

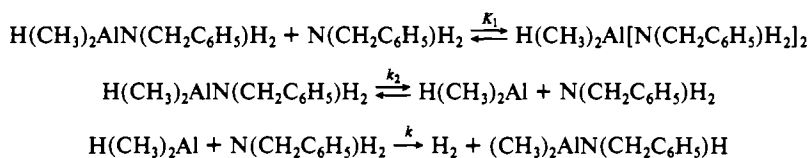
Contribution from the Department of Chemistry,
State University of New York at Buffalo, Buffalo, New York 14214

Kinetics and Mechanism for the Elimination of Hydrogen between Dimethylaluminum Hydride and Benzylamine

O. T. BEACHLEY, JR.

Received September 22, 1980

The rate of elimination of hydrogen from dimethylaluminum hydride and benzylamine has been measured at -63°C in toluene solution. All experimental data are consistent with a second-order rate law which is complicated by a series of equilibria. Initial rate data were correlated with a rate law and fitted to an appropriate mechanism. The following steps of the mechanism determine the rate of elimination of hydrogen during the early stages of the reaction:

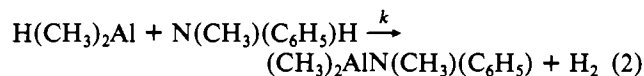
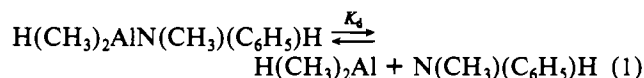


Additional equilibria which involve the aluminum-nitrogen product from the elimination reaction are proposed in order to fully describe the chemistry of the system. The large number of equilibria which complicate the kinetics of the reaction are related to the high basicity of benzylamine.

Introduction

The elimination reaction which occurs between an organometallic compound and a protic acid is of fundamental significance and finds many important applications. Despite the importance of this class of reaction to aluminum chemistry, only one kinetics study¹ of a reaction has led to a proposed mechanism. However, additional kinetics studies with a variety of acid-base pairs are necessary to elucidate the general nature of the elimination step in the mechanism as well as the factors which influence the rate of the elimination reaction and the degree of polymerization of the organometallic product.

The kinetics data for the elimination reaction which occurs between dimethylaluminum hydride and *N*-methylaniline¹ in toluene at -63°C were consistent with a second-order rate law which was complicated by an equilibrium. The reactions 1 and 2 of the mechanism determined the rate of elimination



of hydrogen. The adduct was assumed to be rapidly formed upon mixing of alane and amine. All results were consistent with the conclusion that adduct formation was a dead-end path for elimination. Since the elimination reaction is not a reaction of a preformed adduct, both K_d and k alter the rate of formation of hydrogen. The second pertinent conclusion derived from this kinetics study related to the observed formation of only a dimeric product, $[(\text{CH}_3)_2\text{AlN}(\text{CH}_3)(\text{C}_6\text{H}_5)]_2$, and the predominance of the *cis* isomer (80%), the kinetically preferred isomer. A $2\pi_s + 2\pi_a$ cycloaddition reaction which minimized interactions between bulky phenyl groups was proposed and, therefore, precluded the formation of higher aluminum-nitrogen polymers.

In this paper we report the kinetics of and propose a mechanism for the elimination reaction which occurs between dimethylaluminum hydride and benzylamine, $\text{N}(\text{CH}_2\text{C}_6\text{H}_5)\text{H}_2$, in toluene solution at -63°C . Benzylamine is a significantly stronger base with less bulky substituents than the previously studied *N*-methylaniline. The goals of our exper-

Table I. ^1H NMR Spectral Data^a $[(\text{CH}_3)_2\text{AlNH}(\text{CH}_2\text{C}_6\text{H}_5)]_2$

| assignt | solvent | | |
|------------------------|-----------------------------------|---------------------------|--------------------------|
| | $\text{C}_6\text{H}_5\text{CH}_3$ | C_5H_{10} | CH_2Cl_2 |
| AlCH_3 | | | |
| <i>cis</i> | 10.30 | 10.64 | 10.61 |
| <i>trans</i> | 10.33 | 10.72 | 10.66 |
| <i>cis</i> | 10.36 | 10.80 | 10.71 |
| N-H | 8.78 | <i>b</i> | 8.64 |
| CH_2 | 6.03 | 6.11, 6.13 | 5.97, 6.01 |
| | 6.12 | 6.19, 6.21 | 6.07 |
| C_6H_5 | 2.73, 2.78 | 2.82 | 2.43 |

^a All data are given as τ (ppm) and are referenced to tetramethylsilane (10.00 ppm). The spectra were recorded at 90 MHz and ambient temperature with a Varian Model EM-390 spectrometer.

^b The N-H line was not observed due to interference from cyclopentane.

iments were to determine the nature the aluminum-nitrogen product and the mechanism of the elimination reaction and to compare the kinetic data for the two amines.

Experimental Section

All compounds were manipulated in a vacuum line or a purified argon atmosphere. Benzylamine was dried over molecular sieves and distilled just prior to use. All other reagents or solvents were prepared or purified as previously described.¹

Reaction of $(\text{CH}_3)_2\text{AlH}$ with $\text{N}(\text{CH}_2\text{C}_6\text{H}_5)\text{H}_2$. The stoichiometry of the elimination reaction between $(\text{CH}_3)_2\text{AlH}$ and $\text{N}(\text{CH}_2\text{C}_6\text{H}_5)\text{H}_2$ was examined, and the product was fully characterized. When 0.1890 g (3.26 mmol) of $(\text{CH}_3)_2\text{AlH}$ was combined with 0.3508 g (3.27 mmol) of $\text{N}(\text{CH}_2\text{C}_6\text{H}_5)\text{H}_2$ in toluene solution, 3.24 mmol of H_2 (measured with a Toepler pump and gas buret assembly) was formed. No methane was observed as a product. Additional experiments with excess benzylamine confirmed the stoichiometry.

The aluminum-nitrogen product, $[(\text{CH}_3)_2\text{AlN}(\text{CH}_2\text{C}_6\text{H}_5)]_2$, was fully characterized. The colorless, crystalline solid has a melting point of $65-68^\circ\text{C}$. Decomposition as evidenced by bubbling started at about 140°C . Cryoscopic molecular weight measurements in benzene solution using an apparatus similar to that described by Shriver² demonstrated the compound to exist as a dimer. The following experimental data were observed for $[(\text{CH}_3)_2\text{AlNH}(\text{CH}_2\text{C}_6\text{H}_5)]_2$ (formula weight 327) [calculated molality (observed molecular weight)]: 0.0968 (327); 0.0604 (318); 0.0439 (317). Our ^1H NMR measurements of $[(\text{CH}_3)_2\text{AlNH}(\text{CH}_2\text{C}_6\text{H}_5)]_2$ dissolved in toluene,

(1) Beachley, O. T., Jr.; Tessier-Youngs, C. *Inorg. Chem.* 1979, 18, 3188.

(2) Shriver, D. F. "The Manipulation of Air Sensitive Compounds"; McGraw-Hill: New York, 1969; p 95.

Table II. Kinetic Data for the $(\text{CH}_3)_2\text{AlH}-\text{N}(\text{CH}_2\text{C}_6\text{H}_5)_2$ Reaction

| $[(\text{CH}_3)_2\text{AlH}]_T,^a$ M | $[\text{N}(\text{CH}_2\text{C}_6\text{H}_5)_2]_T,$ M | $10^3 \times$ initial rate, mm/s | $10^5 k_0,^b$ s^{-1} | $10^4 kK_2,^c$ s^{-1} |
|---|---|---|----------------------------------|-----------------------------------|
| 0.123 | 1.94 | 5.23 | 5.92 | 1.95 |
| 0.0891 | 1.68 | 3.83 | 5.99 | 1.82 |
| 0.0833 | 1.23 | 4.38 | 7.31 | 1.82 |
| 0.0819 | 1.07 | 4.52 | 7.67 | 1.76 |
| 0.0819 | 2.00 | 3.13 | 5.32 | 1.82 |
| 0.0776 | 1.44 | 3.42 | 6.12 | 1.68 |
| 0.0675 | 0.924 | 4.27 | 8.79 | 1.86 |
| 0.0603 | 1.39 | 2.68 | 6.19 | 1.66 |
| 0.0546 | 0.720 | 4.07 | 10.36 | 1.94 |
| 0.0575 | 2.03 | 2.08 | 5.03 | 1.74 |

^a Concentrations of $(\text{CH}_3)_2\text{AlH}$ are based on the number of moles of the monomeric unit. ^b Calculated by dividing the initial rate, converted to units of M/s, by $[(\text{CH}_3)_2\text{AlH}]_T$ (see text). ^c Calculated from the rate law by using the calculated value of K_1 (1.21 M^{-1}), initial rate, $[(\text{CH}_3)_2\text{AlH}]_T$, and $[\text{N}(\text{CH}_2\text{C}_6\text{H}_5)_2]_T$ (see text).

cyclopentane, and CH_2Cl_2 suggest that the compound exists as a mixture of cis and trans isomers, but the ratio of isomers has essentially no dependence on the polarity of the solvent (Table I). The infrared spectrum of $[(\text{CH}_3)_2\text{AlNH}(\text{CH}_2\text{C}_6\text{H}_5)]_2$ was recorded in the range $4000\text{--}250 \text{ cm}^{-1}$ by means of a Perkin-Elmer Model 457 spectrometer as a Nujol mull using CsI plates. The spectral data (bands due to the Nujol have been omitted) are as follows: 3262 (m), 1264 (m), 1192 (vs), 1167 (sh), 1082 (sh), 1044 (sh), 1017 (vs), 970 (m), 895 (w), 842 (sh), 802 (s), 737 (sh), 685 (vs), 632 (sh), 562 (m), 522 (w), 492 (w), 452 (m) cm^{-1} .

Kinetics Experiments. The kinetics of the reaction between dimethylaluminum hydride and benzylamine in toluene at -63°C was monitored by following the rate of evolution of hydrogen manometrically. The experimental procedure for adding the amine to the alane solution and following the reaction was identical with that previously described.¹ As in the earlier study all experimental variables which might alter pressure measurements were maintained as constant as possible.

Results and Discussion

The general elimination reaction which occurs between dimethylaluminum hydride and benzylamine can be summarized by eq 3. The kinetics of this reaction were investigated $[(\text{CH}_3)_2\text{AlH}]_3 + 3\text{N}(\text{CH}_2\text{C}_6\text{H}_5)_2 \rightarrow \frac{3}{2}[(\text{CH}_3)_2\text{AlN}(\text{CH}_2\text{C}_6\text{H}_5)\text{H}]_2 + 3\text{H}_2$ (3)

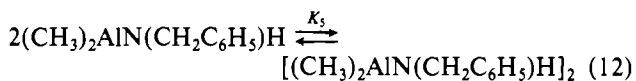
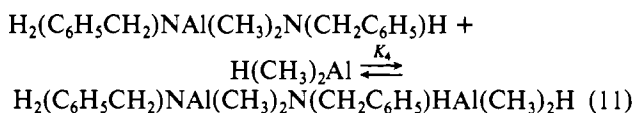
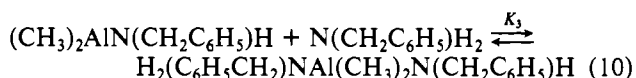
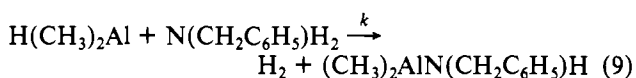
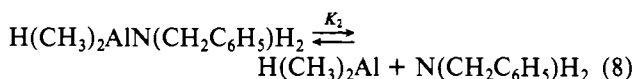
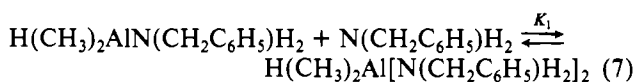
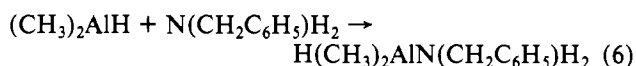
by following the rates of evolution of hydrogen at -63°C in toluene solution. A variety of experimental conditions were attempted. When the amine was in excess of the alane, a clear solution was formed and hydrogen was evolved smoothly. However, when the initial concentration of the alane and amine were equal, a white precipitate was observed in the reaction vessel but no hydrogen was formed. Experiments using an excess of the alane were prohibited because a different final product would be formed.³ Thus, all kinetics data had to be derived from experiments which employed a greater than 10-fold excess of amine.

The kinetics data are summarized in Table II. Only plots of hydrogen pressure vs. time for the early part of the reaction give data which can be correlated with a rate law and fitted to an appropriate mechanism. First-, second- and fractional-order kinetic plots had distinct curvatures. The slope of the linear portion of pressure vs. time plots gives an observed rate which is proportional to the initial dimethylaluminum hydride concentration for a given amine concentration. Thus, the alane dependence is given by eq 4. A plot of $1/k_0$ vs. $[\text{N}(\text{CH}_2\text{C}_6\text{H}_5)_2]_T$ is linear and demonstrates the inverse de-

$$\frac{\Delta P_{\text{H}_2}}{\Delta t} = k_0 [(\text{CH}_3)_2\text{AlH}]_T \quad (\text{constant } [\text{N}(\text{CH}_2\text{C}_6\text{H}_5)_2]_T) \quad (4)$$

pendence of the rate of hydrogen evolution on the amine concentration. The terms $[(\text{CH}_3)_2\text{AlH}]_T$ and $[\text{N}(\text{CH}_2\text{C}_6\text{H}_5)_2]_T$ express the total dimethylaluminum hydride and benzylamine concentrations before elimination.

Equations 5–12 can be used to explain all of the kinetic data



$$\frac{dP_{\text{H}_2}}{dt} = \frac{-d[(\text{CH}_3)_2\text{AlH}]_T}{dt} = \frac{k[(\text{CH}_3)_2\text{AlH}]_T[\text{N}(\text{CH}_2\text{C}_6\text{H}_5)_2]_T}{\frac{k_1[\text{N}(\text{CH}_2\text{C}_6\text{H}_5)_2]_T^2}{K_2} + \frac{[\text{N}(\text{CH}_2\text{C}_6\text{H}_5)_2]_T}{K_2} + 1} \quad (13)$$

and experimental observations, and are totally consistent with the chemistry of the system. The only assumption which must be made for this mechanism is that the initial formation of adduct is extremely rapid.^{1,4,5} The rate law is appropriate during the early stages of a reaction which utilizes a large excess of amine. Equilibria for K_3 and K_4 (eq 10 and 11) are included in the mechanism in order to describe the overall chemistry of the system but have been eliminated from the rate law in order to fit the observed initial rate data. If K_2 is assumed to be small, the rate law can be simplified even further to give eq 14 which is consistent with the data. The

$$\frac{dP_{\text{H}_2}}{dt} = \frac{kK_2[(\text{CH}_3)_2\text{AlH}]_T}{K_1[\text{N}(\text{CH}_2\text{C}_6\text{H}_5)_2]_T + 1} \quad (14)$$

calculated kinetic constants

$$kK_2 = 1.80 \times 10^{-4} \text{ s}^{-1} \quad K_1 = 1.21 \text{ M}^{-1}$$

kinetic constants kK_2 and K_1 are calculated from the slope and intercept of the $1/k_0$ vs. $[\text{N}(\text{CH}_2\text{C}_6\text{H}_5)_2]_T$ plot. With use of this value of K_1 , kK_2 can be recalculated from the initial concentrations and rate data for the individual experiments (Table II). The results of these calculations support the proposed mechanism and rate law. It is regrettable that it is

(3) Bernstein, J. D. Ph.D. Thesis, SUNY-Buffalo, Buffalo, NY, 1975.

(4) Eisch, J. J.; Rhee, S.-G. *J. Am. Chem. Soc.* **1974**, *96*, 7276.

(5) Eisch, J. J.; Rhee, S.-G. *J. Am. Chem. Soc.* **1975**, *97*, 4673.

not possible to calculate values of k and K_2 from the available data.

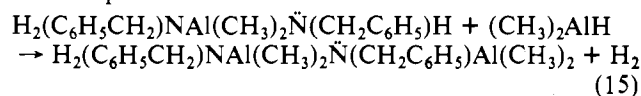
The proposed mechanism for the elimination reaction between dimethylaluminum hydride and benzylamine is analogous to that proposed for the *N*-methylaniline reaction¹ except that equilibria (K_1 , K_3 , and K_4) have been added. The steps of the mechanism which are required for H_2 formation (eq 8 and 9) are identical with those proposed for the $\text{H}(\text{CH}_3)_2\text{Al}-\text{N}(\text{CH}_3)(\text{C}_6\text{H}_5)\text{H}$ reaction.¹ The equilibrium K_1 involving the bis(amine) adduct, $\text{H}(\text{CH}_3)_2\text{Al}[\text{N}(\text{CH}_2\text{C}_6\text{H}_5)_2\text{H}_2]_2$, is necessary to explain the inverse dependence of the rate of hydrogen evolution on the amine concentration under the pseudo-first-order conditions (excess amine). Equilibria K_3 and K_4 , which occur after H_2 has been eliminated, pertain to overall chemistry of the system. The complications of five equilibria in the mechanism are responsible for the reaction not following simple first-order kinetics under pseudo-first-order conditions. The occurrence of these equilibria for the benzylamine reaction are consistent with its significantly high basicity due to the electronic and steric effects. For comparison purposes, equilibrium constants⁶ which describe the basicity of benzylamine and *N*-methylaniline toward the proton in aqueous solution differ by 10^5 .

The observed decreasing initial rate of hydrogen evolution with increasing benzylamine concentration at constant alane concentration is a consequence of equilibrium K_1 (eq 7). The excess amine reduces the concentration of the adduct $\text{H}(\text{C}-\text{H}_3)_2\text{AlN}(\text{CH}_2\text{C}_6\text{H}_5)_2\text{H}_2$, the compound which must dissociate to form the species required for the elimination reaction, the monomeric alane, and the amine. Bis(amine) adducts which involve five-coordinate aluminum are known,⁷⁻¹² but a strong base and minimum steric interactions between the acid and base are necessary. Two compounds,^{13,14} $\text{H}_3\text{Al}[\text{N}(\text{CH}_3)_2]_2$ and $\text{H}_3\text{Al}[(\text{CH}_3)_2\text{NC}_2\text{H}_4\text{N}(\text{CH}_3)_2]_2$, have been characterized by X-ray structural studies. However, in the case of dimethylaluminum hydride-amine compounds, no bis(amine) adducts have been previously observed. Apparently, $\text{N}(\text{CH}_3)_3$ ¹⁵ and $\text{N}(\text{C}_6\text{H}_5)(\text{CH}_3)\text{H}$ ¹ have too many steric interactions or are too weak a base toward $(\text{CH}_3)_2\text{AlH}$ for a bis(amine) adduct to be formed even at -46 or -63 °C, respectively.

The step in the mechanism which leads to the formation of hydrogen (eq 9) is considered to be a second-order reaction between a monomeric alane and the amine. It was not possible to obtain direct kinetic data for this second-order process by following the formation of hydrogen when the alane and amine concentrations were equal.¹ However, other experimental observations support our hypothesis. When the alane and benzylamine are in equal concentrations, an insoluble solid is formed upon mixing at -63 °C, but no hydrogen is eliminated. The insoluble solid is most likely the adduct $\text{H}(\text{CH}_3)_2\text{AlN}(\text{CH}_2\text{C}_6\text{H}_5)_2\text{H}_2$, a very polar compound. The insolubility of this adduct and the equilibria which precede the actual elimination reaction (eq 7 and 8, K_1 and K_2) must reduce the concentrations of the reactive monomeric alane and amine to effectively hinder the formation of hydrogen. If the elimination reaction was a first-order reaction of the preformed adduct,

hydrogen formation should have been observed even if the adduct were insoluble. Second-order reactions of the adduct are inconsistent with the kinetic data.

The equilibria represented by K_3 , K_4 , and K_5 (eq 10-12) have been added to the overall mechanism of the total reaction in order to fully describe the chemistry of the system. These equilibria occur after hydrogen has been formed and involve the aluminum-nitrogen products of the reaction. Thus, they are not required to explain our kinetic observations for the initial part of the reaction. However, these complicating equilibria help to explain why the full reaction does not exhibit simple first-order kinetics under pseudo-first-order conditions. The fact that these equilibria occur in the benzylamine-alane elimination reaction but not in the corresponding *N*-methylaniline reaction¹ must be related to the higher basicity of benzylamine. The reaction of $(\text{CH}_3)_2\text{AlN}(\text{CH}_2\text{C}_6\text{H}_5)\text{H}$ with $\text{N}(\text{CH}_2\text{C}_6\text{H}_5)_2\text{H}_2$ (eq 10, K_3) is clearly supported by ¹H NMR data (see following discussion). The subsequent reaction of $\text{H}_2(\text{C}_6\text{H}_5\text{CH}_2)\text{NAl}(\text{CH}_3)_2\text{N}(\text{CH}_2\text{C}_6\text{H}_5)\text{H}$ with $(\text{CH}_3)_2\text{AlH}$ would be a function of the increased basicity of the benzylamino group after elimination. This suggestion that the benzylamino group can effectively compete with benzylamine for $(\text{CH}_3)_2\text{AlH}$ is based on related observations in aluminum-nitrogen chemistry.^{16,17} The analogous effect is considered to be responsible for the dimerization of $(\text{CH}_3)_2\text{AlN}(\text{CH}_3)\text{C}_2\text{H}_4\text{N}(\text{CH}_3)_2$ with free $\text{N}(\text{CH}_3)_2$ groups, rather than the formation of the chelated monomer.¹⁷ Additional complications in the overall mechanism can be envisioned if a second elimination reaction occurred as shown in eq 15. A subsequent proton-transfer reaction and then dissociation of this product would give $(\text{CH}_3)_2\text{AlN}(\text{CH}_2\text{C}_6\text{H}_5)\text{H}$, the typical reaction product.



The comparisons of the calculated kinetic constants for the analogous benzylamine- and *N*-methylaniline¹-dimethylaluminum hydride elimination reactions are of interest to determine how the amine effects the rate of elimination. Qualitatively, benzylamine reacts faster than *N*-methylaniline. Similarly, these observations are reflected in the calculated values of kK_2 ($1.80 \times 10^{-4} \text{ s}^{-1}$ for $\text{N}(\text{CH}_2\text{C}_6\text{H}_5)_2\text{H}_2$, $5.46 \times 10^{-5} \text{ s}^{-1}$ for $\text{N}(\text{C}_6\text{H}_5)(\text{CH}_3)\text{H}$). Benzylamine is a much stronger base than *N*-methylaniline. Thus, K_2 should be smaller for benzylamine, probably less than $9.09 \times 10^{-3} \text{ M}$, the observed value of K_2 for the $\text{H}(\text{CH}_3)_2\text{AlN}(\text{C}_6\text{H}_5)(\text{CH}_3)\text{H}$ dissociation equilibrium.¹ In order for kK_2 to be larger for the benzylamine reaction, the rate constant for its elimination reaction (k_2) must be greater than $6.01 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$, the value calculated for the *N*-methylaniline reaction.¹ There are many reasons why dimethylaluminum hydride-benzylamine would eliminate hydrogen faster than *N*-methylaniline. There are twice as many reactive N-H bonds with less steric hindrance for the formation of the transition state for the proposed four-centered $\text{S}_{\text{E}1}$ process.¹ Our current limited data does not warrant more detailed comparisons at this time.

The final product from the elimination reaction in the absence of excess amine is an aluminum-nitrogen dimer $[(\text{C}-\text{H}_3)_2\text{AlN}(\text{CH}_2\text{C}_6\text{H}_5)\text{H}]_2$, which exists as a 1:1 mixture of cis/trans geometrical isomers. This isomer ratio is not significantly affected by solvent polarity. The ¹H NMR data indicate 49.5% cis isomer in cyclopentane, 47.9% cis isomer in toluene and 51.8% cis isomer in methylene chloride. If a $2\pi_s + 2\pi_a$ concerted cycloaddition reaction of two $(\text{CH}_3)_2\text{AlN}(\text{CH}_2\text{C}_6\text{H}_5)\text{H}$ monomer units is the mechanism for dimer-

(6) "Handbook of Chemistry and Physics"; CRC Press: Cleveland, Ohio, 1974; p D-147.

(7) Wiberg, E.; Graf, H.; Schmidt, M.; Uson, R. *Z. Naturforsch. B: Anorg. Chem., Org. Chem.* **1952**, *7B*, 578.

(8) Fetter, N. R.; Bartocha, B.; Brinckman, F. E.; Moore, D. W. *Can. J. Chem.* **1963**, *41*, 1359.

(9) Davidson, J. M.; Wartik, T. J. *Am. Chem. Soc.* **1960**, *82*, 5506.

(10) Fetter, N. R.; Moore, D. W. *Can. J. Chem.* **1964**, *42*, 885.

(11) Young, A. R.; Ehrlich, R. *Inorg. Chem.* **1965**, *4*, 1358.

(12) Ashby, E. C. J. *Am. Chem. Soc.* **1964**, *86*, 882.

(13) Heitsch, C. W.; Nordman, C. E.; Parry, R. W. *Inorg. Chem.* **1963**, *2*, 508.

(14) Palenik, G. J. *Acta Crystallogr.* **1964**, *17*, 1573.

(15) Beachley, O. T., Jr.; Bernstein, J. D. *Inorg. Chem.* **1973**, *12*, 183.

(16) Beachley, O. T., Jr.; Racette, K. C. *Inorg. Chem.* **1975**, *14*, 2534.

(17) Beachley, O. T., Jr.; Racette, K. C. *Inorg. Chem.* **1976**, *15*, 2110.

ization,¹ only small differences can exist between the relative energies of the transition states for the formation of the two isomers. The benzyl group would be expected to have small steric effects in the proposed transition state. However, if the monomer, $(\text{CH}_3)_2\text{AlN}(\text{CH}_2\text{C}_6\text{H}_5)\text{H}$, reacts with $\text{N}(\text{CH}_2\text{C}_6\text{H}_5)_2\text{H}_2$ as proposed in eq 10 (K_3), subsequent sequential reactions can also be envisioned to produce the dimer. The current kinetic study does not permit us to distinguish between these two paths, but the concerted cycloaddition reaction seems more plausible, especially when the alane and amine are reacted in equal amounts. When excess benzylamine is added to a cyclopentane solution of the dimer, the unique aluminum-methyl lines of the *cis/trans* isomers in the ¹H NMR spectrum are lost. Only one Al-CH₃ line is observed, which is consistent with fast exchange. As previously mentioned, the equilibria represented by eq 10 and 12 (K_3 and K_5) are consistent with these observations.

The reaction between an alane and amine cannot be considered simple or straightforward. Many factors must influence the various steps of the reaction mechanism. As the basicity and steric effects of the amine change, many equilibria involving reactants and products are apparently introduced into the mechanism. More kinetics studies will be required to elucidate the relative importance of the different equilibria and the factors influencing the magnitude of the second-order rate constant for elimination.

Acknowledgment. This work was supported in part by the Office of Naval Research. We are indebted to Professor Gordon M. Harris for many helpful discussions on the interpretation of the kinetic data.

Registry No. $(\text{CH}_3)_2\text{AlH}$, 865-37-2; $\text{N}(\text{CH}_2\text{C}_6\text{H}_5)_2$, 100-46-9; *cis*- $[(\text{CH}_3)_2\text{AlN}(\text{CH}_2\text{C}_6\text{H}_5)\text{H}]_2$, 77827-45-3; *trans*- $[(\text{CH}_3)_2\text{AlN}(\text{CH}_2\text{C}_6\text{H}_5)\text{H}]_2$, 77880-80-9.

Contribution from the Department of Chemistry, Stanford University, Stanford, California 94305

N-Macrocyclic Complexes of Ruthenium(II) and Ruthenium(III)

DARREL D. WALKER and HENRY TAUBE*

Received November 5, 1980

The following new macrocycle ligand complexes of ruthenium have been synthesized: $[\text{Ru}(\text{mac})\text{Cl}_2]\text{Cl}$ (mac = 2,3-dimethyl-1,4,8,11-tetraazacyclotetradecane (I), 1,4,8,12-tetraazacyclopentadecane (II), and 1,5,9,13-tetraazacyclohexadecane (III)). Compounds II and III, along with the previously reported $[\text{Ru}([\text{14}]\text{aneN}_4)\text{Cl}_2]\text{Cl}$ ([14]aneN₄ = 1,4,8,11-tetraazacyclotetradecane) comprise a series differing in the ring size of the macrocycle. Changes in ring size do not appreciably affect the charge-transfer electronic spectra or the Ru-Cl infrared stretching vibration. A small cathodic shift in the formal potential of the $\text{Ru}(\text{mac})\text{Cl}_2^{+/0}$ couple and a decrease in the chloride affinity of the Ru(II) is observed as the ring size is increased. The structure of $[\text{Ru}([\text{14}]\text{aneN}_4)\text{Cl}_2]\text{Br}$ was determined from three-dimensional X-ray diffraction analysis, and the *trans* geometry of the chloro ligands was verified. Revealed in the structure are nonbonded interactions within the cation between the chloro ligands and the nitrogen-bound hydrogen atoms, which affect the charge-transfer spectra of the Ru(III) form.

Introduction

Since the discovery of the metal template synthesis by Curtis¹ and Busch² 20 years ago, the field of macrocyclic ligands has become a major area of research. The chemistry of first-row transition-metal ions complexed by macrocyclic ligands has been extensively developed and exhibits many unusual features compared to noncyclic analogues. The macrocycles have been shown to stabilize high oxidation states of metal ions such as Ag(II)³ and Ni(III),⁴ they exhibit unusual ligand field strengths compared to noncyclic ligands with similar donor atoms,⁵ and the formation constants of their metal complexes are often unusually high (the macrocycle effect).⁶

One of the fundamental properties of these ligands is the size of the macrocycle ring. A change in ring size on high-spin, six-coordinate nickel(II)⁷ and on low-spin, six-coordinate cobalt(III)⁸ has been shown to affect the electronic spectra, redox potentials, and reactivity of the complexes markedly.

In an effort to extend such studies to a second-row transition-metal ion, we undertook the synthesis and characteri-

zation of a series of ruthenium macrocycle complexes. Ruthenium features two readily accessible oxidation states both of which are usually low spin and six coordinate. Additionally, its simple ammine complexes are well characterized and provide a basis for comparison to the macrocycle ligand complexes.

The ligands used in this study are shown in Figure 1 with their abbreviated names.⁹ They are all fully saturated, tetraaza macrocycles, and except for $\text{Me}_2[\text{14}]\text{aneN}_4$, they lack peripheral alkyl groups. They are σ donors only and their electronic spectra will not show complications from π bonding. The series [14]-, and [15]-, and [16]aneN₄ provides a systematic change in the macrocycle hole size, and thus the effect of this parameter on the physical and chemical properties of the complexes may be determined. One member of the series $\text{Ru}([\text{14}]\text{aneN}_4)\text{Cl}_3$ has been reported previously.¹⁷

Experimental Section

Materials. $\text{K}_2[\text{RuCl}_5(\text{OH}_2)]$ was prepared from $\text{K}_3[\text{RuCl}_6]$ (Matthey-Bishop, Inc.)¹⁰ and $\text{K}_2[\text{RuBr}_5(\text{OH}_2)]$ from ruthenium

- (1) House, D. A.; Curtis, N. F. *Chem. Ind. (London)* **1961**, 1708.
- (2) Blinn, E.; Busch, D. H. *Inorg. Chem.* **1968**, *7*, 820.
- (3) Kestner, M. O.; Allred, A. L. *J. Am. Chem. Soc.* **1972**, *94*, 7189.
- (4) Barefield, E. K.; Mocella, M. T. *Inorg. Chem.* **1973**, *12*, 2829.
- (5) Gore, E. S.; Busch, D. H. *Inorg. Chem.* **1973**, *12*, 1.
- (6) Busch, D. H. *Acc. Chem. Res.* **1978**, *11*, 392.
- (7) Cabiness, D. K.; Margerum, D. W. *J. Am. Chem. Soc.* **1970**, *92*, 2151.
- (8) Martin, L. Y.; Sperati, C. R.; Busch, D. H. *J. Am. Chem. Soc.* **1977**, *99*, 2969.
- (9) Hung, Y.; Martin, L. Y.; Jackels, S. C.; Tait, A. M.; Busch, D. H. *J. Am. Chem. Soc.* **1977**, *99*, 4029.

- (9) An explanation of the derivation of the abbreviations for the macrocycle ligands may be found in the following papers: Goedken, V. L.; Merrell, P. H.; Busch, D. H. *J. Am. Chem. Soc.* **1972**, *94*, 3397. Dabrowiak, J. C.; Merrell, P. H.; Busch, D. H. *Inorg. Chem.* **1972**, *11*, 1979. The systematic names are as follows: cyclam or [14]aneN₄, 1,4,8,11-tetraazacyclotetradecane; [15]aneN₄, 1,4,8,12-tetraazacyclopentadecane; [16]aneN₄, 1,5,9,13-tetraazacyclohexadecane; Me_2cyclam or $\text{Me}_2\text{[14]aneN}_4$, 2,3-dimethyl-1,4,8,11-tetraazacyclotetradecane. Other abbreviations used in this paper are as follows: PPh₃, triphenylphosphine; DSS, 3-(trimethylsilyl)-1-propanesulfonic acid disodium salt; HTFMS, trifluoromethanesulfonic acid; en, ethylenediamine.
- (10) Raichart, D. W. Ph.D. Thesis, Stanford University, July 1972.