.0(4)	$Ni-N_2-C_{10}$ 125.6(2)
	$C_1-N_1-C_5$	118.5(3)	$C_6-N_2-C_{10}$ 118.5(3)
	$N_1-C_1-C_2$	122.3(4)	$N_2-C_6-C_7$ 121.8(4)
	$C_1-C_2-C_3$	118.6(4)	$C_6-C_7-C_8$ 119.1(4)
	$C_2-C_3-C_4$	119.3(2)	$C_7-C_8-C_9$ 119.6(3)
	$C_3-C_4-C_5$	118.9(5)	$C_8-C_9-C_{10}$ 118.4(4)
	$C_4-C_5-N_1$	122.1(7)	$C_9-C_{10}-N_2$ 122.7(3)
	$C_4-C_5-C_6$	122.9(3)	
	$N_1-C_5-C_6$	115.7(3)	

N_1-Ni-N_3 98.5(1)
N_1-Ni-N_4 172.9(1)
N_1-Ni-N_5 90.0(1)
N_1-Ni-N_6 95.5(1)

$C(NO_2)_3$ 1:

$N_7-C_{31}-N_8$	125.3(4)	$C_{31}-N_7-O_1$	117.8(3)
		$C_{31}-N_7-O_2$	121.6(3)
		$O_1-N_7-O_2$	120.6(4)
$N_8-C_{31}-N_9$	116.5(4)	$C_{31}-N_8-O_3$	120.1(5)
		$C_{31}-N_8-O_4$	116.0(4)
		$O_3-N_8-O_4$	123.9(4)
$N_9-C_{31}-N_7$	117.7(3)	$C_{31}-N_9-O_5$	117.0(4)
		$C_{31}-N_9-O_6$	118.8(4)
		$O_5-N_9-O_6$	124.1(4)

$C(NO_2)_3$ 2:

$N_{10}-C_{32}-N_{11}$	115.2(4)	$C_{32}-N_{10}-O_7$	120.3(4)
		$C_{32}-N_{10}-O_8$	117.1(3)
		$O_7-N_{10}-O_8$	122.6(4)
$N_{11}-C_{32}-N_{12}$	116.6(4)	$C_{32}-N_{11}-O_9$	118.1(3)
		$C_{32}-N_{11}-O_{10}$	116.8(4)
		$O_9-N_{11}-O_{10}$	125.0(3)
$N_{12}-C_{32}-N_{10}$	128.0(4)	$C_{32}-N_{12}-O_{11}$	115.8(3)
		$C_{32}-N_{12}-O_{12}$	121.7(3)
		$O_{11}-N_{12}-O_{12}$	122.5(4)

Torsion Angles:

$N_7-C_{31}-N_8-O_3$	12.0(6)	$N_{10}-C_{32}-N_{11}-O_9$	94.9(6)
$N_7-C_{31}-N_8-O_4$	168.6(4)	$N_{10}-C_{32}-N_{11}-O_{10}$	85.5(6)
$N_7-C_{31}-N_9-O_5$	63.1(6)	$N_{10}-C_{32}-N_{12}-O_{11}$	178.2(4)
$N_7-C_{31}-N_9-O_6$	115.9(5)	$N_{10}-C_{32}-N_{12}-O_{12}$	1.3(8)
$N_8-C_{31}-N_7-O_1$	168.9(4)	$N_{11}-C_{32}-N_{10}-O_7$	178.5(4)
$N_8-C_{31}-N_7-O_2$	11.7(7)	$N_{11}-C_{32}-N_{10}-O_8$	175.1(5)
$N_9-C_{31}-N_7-O_1$	3.0(6)	$N_{12}-C_{32}-N_{11}-O_9$	89.5(6)
$N_9-C_{31}-N_7-O_2$	176.3(4)	$N_{12}-C_{32}-N_{11}-O_9$	90.1(5)
$N_9-C_{31}-N_8-O_3$	160.1(4)	$N_9-C_{31}-N_8-O_4$	19.3(6)

Position and Thermal Parameters for $(bipy)Ni[C(NO_2)_3]$

ATOM	X/A	Y/B	Z/C	K	U11	U22	U33	U23	U13	U12	U(EQUIV)
NIC	41038	00457	24350	1 0000	0170	0185	0183	-0003	-0016	-0062	0182
	00005	00005	00003	0000	0003	0003	0003	0002	0002	0002	0002
N1	35293	29586	20391	1 0000	0224	0247	0209	-0005	0008	-0106	0223
	00033	00031	00016	0000	0016	0018	0017	0014	0014	0015	0012
N2	19822	10423	29019	1 0000	0200	0234	0200	-0013	-0014	-0103	0206
	00033	00031	00016	0000	0016	0018	0018	0014	0014	0015	0013
N3	51795	01366	33897	1 0000	0217	0192	0227	-0034	0003	-0075	0214
	00033	00030	00016	0000	0017	0017	0017	0014	0014	0014	0012
N4	44716	-13445	29285	1 0000	0179	0203	0211	-0009	0008	-0074	0199
	00032	00029	00016	0000	0017	0017	0017	0013	0013	0014	0012
N5	33472	-04203	14589	1 0000	0202	0231	0221	0014	-0047	-0087	0218
	00033	00030	00016	0000	0017	0018	0017	0014	0014	0014	0012
N6	61129	-08021	13254	1 0000	0203	0168	0245	0010	-0001	-0072	0207
	00032	00029	00016	0000	0017	0017	0018	0013	0014	0014	0012
C1	43453	24858	15702	1 0000	0273	0284	0229	-0019	0027	-0128	0257
	00044	00039	00020	0000	0022	0023	0021	0017	0018	0019	0016
H1	53641	18865	14916	1 0000	0325						
	00044	00039	00020	0000	0000						
C2	37773	37475	12125	1 0000	0352	0309	0285	0040	0045	-0142	0315
	00046	00040	00022	0000	0025	0024	0024	0019	0019	0021	0017
H2	43843	40195	08906	1 0000	0391						
	00046	00040	00022	0000	0000						
C3	23123	46096	13468	1 0000	0435	0276	0365	0110	-0042	-0113	0371
	00043	00043	00023	0100	0028	0024	0026	0020	0021	0022	0018
H3	13795	54790	10956	1 0000	0440						
	00049	00043	00023	0000	0000						
C4	14554	42069	13536	1 0000	0243	0297	0360	0020	0003	-0050	0323
	00045	00041	00022	0000	0023	0024	0025	0019	0019	0019	0017
H4	04509	48095	19685	1 0000	0410						
	00045	00041	00022	0000	0000						
C5	20975	23224	21360	1 0000	0248	0224	0186	-0018	-0022	-0095	0218
	00041	00037	00019	0000	0021	0021	0020	0016	0016	0018	0015

END

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DTIC

MICROCOPY RESOLUTION TEST CHART

NATIONAL BUREAU OF STANDARDS-1963-A

C6	.12721 .00040	.23879 .00038	.27241 .00020	1.0000 .0000	.0192 .0020	.0246 .0021	.0214 .0020	-.0042 .0016	-.0041 .0016	-.0098 .0017	.0216 .0015
C7	-.00846 .00043	.32006 .00041	.30467 .00022	1.0000 .0000	.0244 .0022	.0264 .0023	.0337 .0024	-.0034 .0018	-.0003 .0018	-.0073 .0018	.0290 .0016
H7	-.05556 .00043	.41543 .00041	.29219 .00022	1.0000 .0000	.0368 .0000						
C8	-.07388 .00046	.26105 .00044	.35524 .00022	1.0000 .0000	.0219 .0023	.0383 .0027	.0306 .0024	-.0064 .0020	.0074 .0019	-.0086 .0021	.0314 .0018
H8	-.16735 .00045	.31522 .00044	.37776 .00022	1.0000 .0000	.0373 .0000						
C9	-.00386 .00044	.12320 .00041	.37270 .00022	1.0000 .0000	.0284 .0023	.0354 .0025	.0283 .0023	-.0028 .0019	.0088 .0018	-.0138 .0020	.0305 .0017
H9	-.04772 .00044	.08847 .00041	.40719 .00022	1.0000 .0000	.0377 .0000						
C10	.13267 .00042	.04800 .00040	.33908 .00021	1.0000 .0000	.0242 .0022	.0252 .0022	.0288 .0022	.0028 .0018	-.0007 .0018	-.0104 .0018	.0260 .0016
H10	.18179 .00042	-.04747 .00040	.35096 .00021	1.0000 .0000	.0320 .0000						
C11	.54574 .00044	.11998 .00040	.36040 .00022	1.0000 .0000	.0273 .0023	.0241 .0022	.0269 .0023	-.0029 .0018	.0016 .0018	-.0092 .0019	.0264 .0016
H11	.50536 .00044	.20338 .00040	.33184 .00022	1.0000 .0000	.0331 .0000						
C12	.63001 .00043	.11539 .00043	.42143 .00022	1.0000 .0000	.0274 .0023	.0337 .0025	.0351 .0025	-.0057 .0020	-.0030 .0019	-.0160 .0020	.0307 .0017
H12	.64497 .00043	.19397 .00043	.43552 .00022	1.0000 .0000	.0371 .0000						
C13	.69119 .00046	-.00637 .00043	.46110 .00022	1.0000 .0000	.0327 .0024	.0450 .0027	.0237 .0022	-.0017 .0020	-.0074 .0018	-.0196 .0021	.0323 .0018
H13	.75258 .00046	-.01445 .00043	.56254 .00022	1.0000 .0000	.0417 .0000						
C14	.66259 .00044	-.11737 .00041	.44026 .00021	1.0000 .0000	.0314 .0024	.0305 .0024	.0281 .0023	.0046 .0018	.0075 .0018	-.0121 .0020	.0302 .0017
H14	.70293 .00044	-.20177 .00041	.46795 .00021	1.0000 .0000	.0375 .0000						
C15	.57517 .00039	-.10512 .00037	.37910 .00020	1.0000 .0000	.0151 .0019	.0222 .0021	.0232 .0021	-.0023 .0016	.0023 .0016	-.0064 .0017	.0205 .0014

C16	.53185 .00039	-.21534 .00037	.35364 .00019	1.0000 .0000	.0131 .0030	.0344 .0021	.0191 .0020	-.0010 .0016	-.0003 .0016	-.0084 .0017	.0206 .0014
C17	.57060 .00043	-.34070 .00039	.39099 .00022	1.0000 .0000	.0262 .0023	.0295 .0023	.0295 .0023	.0022 .0018	-.0043 .0018	-.0109 .0019	.0281 .0016
H17	.63246 .00043	-.36229 .00039	.43342 .00022	1.0000 .0000	.0363 .0000	.0199 .0021	.0364 .0025	.0064 .0018	.0019 .0019	-.0073 .0018	.0289 .0016
C18	.51874 .00043	-.43476 .00039	.36498 .00022	1.0000 .0000	.0276 .0023						
H18	.54338 .00043	-.52093 .00039	.39018 .00022	1.0000 .0000	.0361 .0000	.0239 .0022	.0306 .0023	-.0001 .0018	-.0007 .0018	-.0114 .0018	.0267 .0016
C19	.43139 .00042	-.40247 .00038	.38286 .00021	1.0000 .0000	.0269 .0023	.0245 .0022	.0269 .0022	-.0043 .0018	-.0026 .0018	-.0141 .0019	.0248 .0016
H19	.39486 .00042	-.46545 .00038	.28438 .00021	1.0000 .0000	.0340 .0000						
C20	.39078 .00043	-.27713 .00038	.26020 .00022	1.0000 .0000	.0271 .0023	.0343 .0024	.0243 .0022	-.0001 .0018	.0017 .0018	-.0133 .0020	.0279 .0017
H20	.33926 .00043	-.25455 .00038	.22493 .00022	1.0000 .0000	.0311 .0000	.0383 .0026	.0288 .0024	.0070 .0020	-.0131 .0020	-.0166 .0021	.0327 .0018
C21	.19293 .00044	-.82190 .00040	.13136 .00021	1.0000 .0000	.0262 .0023	.0417 .0027	.0289 .0024	-.0055 .0020	.0106 .0021	-.0188 .0023	.0378 .0019
H21	.11689 .00044	.82113 .00040	.16700 .00021	1.0000 .0000	.0344 .0000						
C22	.15260 .00049	-.86162 .00044	.06623 .00022	1.0000 .0000	.0332 .0025	.0358 .0026	.0267 .0023	-.0040 .0019	-.0020 .0020	-.0094 .0021	.0341 .0018
H22	.85170 .00049	-.85048 .00043	.05889 .00022	1.0000 .0000	.0416 .0000						
C23	.25991 .00049	-.11746 .00044	.01294 .00023	1.0000 .0000	.0449 .0028	.0152 .0020	.0214 .0020	.0005 .0016	.0012 .0017	-.0067 .0017	.0215 .0015
H23	.23388 .00049	-.14116 .00044	-.03306 .00023	1.0000 .0000	.0447 .0000						
C24	.40691 .00049	-.13795 .00043	.02731 .00023	1.0000 .0000	.0353 .0026	.0167 .0020	.0286 .0021	.0025 .0016	.0008 .0017	-.0074 .0017	.0221 .0015
H24	.48389 .00049	-.17759 .00043	-.00841 .00023	1.0000 .0000	.0425 .0000						
C25	.44119 .00041	-.10027 .00035	.09421 .00020	1.0000 .0000	.0262 .0022						
C26	.59744 .00042	-.12623 .00037	.11535 .00020	1.0000 .0000	.0272 .0022						

Atom	x	y	z	occ	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{eq}
C27	.72079(44)	-.19501(40)	.87143(22)	1.0000(0)	.0291(24)	.0249(33)	.0233(33)	-.0004(18)	.0010(19)	-.0059(19)	.0291(17)
N27	.76827(44)	-.22532(40)	.02451(22)	1.0000(0)	.0370(0)						
C28	.86363(47)	-.21949(43)	.09668(24)	1.0000(0)	.0295(25)	.0311(26)	.0367(26)	.0033(20)	.0078(20)	-.0039(20)	.0354(18)
N28	.94995(47)	-.16608(43)	.06714(24)	1.0000(0)	.0429(0)						
C29	.87841(43)	-.17449(39)	.16501(22)	1.0000(0)	.0188(21)	.0280(23)	.0378(25)	.0087(19)	.0015(18)	-.0040(18)	.0302(16)
N29	.97318(43)	-.19952(39)	.18333(22)	1.0000(0)	.0396(0)						
C30	.74973(42)	-.10529(38)	.26614(22)	1.0000(0)	.0281(23)	.0241(22)	.0276(22)	.0020(17)	.0037(18)	-.0115(19)	.0263(16)
N30	.76028(42)	-.07450(38)	.25325(22)	1.0000(0)	.0334(0)						
C31	.87134(48)	-.63081(42)	.58640(23)	1.0000(0)	.0405(26)	.0266(24)	.0327(25)	.0022(19)	-.0095(21)	-.0144(21)	.0329(18)
N7	.80550(39)	-.69063(34)	.54165(18)	1.0000(0)	.0365(21)	.0297(20)	.0256(19)	.0002(16)	.0006(17)	-.0152(17)	.0300(14)
N8	.96981(41)	-.69761(35)	.64313(20)	1.0000(0)	.0470(24)	.0295(20)	.0413(23)	-.0032(17)	-.0158(19)	-.0192(18)	.0377(16)
N9	.82150(45)	-.48442(38)	.58060(23)	1.0000(0)	.0583(27)	.0354(23)	.0495(26)	.0076(19)	-.0207(21)	-.0227(21)	.0464(18)
O1	.70195(33)	-.61390(31)	.50092(16)	1.0000(0)	.0379(18)	.0452(19)	.0318(17)	.0041(15)	-.0101(15)	-.0146(16)	.0390(13)
O2	.84741(41)	-.81643(38)	.54072(20)	.7400(0)	.0338(9)						
O3	.98536(50)	-.81384(43)	.66445(24)	.7400(0)	.0346(12)						
O4	1.03718(42)	-.63284(33)	.66990(21)	.7400(0)	.0355(10)						
O5	.84262(51)	-.43539(39)	.52152(23)	1.0000(0)	.1192(37)	.0562(25)	.0762(30)	.0279(22)	.0228(26)	-.0405(25)	.0827(22)
O6	.75987(43)	-.41690(44)	.63333(24)	.7400(0)	.0473(11)						

	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10	C11
034	1.03296 .00208	-.82981 .00175	.64438 .00099	.1300 .0000	.0042 .0041						
038	.93664 .00195	-.79085 .00178	.69428 .00096	.1300 .0000	.0145 .0041						
044	1.00316 .00192	-.62504 .00173	.63299 .00096	.1300 .0000	.0145 .0040						
064	.76786 .00196	-.43367 .00178	.66060 .00100	.1300 .0000	.0202 .0042						
060	.76049 .00235	-.40093 .00219	.60671 .00122	.1300 .0000	.0394 .0053						
024	.89991 .00201	-.82003 .00171	.53743 .00091	.1300 .0000	.0127 .0039						
028	.80709 .00207	-.81023 .00175	.55138 .00094	.1300 .0000	.0134 .0040						
048	1.07362 .00216	-.64556 .00193	.65197 .00107	.1300 .0000	.0232 .0046						
C32	-.21747 .00051	.37804 .00044	.14131 .00025	1.0000 .0000	.0419 .0028	.0287 .0026	.0400 .0027	.0022 .0021	.0085 .0022	-.0114 .0022	.0300 .0019
N10	-.12527 .00041	.35995 .00038	.08047 .00019	1.0000 .0000	.0460 .0024	.0349 .0023	.0323 .0021	-.0064 .0018	.0049 .0018	-.0164 .0020	.0377 .0016
N11	-.31201 .00042	.52124 .00036	.15674 .00021	1.0000 .0000	.0398 .0024	.0271 .0021	.0418 .0023	.0029 .0018	.0074 .0019	-.0134 .0019	.0365 .0016
N12	-.23814 .00037	.28131 .00034	.18516 .00019	1.0000 .0000	.0286 .0020	.0265 .0021	.0356 .0021	-.0004 .0016	-.0026 .0017	-.0114 .0017	.0301 .0015
07	-.03798 .00040	.24260 .00034	.06344 .00019	1.0000 .0000	.0688 .0024	.0422 .0021	.0553 .0023	.0153 .0017	.0222 .0019	.0211 .0019	.0558 .0016
08	-.13173 .00039	.46429 .00034	.04552 .00018	1.0000 .0000	.0731 .0025	.0465 .0021	.0447 .0020	.0123 .0017	.0129 .0018	-.0285 .0019	.0539 .0016
09	-.26644 .00034	.57952 .00030	.20081 .00017	1.0000 .0000	.0415 .0019	.0320 .0018	.0498 .0021	-.0045 .0015	.0015 .0016	-.0148 .0015	.0410 .0013
010	-.43223 .00036	.57319 .00031	.12448 .00018	1.0000 .0000	.0418 .0021	.0379 .0019	.0639 .0023	.0091 .0017	-.0097 .0018	-.0146 .0017	.0485 .0015
011	-.33226 .00032	.32527 .00029	.23668 .00016	1.0000 .0000	.0334 .0017	.0380 .0018	.0371 .0018	-.0012 .0014	.0051 .0014	-.0149 .0015	.0361 .0012
012	-.16933 .00033	.15786 .00029	.17440 .00017	1.0000 .0000	.0437 .0019	.0244 .0018	.0555 .0021	-.0019 .0015	.0041 .0016	-.0118 .0015	.0419 .0013

Appendix F

PREPARATION AND PROPERTIES
OF ALUMINUM NITROALKOXIDES

PREPARATION AND PROPERTIES OF ALUMINUM NITROALKOXIDES[1]

Donald A. Levins

Abstract: Three aluminum nitroalkoxides were prepared by the reaction
of triethyl or triisobutylaluminum with nitroalcohols. Aluminum 2-
nitro-ethoxide, aluminum 2,2-dinitropropoxide, and aluminum 2-fluoro-
2,2-dinitroethoxide were found by NMR studies to be monomeric in donor
solvents such as pyridine and dioxane and, unlike aluminum halo-
alkoxides, monomeric in chloroform and benzene. The infrared spectra of
donor-acceptor complexes with xanthone showed the Lewis acid strength of
the aluminum nitroalkoxides to be comparable to similarly substituted
aluminum halo alkoxides and the aluminum alkyls and significantly
greater than that of unsubstituted aluminum alkoxides. The aluminum
polynitroalkoxides detonated on impact. Hydrolytic stability increased
with increasing substitution.

INTRODUCTION

Three aluminum nitroalkoxides were prepared and their physical and chemical properties investigated. Of particular interest were the factors affecting the hydrolytic stability of these compounds, such as hindering attack on the aluminum atom by increasing substitution or by postulated partial bonding of nitro group oxygens to the central aluminum atoms, as shown in Figure 1. The Lewis acid strength of the
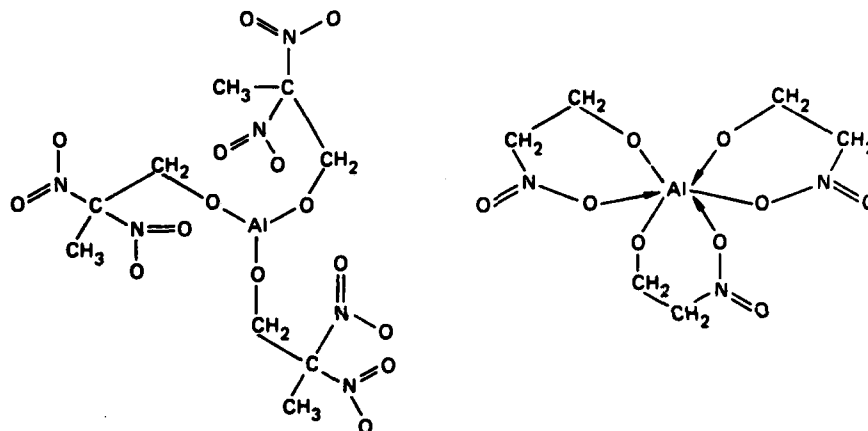

FIGURE 1   TWO MEANS OF OBSTRUCTING ATTACK ON THE ALUMINUM ATOM
OF ALUMINUM NITROALKOXIDES

aluminum nitroalkoxides was assessed and compared with that of the aluminum haloalkoxides and the unsubstituted aluminum alkoxides.

RESULTS AND DISCUSSION

Aluminum 2-nitroethoxide, aluminum 2,2-dinitropropoxide, and aluminum 2-fluoro-2,2-dinitroethoxide were prepared by the reaction of triethyl or triisobutyl aluminum and the appropriate alcohol in methylenechloride. Elemental analyses were satisfactory. Each of the aluminum compounds prepared was isolated as a white powder. Decom-

position points and times to complete hydrolysis of samples exposed to air are given in Table I. Resistance to hydrolysis

Table I

DECOMPOSITION POINTS AND TIMES TO
COMPLETE HYDROLYSIS

Aluminum Compound	Decomposition Point (°C)	Time to Complete Hydrolysis
2-Nitroethoxide	136	20 min
2,2-Dinitropropoxide	142	45 min
2-Fluoro-2,2-dinitro-ethoxide	137	2 days

parallels both increasing electronegative substitution and increasing steric hindrance to attack on the central aluminum atom.

Aluminum 2-nitroethoxide (Figure 2) and aluminum 2,2-dinitropropoxide were both insoluble in ether and methylenechloride, slightly soluble in benzene and chloroform, and soluble in pyridine and tetrahydrofuran.

Proton and carbon-13 magnetic resonance spectra of these two aluminum compounds in benzene, pyridine, and chloroform revealed absorptions attributable only to the monomeric form of the aluminum alkoxides. In contrast, aluminum 2,2,2-trichloroethoxide associated[1] in non-donor solvents and monomeric in donor solvents. Unsubstituted aluminum alkoxides, such as aluminum isopropoxide, are associated in various solvents including donor solvents. Decreased nucleophilicity of the alkoxy compounds, and steric hindrance explain to some extent this observed failure to associate.
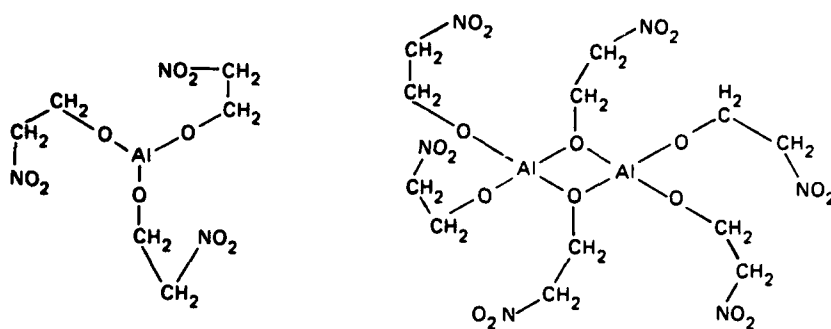
FIGURE 2 MONOMERIC AND DIMERIC FORMS OF ALUMINUM 2-NITROETHOXIDE

The Lewis acid strength of the aluminum nitroalkoxides was assessed by the infrared techniques of Cook,[2] in which a shift in xanthone carbonyl absorption due to xanthone coordination to aluminum is determined and used as a measure of acid strength. Table II lists the measured shift in the xanthone carbonyl stretch absorptions for aluminum nitroalkoxide, aluminum haloalkoxide, unsubstituted aluminum alkoxide, and aluminum alkyl complexes with xanthone.

Table II

SHIFT IN XANTHONE CARBOXYL ABSORPTION DUE TO
COORDINATION WITH VARIOUS ALUMINUM COMPOUNDS

Lewis Acids	Carbonyl Absorption Shift (cm^{-1})	Reference
$Al(OCH_2CH_2NO_2)_3$	30	This work
$Al[OCH_2C(NO_2)_2CH_3]_3$	39	"
$Al[OCH_2C(NO_2)_2F]_3$	43	"
$Al(OCH_2CCl_3)_3$	90	2
$Al(OCH_2CH_3)_3$	0	This work
$Al(CH_2CH_3)_3$	83	3
$Al(CH_2CH_3)Cl_2$	108	3

As with aluminum 2,2,2-trichloroethoxide, the enhanced Lewis acid strength of the aluminum nitroalkoxides compared with the unsubstituted aluminum alkoxides is probably due to the electron-withdrawing effect of the electronegative substituents, resulting in enhancement of the electrophilicity of the central aluminum atom. The carbonyl absorption shift of xanthane complexes of the aluminum nitroalkoxides are probably reduced to some extent by steric hindrance of approach of the coordinated xanthane.

Infrared spectra gave no indication[3] of interaction between central aluminum atoms and nitro substituents in these compounds, in the form of backbonding as shown in Figure 1. The two polynitroalkoxy aluminum compounds to detonated on moderate impact.

EXPERIMENTAL

Warning! All polynitro and aluminum nitroalkoxy compounds should be considered toxic and potentially explosive and should be handled with appropriate precautions. Decomposition points were determined in sealed glass capillaries. Infrared spectra were determin' with Perkin-Elmer Models 281 and 735B spectrophotometers. Nuclear ı netic resonance (NMR) spectra were determined with Varian Associat EM-360 and JEOL FX-90Q spectrophotometers, and chemical shifts are re ted in parts per million (δ) relative to internal reference compoui ˌ Microanalyses were performed by Galbraith Laboratories, Inc., and in our laboratory with a Perkin-Elmer 240 elemental analyzer.

All solvents were carefully dried, distilled, and degassed. The nitroalcohols were carefully dried by liquid-liquid extraction and distilled or recrystallized. All procedures were performed under argon in flame-dried glassware.

Aluminum 2-nitroethoxide was synthesized by adding 5 mL of a 25% solution of triisobutylaluminum in toluene (1.17 g, 0.006 mol) in 20 mL methylenechloride cooled to 5°C. The reaction mixture was then allowed to warm slowly to room temperature and stirred overnight. The desired product precipitated as a white powder and was isolated by filtration, washed with ether, and dried at room temperature under vacuum. Yield, 1.30 g (73%). Decomposition point, 136°C. IR (Nujol) 1540 (NO_2), 1150 $(C-O)^5$ cm^{-1}; PMR (p-dioxane) δ 4.1 (m, 2H, CH_2), δ 4.6 (m, 2H, CH_2); 13_C NMR (pyridine-d_5) δ 58.8 (s, CH_2), δ 79.2 (s, CH_2). Anal. Calcd. for $C_6H_{12}N_3O_9Al$: C, 24.3; H, 4.0; N, 14.1; Al, 9.1. Found: C, 26.1; H, 4.2; N, 11.0; Al, 9.0.

Aluminum 2,2-dinitropropoxide was synthesized by adding 1.7 mL of a 25% solution of triethylaluminum in toluene (0.0033 mol) to a solution of 1.5 g of 2,2-dinitropropanol in 20 mL of dichloromethane at 5°C over

a 30-min period. The mixture was allowed to come to room temperature slowly, then stirred overnight. The reaction mixture was partially evaporated under an argon stream, and the desired product as a white powder was isolated by filtration, washed with cold ether, and dried under vacuum at room temperature. Yield, 4.2 g (87%). Decomposition point, 142°C. IR (Nujol) 1550 (NO_2), 1120 (C-O) cm^{-1}; PMR ($CDCl_3$) δ 2.0 (s, 3H, CH_3), δ 4.2 (s, 2H, CH_2); ^{13}C NMR ($CDCl_3$) δ 19.7 (s, CH_3), δ 2.0 64.8 (s, CH_2). Anal. Calcd. for $C_9H_{15}N_6O_{15}$ Al: C, 22.8; H, 3.2; N, 17.7, Al, 5.8. Found: C, 23.0; H, 3.8; N, 14.2; Al, 5.9.

Aluminum 2-fluoro-2,2-dinitroethoxide was synthesized by adding 4 mL of a 25% solution of triethylaluminum in toluene (0.008 mol) over a 30-min period to a solution of 3.7 g of 2-fluoro-2,2-dinitroethanol (0.024 mol) in 20 mL of dichloromethane at 5°C. The reaction mixture was allowed to come to room temperature slowly and stirred 48 hours at room temperature. The solvent was partially evaporated in a stream of argon, revealing a white powder that was isolated by filtration and washed with cold ether. Yield, 3.1 g (80%). Decomposition point, 137°C. IR (Nujol) 1595 (NO_2), 1170 (C-O) cm^{-1}; PMR ($CDCl_3$) δ 4.68 (d, CH_2). Anal. Calcd. for $C_6H_6N_6O_{15}F_3Al$: C, 14.8; H, 1.2; N, 17.3. Found: C, 15.7; H, 1.0; N, 15.4.

Aluminum nitroalkoxide/xanthone complexes were prepared by adding one equivalent of xanthone to a carefully weighed portion of each aluminum nitroalkyl dissolved in dichloromethane, ether, or toluene. The mixture was stirred at room temperature while the solvent was evaporated under an argon stream until a small quantity of the desired complex precipitated. The complexes, isolated as white powders, were washed with cold ether and dried under vacuum. NMR and infrared spectra reveal 1:1 complexes.

Acknowledgment

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