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# The preparation and kinetic studies of two sterically hindered gold (III) complexes

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THE PREPARATION AND KINETIC STUDIES  
OF TWO STERICALLY HINDERED  
GOLD(III) COMPLEXES

by JAMES F. STEVENS, *III* *master* *M.S. 1976*

This thesis is submitted in partial fulfillment of  
the requirements for the degree of Master of Science in  
Chemistry.

UNION COLLEGE  
Schenectady, New York  
July, 1975

Approved Charles F. Weick  
Thesis Advisor

Approved Caron Feinst  
Committee on Graduate Studies

Date June 1976

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This thesis is gratefully dedicated to my wonderful wife, Rosemary, whose continual encouragement and understanding made this work possible.



## ACKNOWLEDGMENT

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## LIST OF ABBREVIATIONS

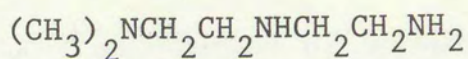
The following abbreviations will be used throughout the text of this paper:

<u>Abbreviation</u>	<u>Name &amp; Formula</u>
amine	any dien or substituted dien
amine-H	the conjugate base of amine
dien	Diethylenetriamine $\text{NH}_2\text{CH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}_2$
dien-H	the conjugate base of dien $\text{NH}_2\text{CH}_2\text{CH}_2\text{NCH}_2\text{CH}_2\text{NH}_2^-$
Et <sub>4</sub> dien	1,1',7,7' - tetraethyldiethylene- tri-amine $(\text{C}_2\text{H}_5)_2\text{NCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{N}(\text{C}_2\text{H}_5)_2$
Et <sub>4</sub> dien-H	the conjugate base of Et <sub>4</sub> dien $(\text{C}_2\text{H}_5)_2\text{NCH}_2\text{CH}_2\text{NCH}_2\text{CH}_2\text{N}(\text{C}_2\text{H}_5)_2^-$
Et <sub>2</sub> dien	1,1'-diethyldiethylenetriamine $(\text{C}_2\text{H}_5)_2\text{NCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}_2$
Et <sub>2</sub> dien-H	the conjugate base of Et <sub>2</sub> dien $(\text{C}_2\text{H}_5)_2\text{NCH}_2\text{CH}_2\text{NCH}_2\text{CH}_2\text{NH}_2^-$
Me <sub>4</sub> dien	1,1',7,7' - tetramethyldiethylene- tri-amine $(\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$
Me <sub>4</sub> dien-H	the conjugate base of Me <sub>4</sub> dien $(\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2^-$



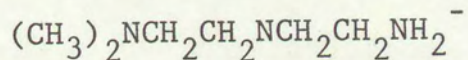
Me<sub>2</sub>dien

1,1'-dimethyldiethylenetriamine



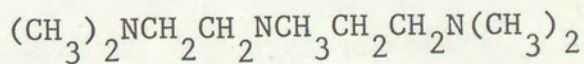
Me<sub>2</sub>dien-H

the conjugate base of Me<sub>2</sub>dien



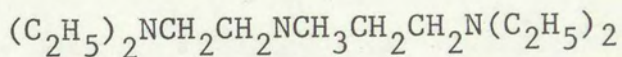
Me<sub>5</sub>dien

1,1',4,7,7'-pentamethyldiethylene-  
triamine



MeEt<sub>4</sub>dien

4-methyl-1,1',7,7'-tetraethyl-  
diethylenetriamine



## ABSTRACT

Previous studies indicate substitution of bromide ion for chloride ion in  $[\text{Au}(\text{Et}_4\text{dien-H})\text{Cl}]^+$  occurs at a rate almost independent of the bromide ion concentration, while similar reactions with  $[\text{Au}(\text{dien-H})\text{Cl}]^+$ ,  $[\text{Au}(\text{Me}_2\text{dien-H})\text{Cl}]^+$  and  $[\text{Au}(\text{Me}_4\text{dien-H})\text{Cl}]^+$  show rates dependent on bromide ion concentration as usually encountered for square planar complexes. There is retardation of the reaction by steric and electronic effects with increased N-alkyl substitution of the triamine. It has also been postulated that substitution of  $[\text{Au}(\text{Et}_2\text{dien-H})\text{Cl}]^+$  proceeds via a ring-opening mechanism.

The purpose of this research was to study further the effect of steric hindrance on rates of substitution of two additional gold(III) complexes. The complexes of  $\text{Me}_5\text{dien}$  and  $\text{MeEt}_4\text{dien}$  with gold(III) were prepared and investigated,

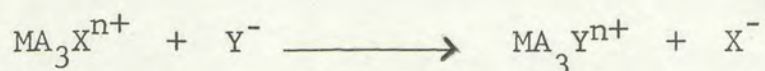
As observed with other less methyl substituted gold(III) dien complexes the substitution reaction of  $[\text{Au}(\text{Me}_5\text{dien})\text{Cl}]^{2+}$  with bromide ion is dependent on the bromide ion concentration. The results of the reaction rate studies on  $[\text{Au}(\text{MeEt}_4\text{dien})\text{Cl}]^{2+}$  with bromide ion can most easily be rationalized in terms of the previously postulated ring-opening mechanism.



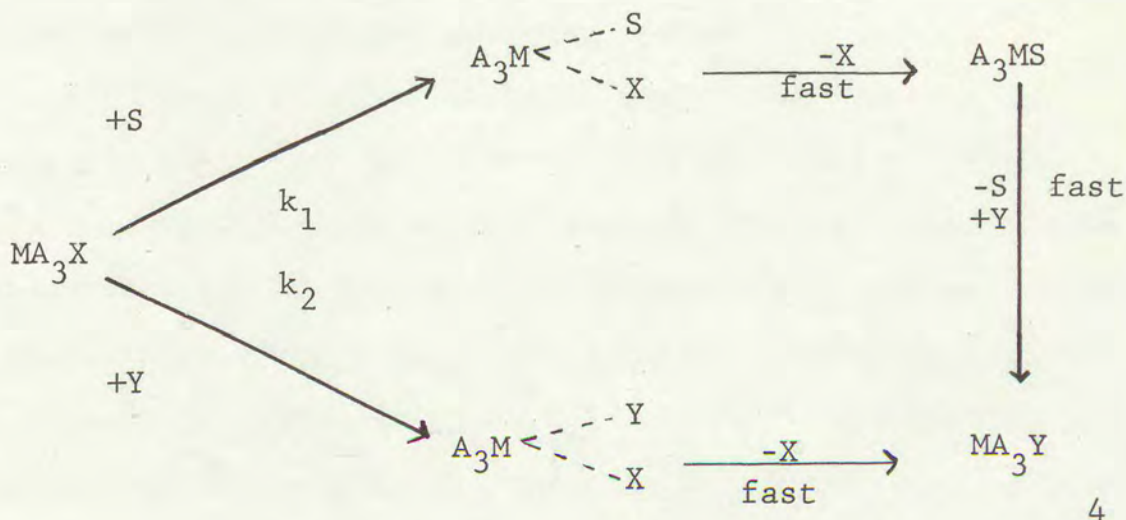
## INTRODUCTION

Extensive quantitative studies on square planar, low spin  $d^8$  complexes, especially those of Pt(II) and Pd(II), have shown that these complexes generally undergo substitution at rates that are reagent dependent.<sup>1</sup>

Square planar substitution reactions of the form:



are believed to follow a bimolecular displacement mechanism which can be represented as:



where S is the solvent and  $k_1$  represents the solvent path rate constant, Y is the substituting nucleophile and  $k_2$  is the substituting nucleophile path rate constant. This mechanism follows the two term rate law:

$$\text{Rate} = k_1 [MA_3X^{n+}] + k_2 [MA_3X^{n+}] [Y^-]$$



which under pseudo first order conditions with excess  $Y^-$  reduces to:

$$\text{Rate} = k_{\text{obs}} [\text{MA}_3\text{X}^{n+}]$$

$$\text{where } k_{\text{obs}} = k_1 + k_2 [Y] \quad 1$$

However, the square planar complexes of Pt(II), Pd(II) and Au(III) with certain N-alkyl-substituted diethylenetriamines undergo substitution at rates that are almost independent of the concentration of the entering ligand.<sup>2,3,4</sup> It has been suggested that the alkyl groups which occupy the regions above and below the plane of the ion sterically hinder the attack of the entering ligand.<sup>1</sup>

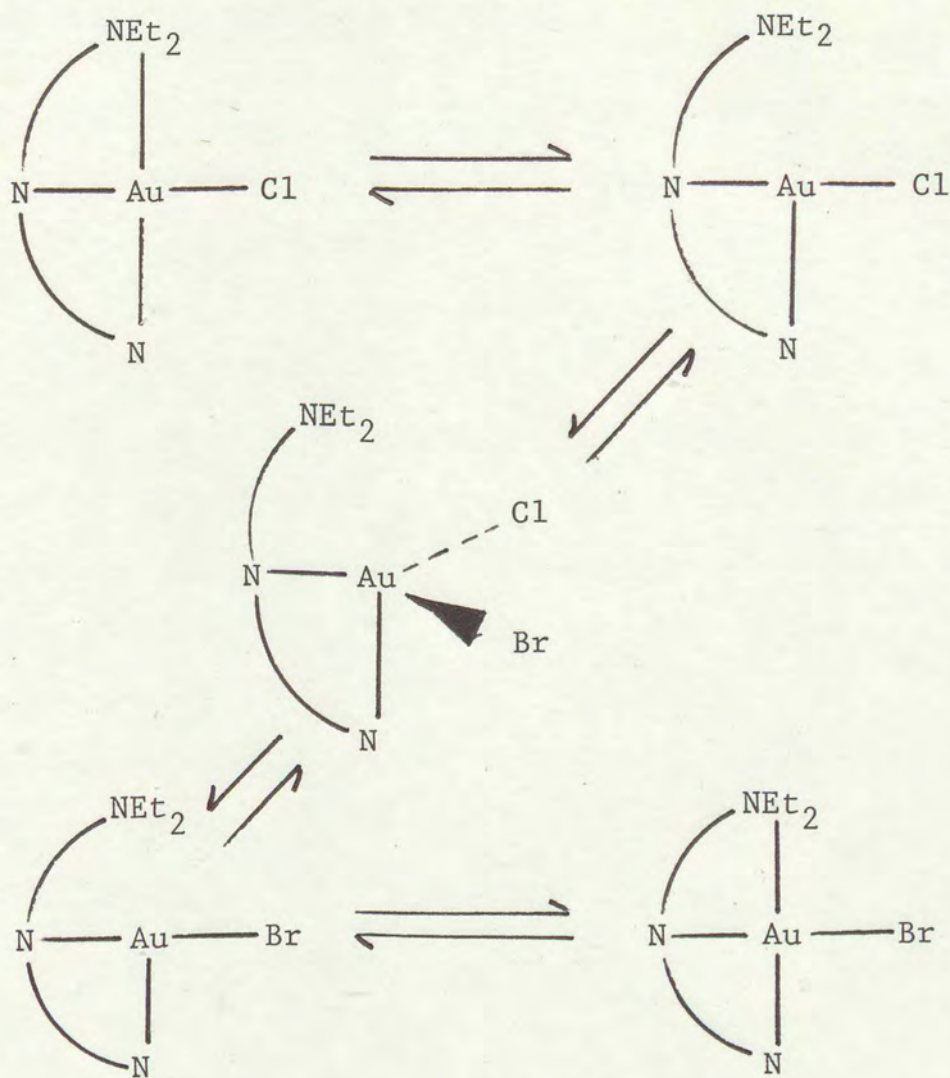
Studies of a series of reactions of the type

$$[\text{Au}(\text{amine-H})\text{Cl}]^+ + \text{Br}^- \longrightarrow [\text{Au}(\text{amine-H})\text{Br}]^+ + \text{Cl}^-$$

with the amines having various degrees of alkyl substitution reveal that the variation in the experimental bromide ion rate dependence as a function of the amine is  $\text{dien-H} > \text{Me}_2\text{dien-H} > \text{Et}_2\text{dien-H} > \text{Me}_4\text{dien-H} \gg \text{Et}_4\text{dien-H}$ . However, examination of space filling molecular models indicates that alkyl-group shielding of the central Au(III) ion increases in the order;  $\text{dien-H} < \text{Me}_2\text{dien-H} < \text{Me}_4\text{dien-H} < \text{Et}_2\text{dien-H} < \text{Et}_4\text{dien-H}$ . Thus, if only steric effects are considered the experimental rate dependence should have shown  $\text{Me}_4\text{dien-H} > \text{Et}_2\text{dien-H}$ .<sup>3,5</sup>

To explain this anomaly between the molecular model indications and the observed kinetics for  $[\text{Au}(\text{Et}_2\text{dien-H})\text{Cl}]^+$

vs  $[\text{Au}(\text{Me}_4\text{dien-H})\text{Cl}]^+$  it has been suggested that the substitution reaction of bromide with the  $[\text{Au}(\text{Et}_2\text{dien-H})\text{Cl}]^+$  complex proceeds by the following ring-opening mechanism.<sup>6</sup>



A similar ring-opening mechanism has been suggested for the reaction of  $[\text{Au}(\text{Et}_4\text{dien-H})\text{Cl}]^+$  with  $\text{N}_3^-$ ,<sup>3</sup> and for  $[\text{Pd}(\text{Et}_4\text{dien})\text{SeCN}]^+$  with  $\text{Br}^-$ .<sup>7</sup>



To investigate further the effects of alkyl substitution, the gold(III) complexes,  $[\text{Au}(\text{Me}_5\text{dien})\text{Cl}]^{2+}$  and  $[\text{Au}(\text{MeEt}_4\text{dien})\text{Cl}]^{2+}$  have been prepared and their bromide substitution reactions studied.



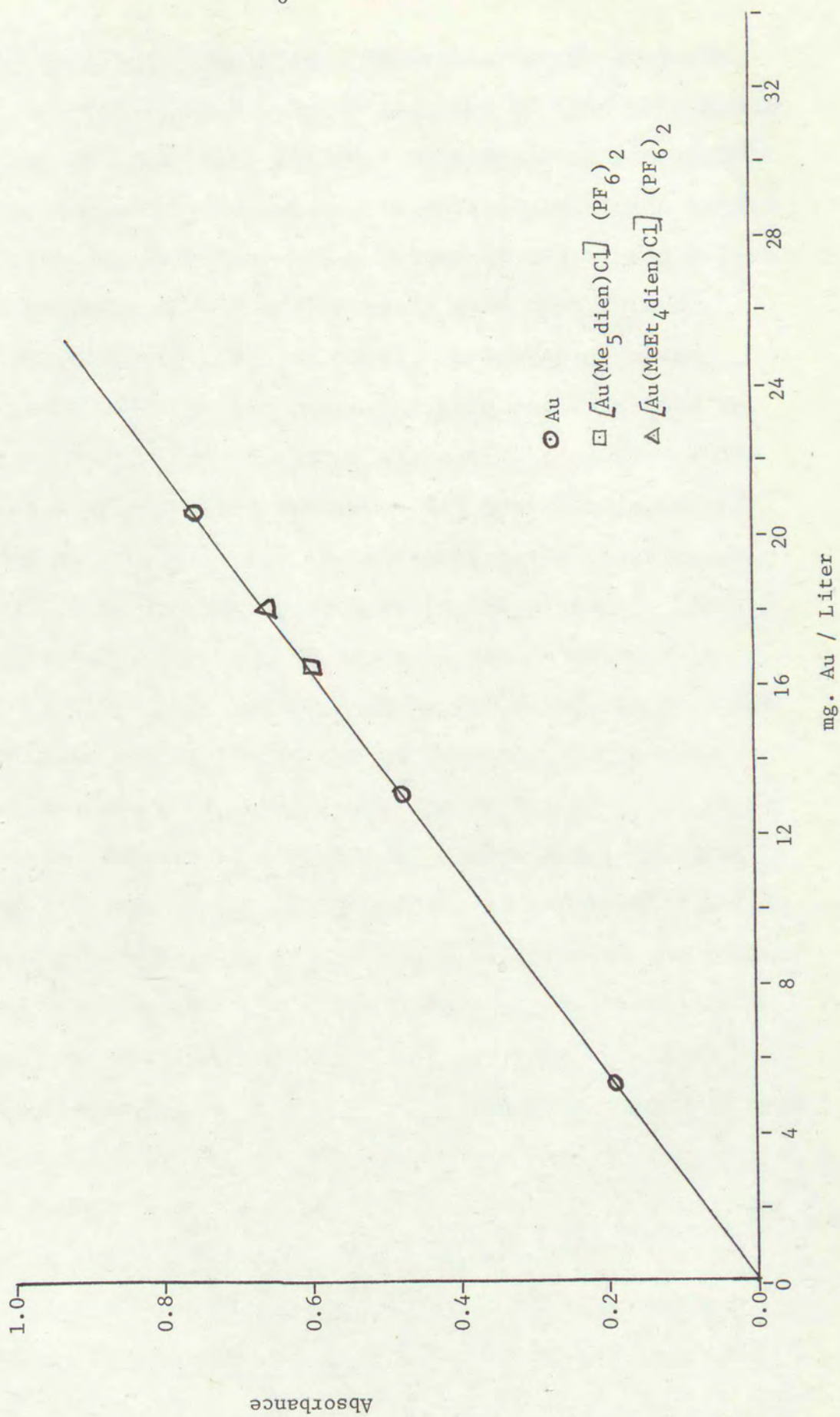
## EXPERIMENTAL

Materials: Fine gold powder, purity better than 99.99%, and ammonium hexafluorophosphate were obtained from Alfa Inorganics, Inc. The 1,1',4,7,7'-pentamethyldiethylenetriamine and the 4-methyl-1,1',7,7'-tetraethyldiethylenetriamine were purchased from Ames Laboratories, Inc. All other chemicals used were reagent grade.

Analyses: The gold analyses of the complexes, prepared as the hexafluorophosphate salts, were performed by dissolving a small accurately weighed quantity of complex in aqua regia followed by repeated evaporation with concentrated HCl to remove all volatile nitrogen oxides. Throughout the evaporation the solutions were not allowed to go to dryness, since dryness caused non-reproducible results by volatilization of gold in the presence of the hexafluorophosphate ion.<sup>3</sup> The tetrachloroauric acid solutions thus obtained were diluted with 1M HCl to obtain solutions with final concentrations in the range of  $10^{-4}$  molar. The absorbance of these solutions was measured at 314 nm using either a Perkin Elmer Model 202 Recording Spectrophotometer or a Cary Recording Spectrophotometer model 14MS. The concentration of the gold was then read from a standard curve of absorbance vs concentration of  $\text{HAuCl}_4$  prepared from pure gold. (Figure 1)

The chloride content of the complexes was determined by the Mohr method.<sup>8</sup>

FIGURE 1

Absorbance of  $\text{AuCl}_4^-$  vs Au Concentration at 313 nm



Preparation of Complexes: Tetrachloroauric acid was prepared by dissolving a weighed quantity of fine gold powder in a few ml of aqua regia followed by a repeated evaporation with concentrated HCl to remove the volatile nitrogen oxides. The solution was evaporated to a volume of 1-2 ml and allowed to cool; crystals of tetrachloroauric acid then formed.

$[\text{Au}(\text{Me}_5\text{dien})\text{Cl}] (\text{PF}_6)_2$ :  $\text{HAuCl}_4$ , prepared as above, equivalent to 0.5 g or 2.5 mmoles of gold was dissolved in 20 ml of cold  $\text{H}_2\text{O}$ . The solution was cooled to  $10^\circ\text{C}$ . While mechanically stirring the solution, 2.5 mmoles or approximately 0.7 ml of 1,1',4,7,7'-pentamethyldiethylenetriamine was added. A yellow precipitate of  $[\text{Au}(\text{Me}_5\text{dien})\text{Cl}] [\text{AuCl}_4]_2$  immediately formed. While maintaining the solution at a temperature below  $10^\circ\text{C}$  and monitoring the pH of the solution with a Fischer Accumet model 120 pH meter, 0.15 M sodium hydroxide was added dropwise not allowing the pH to go above 7. With the addition of the sodium hydroxide the pH first increased and then slowly decreased as the added  $\text{OH}^-$  reacted. The yellow precipitate dissolved. The addition of the sodium hydroxide was continued until the solution remained at pH 5 for five minutes. The solution was filtered and a clear orange filtrate was obtained. The filtrate was cooled to less than  $5^\circ\text{C}$  and 1 g of  $\text{NH}_4\text{PF}_6$  was added. A peach colored precipitate formed which was then collected on filter paper and washed with small portions of ice cold ethanol. This was followed by a wash with cold ether and the product sucked dry. The resulting cream colored crystals were then stored



over  $\text{CaCl}_2$  in a refrigerated desiccator. A yield of 38% was obtained (based on the weight of gold used).

Analysis: Calculated for  $[\text{Au}(\text{Me}_5\text{dien})\text{Cl}] (\text{PF}_6)_2$   
 Au, 28.3%; Cl, 5.11%. Found: Au, 28.1%; Cl, 5.2%.

$[\text{Au}(\text{MeEt}_4\text{dien})\text{Cl}] (\text{PF}_6)_2$ :  $\text{HAuCl}_4$ , prepared as stated above, equivalent to 0.5 g or 2.5 mmols of gold was dissolved in 30 ml of  $\text{H}_2\text{O}$  and cooled to  $10^\circ\text{C}$ . While mechanically stirring the solution, 2.5 mmols or approximately 0.7 ml of 4-methyl-1,1', 7, 7'-tetraethyldiethylenetriamine was added. A yellow precipitate  $[\text{Au}(\text{MeEt}_4\text{dien})\text{Cl}] [\text{AuCl}_4]_2$  immediately formed. This precipitate was slowly dissolved with a dropwise addition of 0.15 M sodium hydroxide, while monitoring the pH and maintaining it below pH 7. The addition of the sodium hydroxide caused the solution to darken to an orange color and then to a gray, presumably because of some decomposition of the yellow precipitate. Sodium hydroxide was added until a pH of 5.5 was maintained for five minutes. The solution and dark residue were filtered to obtain a yellow-orange filtrate. The filtrate was cooled to about  $5^\circ\text{C}$  and 1 g of  $\text{NH}_4\text{PF}_6$  was added. The off-white precipitate produced was collected on filter paper and washed with cold  $\text{H}_2\text{O}$ , cold ethanol and finally cold ether and sucked dry. The compound was stored over  $\text{CaCl}_2$  in a refrigerated desiccator. A yield of 33% (based on the weight of gold used) was obtained.

Analysis: Calculated for  $[\text{Au}(\text{MeEt}_4\text{dien})\text{Cl}] (\text{PF}_6)_2$   
 Au, 26.2%; Cl, 4.72%. Found: Au, 26.3%; Cl, 4.70%

Although these compounds were refrigerated in the absence of light, they slowly darkened and became gummy. Recrystallization was necessary after about one month. Recrystallization was accomplished by dissolving the compound in a small quantity of acetone and water. The mixture was then filtered and the water-acetone filtrate collected. The acetone was removed by vacuum. The resulting recrystallized compound was collected and washed with cold ethanol followed by cold ether and the product sucked dry.



## KINETIC STUDIES

Earlier studies of the aqueous solution chemistry of Au(III) with various diens indicated that: (a) Au(III) dien-H complexes undergo extensive hydrolysis in neutral aqueous solutions; (b) an excess of halide ion represses hydrolysis of these complexes in certain pH ranges; (c) the conjugate acids of these complexes are stable in perchloric acid; and (d) the conjugate acids of these complexes undergo decomposition in hydrohalic acids. 3,6,9

Since  $[\text{Au}(\text{Me}_5\text{dien})\text{Cl}]^{2+}$  and  $[\text{Au}(\text{MeEt}_4\text{dien})\text{Cl}]^{2+}$  are complexes of the Au(III) dien category, their aqueous solution chemistry was briefly examined to determine their behavior at various pH's and to select suitable pH ranges for kinetic study.

Small portions of each complex were dissolved in  $\text{H}_2\text{O}$ , to a final concentration of  $4 \times 10^{-4}\text{M}$ . The solutions were placed in a water jacketed beaker and maintained at  $25^\circ\text{C}$  by circulating water through the jacket from a P.M. Tamson constant temperature bath. The pH of these solutions was measured with a Fischer Accumet pH meter previously calibrated using Bechman pH 4.00 and pH 6.86 buffers. The pH was decreased in small increments using  $\text{HClO}_4$  and increased in small increments using  $\text{NaOH}$ . The spectrum of aliquots of each of the solutions at the various pH's was obtained by using a Perkin-Elmer 202 spectrophotometer and scanning from



250 nm to 390 nm.

It was also of interest to examine the stability of the bromide substituted complexes at various pH's. The examination was similar to that stated above except that the chloro species was allowed to react with a sufficient amount of bromide ion at 25°C before decreasing or increasing the pH at small increments with  $\text{HClO}_4$  or  $\text{NaOH}$  respectively.

Whereas with previously studied gold(III) diens it was possible to form their conjugate bases and measure the dissociation constants, there are no acid-conjugate base relationships with  $[\text{Au}(\text{Me}_5\text{dien})\text{Cl}]^{2+}$  and  $[\text{Au}(\text{MeEt}_4\text{dien})\text{Cl}]^{2+}$  because all amine sites are completely substituted.

The pH of a  $4 \times 10^{-4}$  M solution of  $[\text{Au}(\text{Me}_5\text{dien})\text{Cl}]^{2+}$  in  $\text{H}_2\text{O}$  was 5.5. The pH of a similar concentration of  $[\text{Au}(\text{MeEt}_4\text{dien})\text{Cl}]^{2+}$  in  $\text{H}_2\text{O}$  was 5.8.

Examination of the scans at the various pH's revealed that the  $[\text{Au}(\text{Me}_5\text{dien})\text{Cl}]^{2+}$  complex was stable with the addition of  $\text{HClO}_4$  to an acidic pH of 1.0, at which decomposition occurred with the formation of  $\text{AuCl}_4^-$ . With the addition of  $\text{NaOH}$  the complex was stable to a pH of 6.3, then the hydroxide ion noticeably replaced the chloride ion. The pH studies of the bromide substituted complex,  $[\text{Au}(\text{Me}_5\text{dien})\text{Br}]^{2+}$ , indicated that at a pH less than 5 there was unwrapping of the ligand and replacement with bromide at the amine sites, and at a pH greater than 6.3 hydrolysis takes place. The pH studies of the  $[\text{Au}(\text{MeEt}_4\text{dien})\text{Cl}]^{2+}$  complex indicated that it was less stable than the  $[\text{Au}(\text{Me}_5\text{dien})\text{Cl}]^{2+}$  complex.



Decomposition occurred below a pH of 2.3 and hydrolysis took place above pH 5.8. The bromide substituted species,

$[\text{Au}(\text{MeEt}_4\text{dien})\text{Br}]^{2+}$ , was stable between pH 5.2 and pH 6.2.

Based on the above information it was decided to study the kinetics of both complexes in a pH 5.8 buffer. A  $\text{Na}_2\text{HPO}_4$ — $\text{NaH}_2\text{PO}_4$  buffer was used. Two solutions of each complex were prepared in pH 5.8 buffer, one containing 0.10 M  $\text{Cl}^-$  and the other containing 0.10 M  $\text{Br}^-$ . The spectrum of each solution was then obtained. The results for  $[\text{Au}(\text{Me}_5\text{dien})\text{X}]^{2+}$  are shown in Figure 2. Examination of these spectra show a large difference in absorbance at a wavelength of 330 nm. Therefore, the wavelength of 330 nm was selected as optimum for the kinetic study for the  $\text{Me}_5\text{dien}$  complex.

A wavelength of 340 nm was selected for the kinetic study for the  $\text{MeEt}_4\text{dien}$  complex by a similar procedure. Pertinent spectra for these complexes are shown in Figure 3.

Solutions of the chloro complexes were prepared by dissolving exact amounts of the solid  $[\text{Au}(\text{amine})\text{Cl}] (\text{PF}_6)_2$  in pH 5.8 phosphate buffer. Kinetic runs were carried out by allowing 2 ml of this solution to react with 1 ml of a solution containing bromide ion at various concentrations. The bromide solutions were prepared by dissolving exact amounts of NaBr and  $\text{NaClO}_4$  in pH 5.8 buffer to produce, after mixing, the desired bromide ion concentration and a total ionic strength of NaBr and  $\text{NaClO}_4$  equal to 0.10 M. The concentration

FIGURE 2

Absorption Spectra of the Bromo and Chloro Species of

$[\text{Au}(\text{Me}_5\text{dien})\text{X}]^{2+}$  at Concentrations of  $4 \times 10^{-4}$  M

A  $[\text{Au}(\text{Me}_5\text{dien})\text{Cl}]^{2+}$

B  $[\text{Au}(\text{Me}_5\text{dien})\text{Br}]^{2+}$

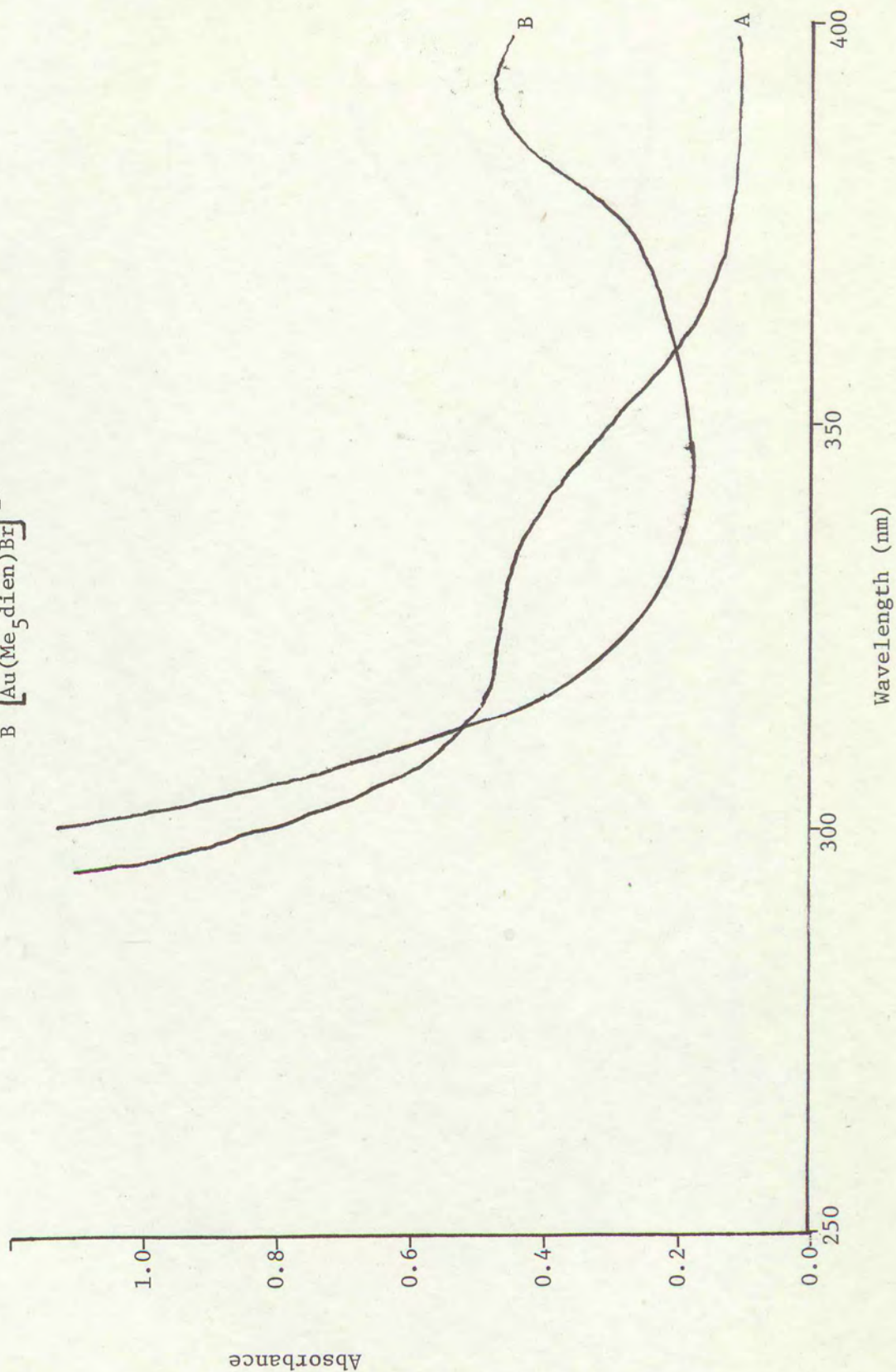




FIGURE 3

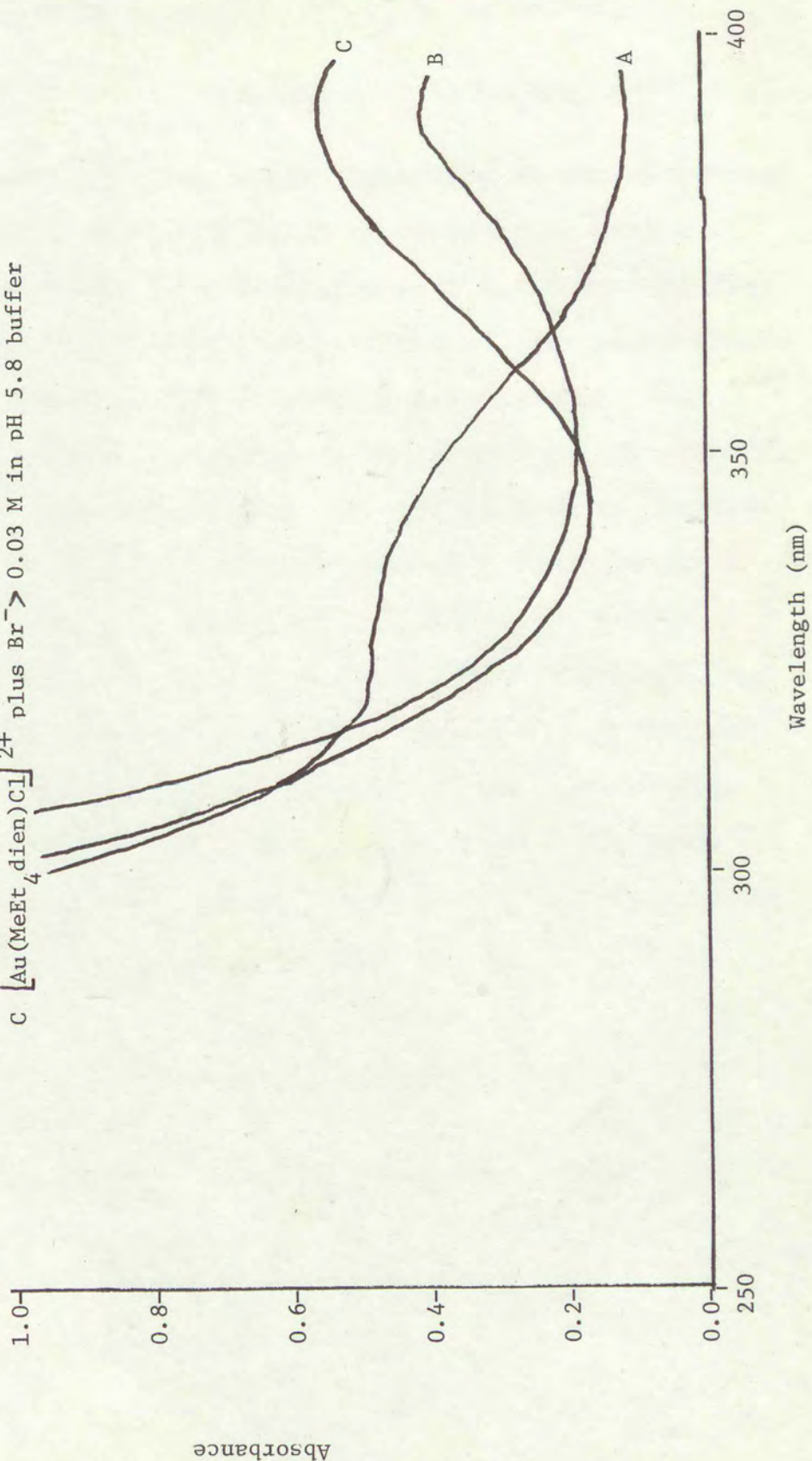
Absorption Spectra of the Bromo and Chloro Species of

$[\text{Au}(\text{MeEt}_4\text{dien})\text{X}]^{2+}$  at Concentrations of  $4 \times 10^{-4}$  M

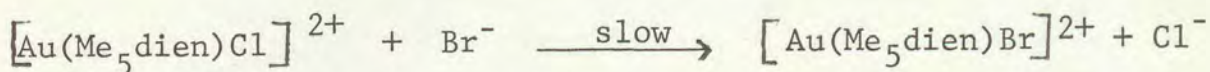
A  $[\text{Au}(\text{MeEt}_4\text{dien})\text{Cl}]^{2+}$  in pH 5.8 buffer

B  $[\text{Au}(\text{MeEt}_4\text{dien})\text{Cl}]^{2+}$  plus  $\text{Br}^- < 0.03$  M in pH 5.8 buffer

C  $[\text{Au}(\text{MeEt}_4\text{dien})\text{Cl}]^{2+}$  plus  $\text{Br}^- > 0.03$  M in pH 5.8 buffer



of the complex after mixing was  $4 \times 10^{-4}$  M. The reaction occurring for  $[\text{Au}(\text{Me}_5\text{dien})\text{Cl}] (\text{PF}_6)_2$  is as follows:



Rates were determined using a Cary Recording Spectrophotometer model 14 MS with 1 cm quartz cells in conjunction with a Temptrol 153 waterbath from Precision Scientific Company that pumped water through the cell compartment of the spectrophotometer to keep the system at a constant temperature. The scans obtained showed the change in absorbance at the specific wavelength as a function of time. A typical scan is shown in Figure 4. All reactions were performed at a temperature of  $25^\circ\text{C} \pm 0.1^\circ\text{C}$ . Bromide concentrations of 0.005 M, 0.01 M, 0.03 M, 0.05 M, 0.08 M and 0.1 M were used for both complexes. Additionally,  $[\text{Au}(\text{MeEt}_4\text{dien})\text{Cl}]^{2+}$  was studied at 0.02 M and 0.04 M bromide ion concentration; also the kinetics of this complex were studied at a wavelength of 380 nm. For each complex, replicate runs were performed at the various bromide concentration levels. Reproducibility was better than 1% absorbance.

Two methods for determining the pseudo-first order rate constant were used:

1. The log of the difference in the absorbance value (obtained from the scan) at time "t" ( $A_t$ ) and at the completion of the reaction ( $A_\infty$ ) was plotted as a function of time.

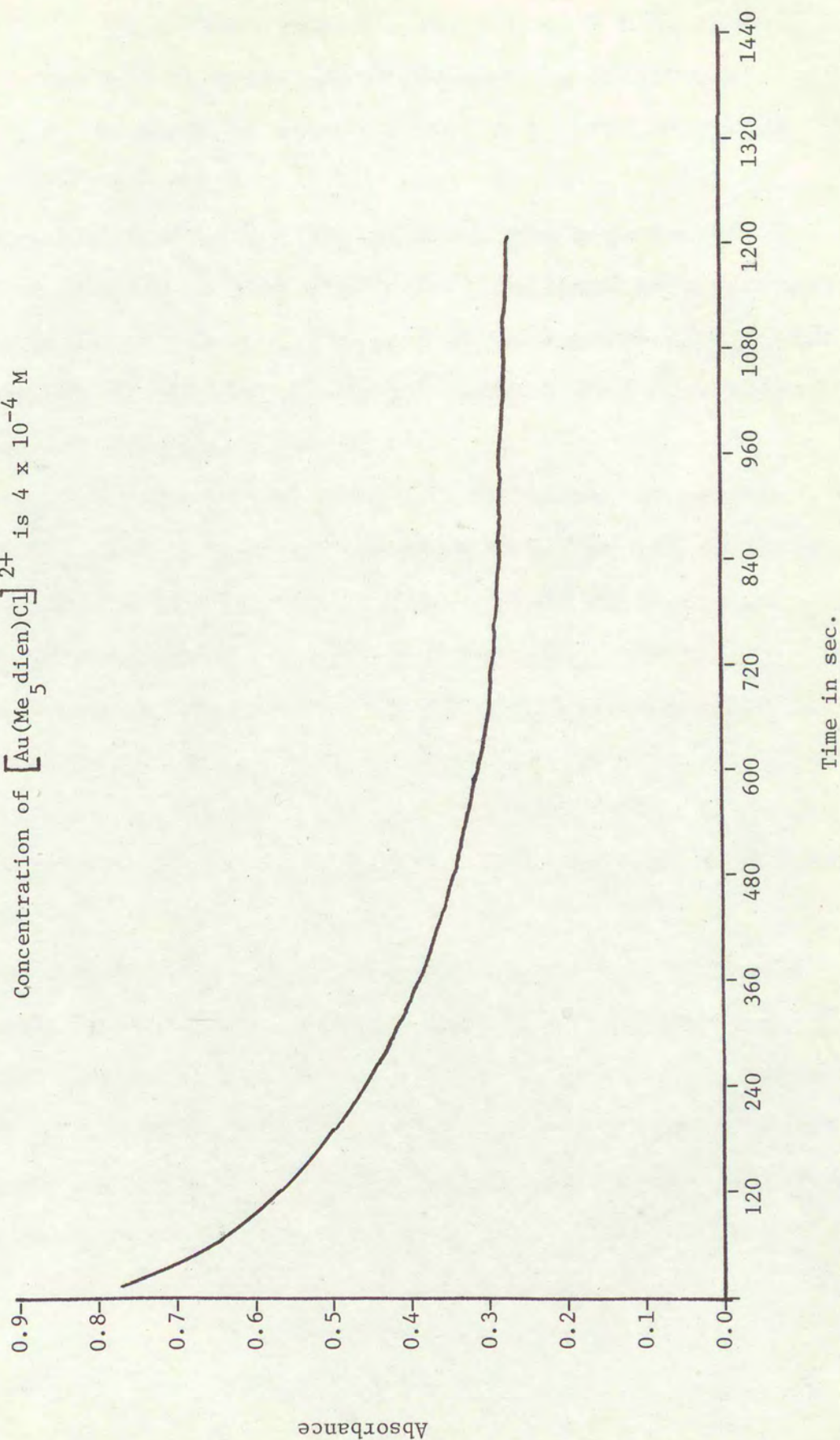


FIGURE 4

A Typical Scan for the Reaction of  $[\text{Au}(\text{Me}_5\text{dien})\text{Cl}]^{2+}$  with  $0.1 \text{ M Br}^-$ ,

Followed as a Decrease in Absorbance at 330 nm with time.

Concentration of  $[\text{Au}(\text{Me}_5\text{dien})\text{Cl}]^{2+}$  is  $4 \times 10^{-4} \text{ M}$



2. The Guggenheim method:<sup>11</sup> The log of  $\Delta A$  vs time where  $\Delta A$  equals the difference in absorbance for a constant time interval  $\Delta t$ . For most runs  $\Delta t = 2$  min.

Figure 5 shows a typical scan for the reaction of  $[\text{Au}(\text{MeEt}_4\text{dien})\text{Cl}]^{2+}$  with  $0.05 \text{ M Br}^-$ , followed as a decrease in absorbance at 340 nm. Figure 6 shows a graph of  $k_{\text{obs}}$  for the reaction of  $[\text{Au}(\text{MeEt}_4\text{dien})\text{Cl}]^{2+}$  with  $0.05 \text{ M Br}^-$ , calculated by the Guggenheim method.

From the linear plot obtained, the slope, or pseudo-first order rate constant, was calculated for the specific bromide concentration being studied. Plots of replicate runs yielded slopes which agreed within 10%. A straight line was obtained from a plot of the observed rate constant as a function of the bromide concentration with an intercept equal to  $k_1$ , the solvent path rate constant, and a slope of  $k_2$ , the bromide path rate constant. (See Figures, 7, 8, and 9)

The Guggenheim method was used because the absorbance at time infinity is not needed to determine the observed rate constant. The absorbance at time infinity was questioned because of the hydrolysis that occurred with time. However, comparison of the two methods showed no significant difference in the calculated observed rate constant.



FIGURE 5

A Typical Scan for the Reaction of  $[\text{Au}(\text{MeEt}_4\text{dien})\text{Cl}]^{2+}$  with  $0.05 \text{ M Br}^-$ ,

Followed as a decrease in Absorbance at  $340 \text{ nm}$  with time.

Concentration of  $[\text{Au}(\text{MeEt}_4\text{dien})\text{Cl}]^{2+}$  is  $4 \times 10^{-4} \text{ M}$

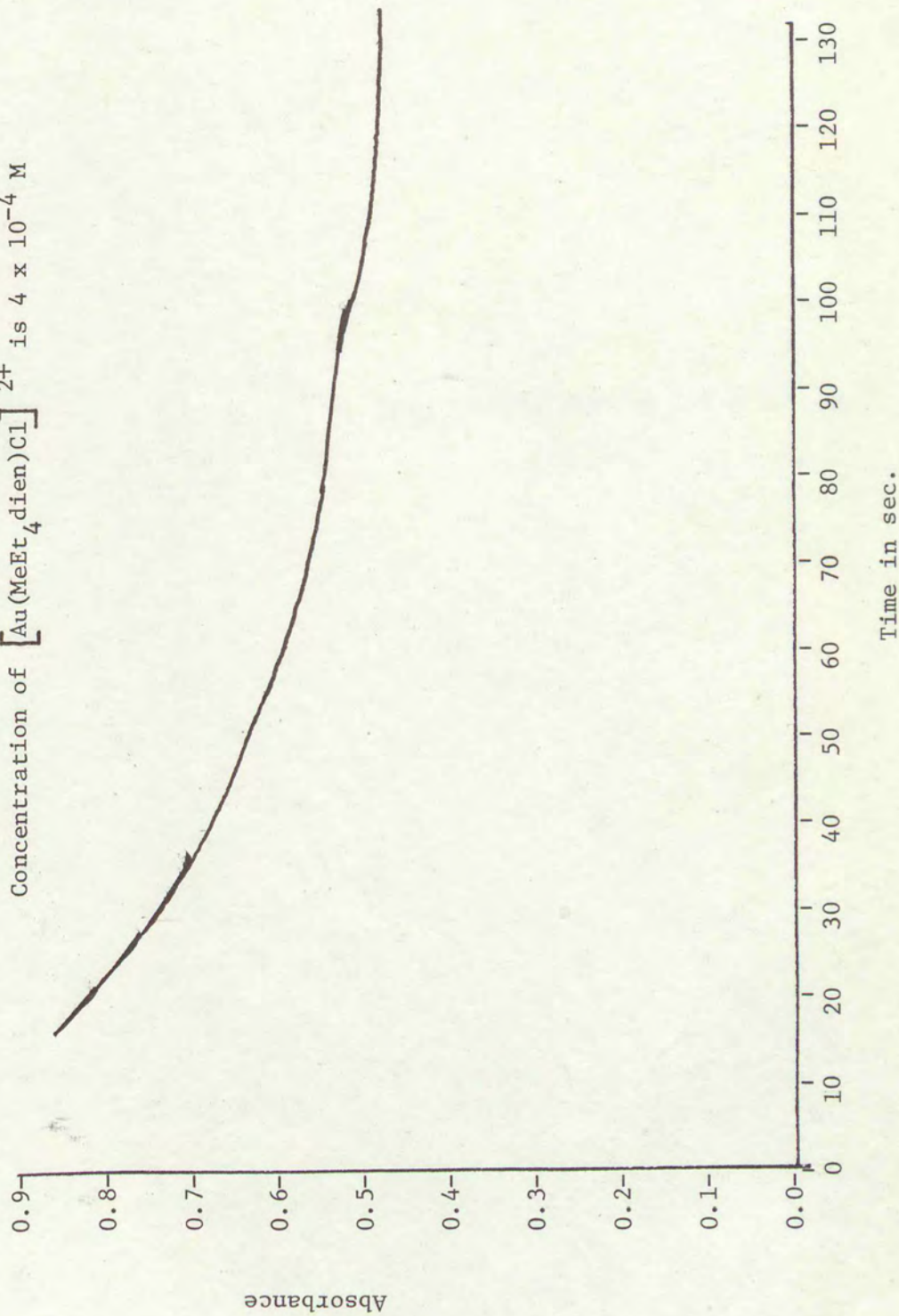


FIGURE 6

Graph of  $k_{\text{obs}}$  for the reaction of  $[\text{Au}(\text{MeEt}_4\text{dien})\text{Cl}]^{2+}$   
with  $0.05 \text{ M Br}^-$

Calculated by Guggenheim Method

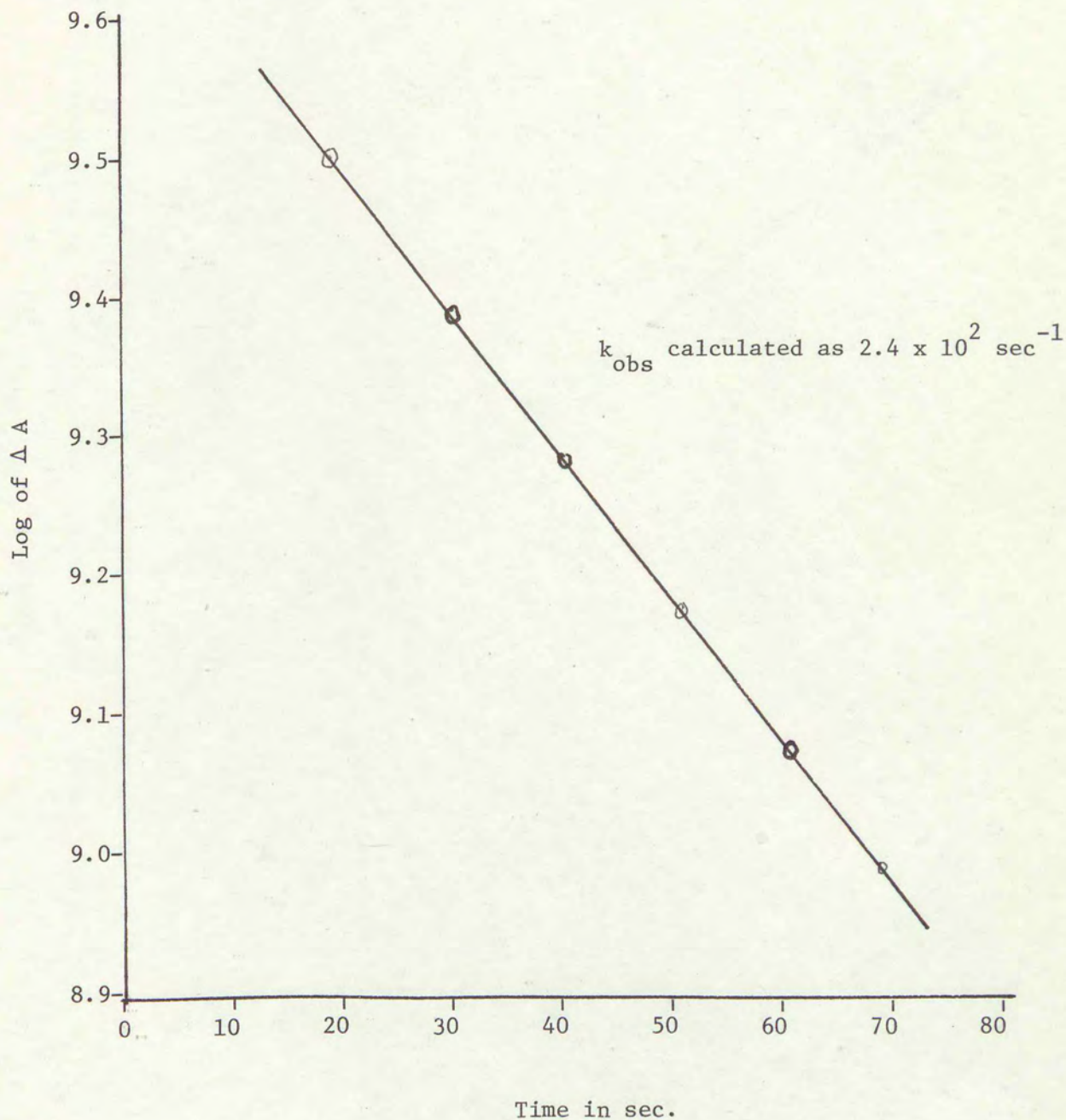




FIGURE 7

Observed Rate Constant for  $[\text{Au}(\text{Me}_5\text{dien})\text{Cl}]^{2+}$

versus Bromide Concentration @  $T = 25^\circ\text{C}$

Data obtained from change in Absorbance at 330 nm

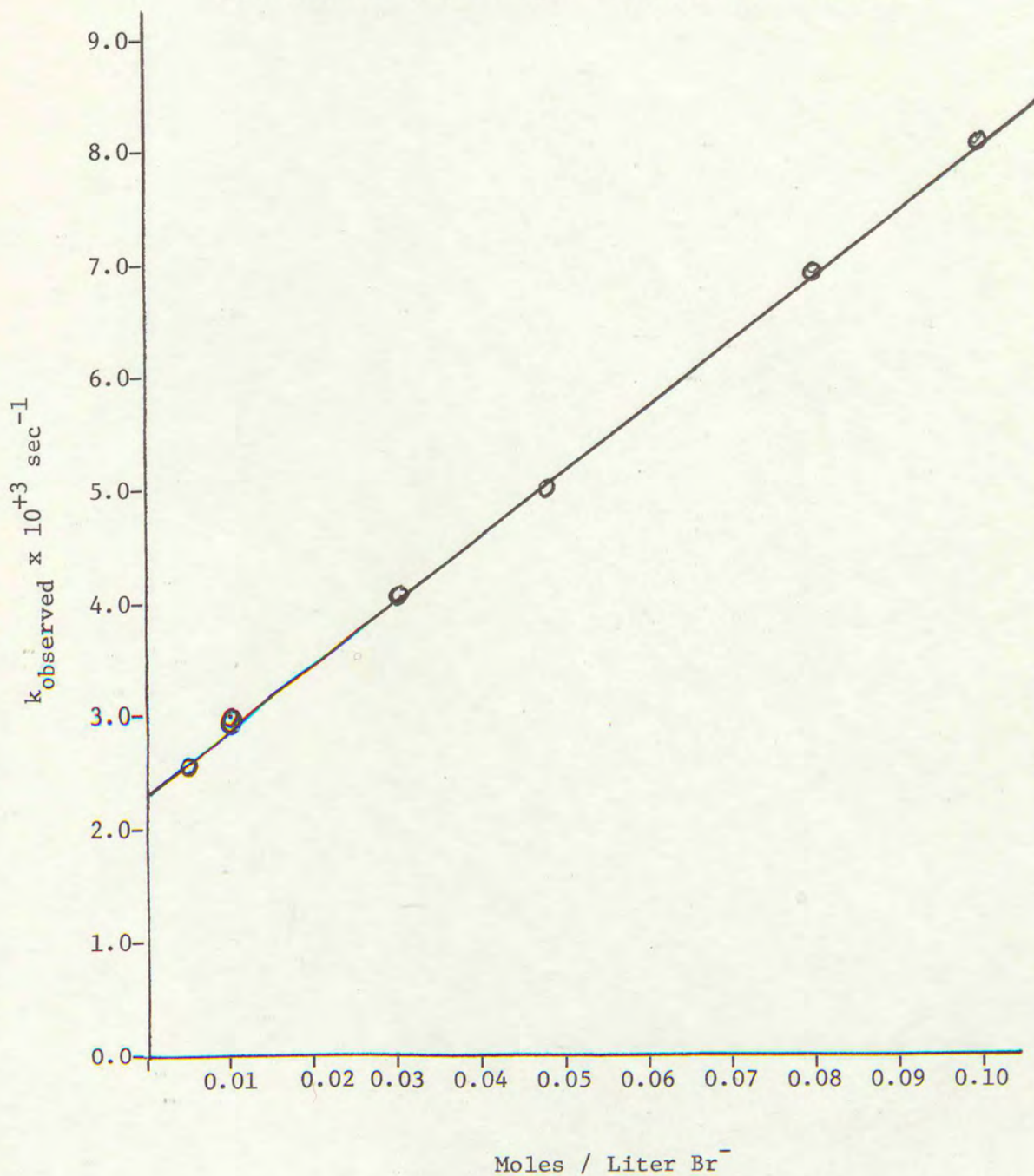


FIGURE 8

Observed Rate Constant for  $[\text{Au}(\text{MeEt}_4\text{dien})\text{Cl}]^{2+}$

versus Bromide Concentration @  $T = 25^\circ\text{C}$

Data Obtained from change in Absorbance at 340 nm

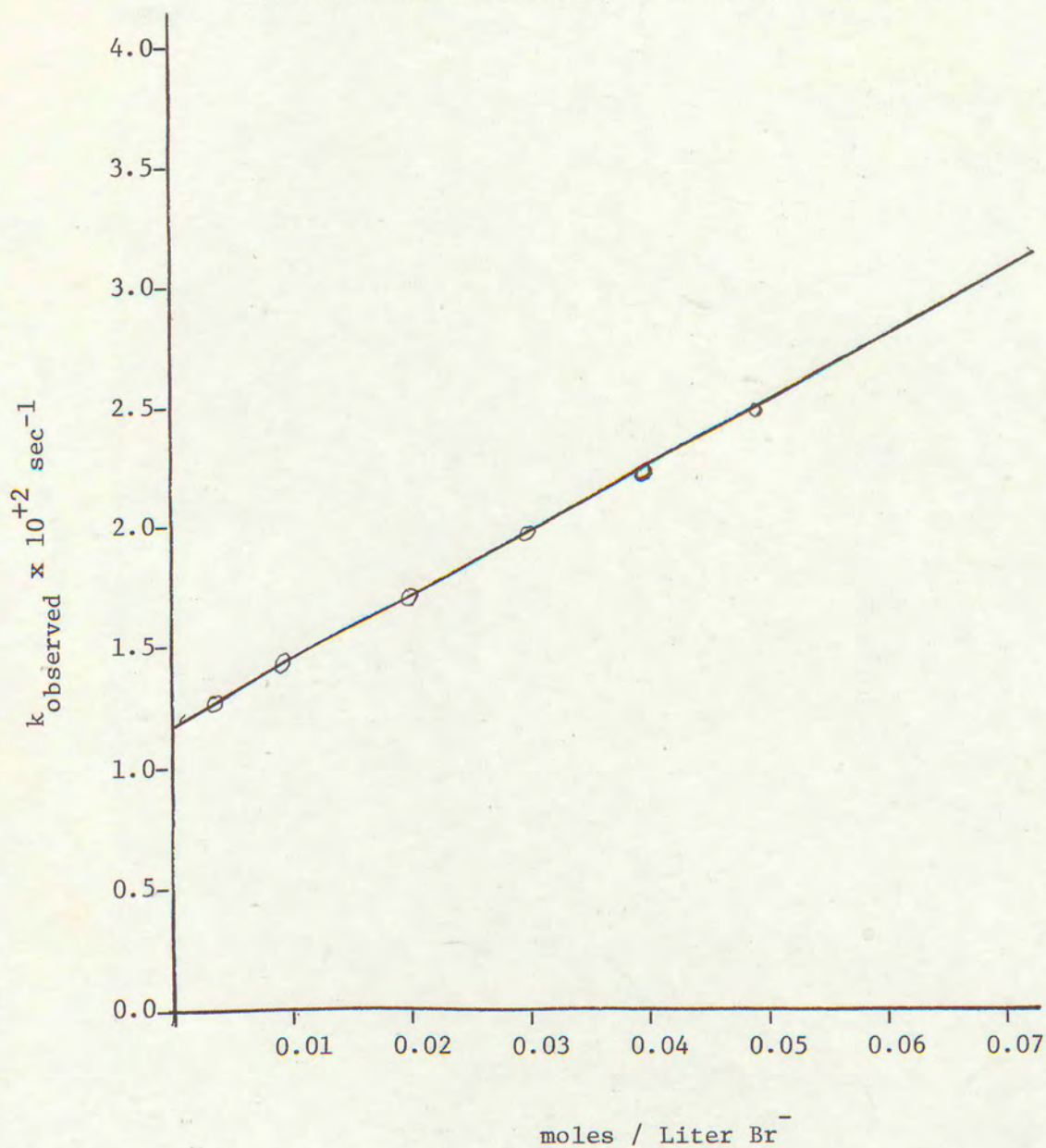


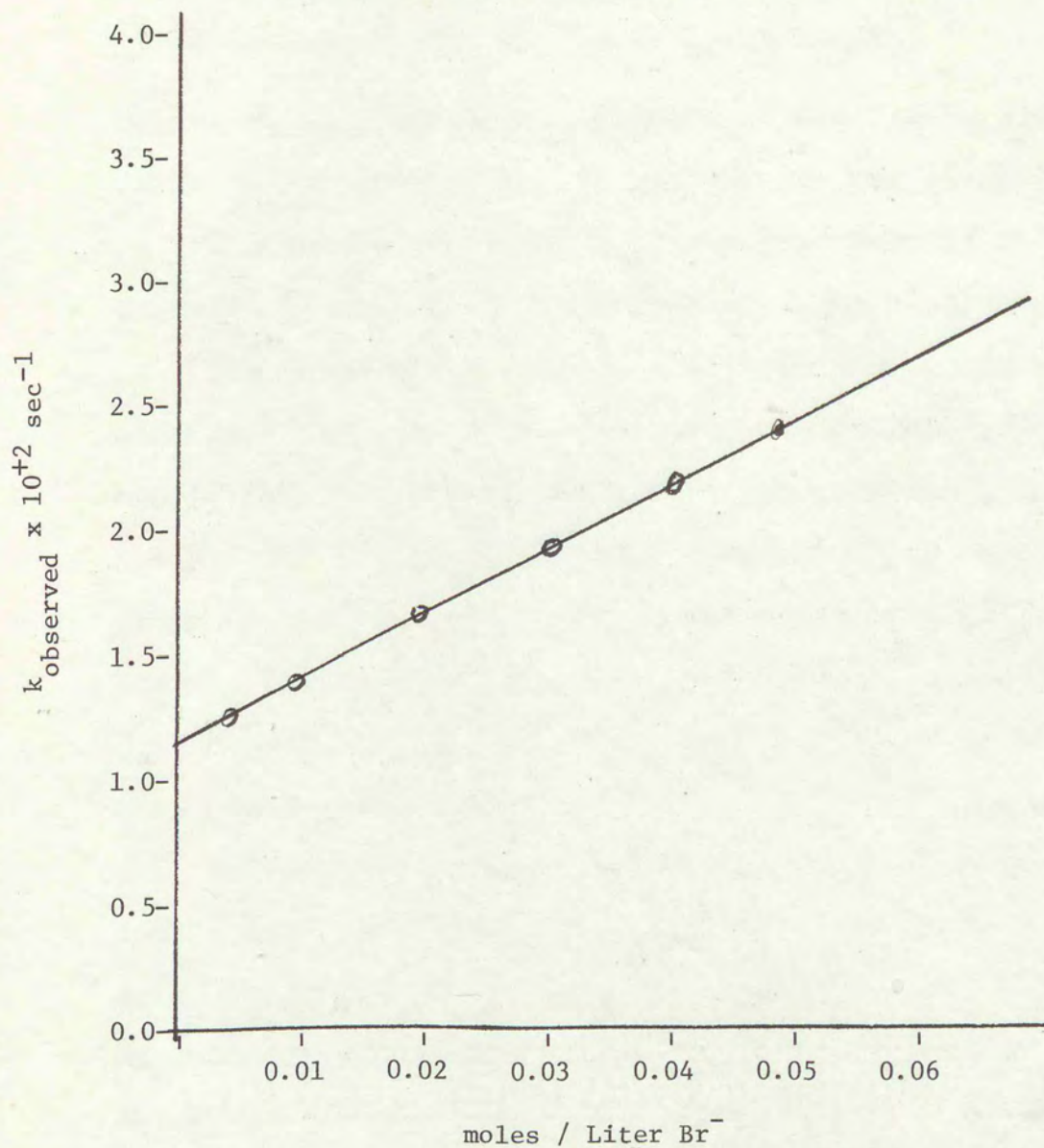


FIGURE 9

Observed Rate Constant for  $[\text{Au}(\text{MeEt}_4\text{dien})\text{Cl}]^{2+}$

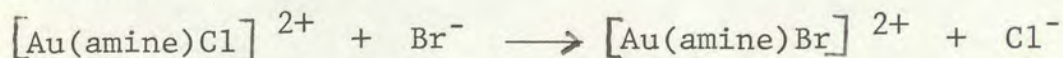
versus Bromide Concentration @  $T = 25^\circ\text{C}$

Data obtained from change in absorbance at 380 nm



## RESULTS AND DISCUSSION

The pseudo-first order rate constants obtained for the reaction:



(where amine = (Me<sub>5</sub>dien), studied at wavelength 330 nm, and (MeEt<sub>4</sub>dien), studied at 340 and 380 nm) are given in Table I.

The values shown for  $k_{\text{obs}}$  are reproducible within 10% and are the average of from four to eight replicate runs.

The estimated values of the first and second order rate constants for  $[\text{Au}(\text{Me}_5\text{dien})\text{Cl}]^{2+}$  and  $[\text{Au}(\text{MeEt}_4\text{dien})\text{Cl}]^{2+}$  are listed in Table II, these represent rate constants for the solvent and bromide paths, respectively. Also listed in Table II are the data for the substitution reactions of  $\text{Br}^-$  for  $\text{Cl}^-$  in the complexes of  $[\text{Au}(\text{dien})\text{Cl}]^{2+}$ ,  $[\text{Au}(\text{dien-H})\text{Cl}]^+$ ,  $[\text{Au}(\text{Me}_2\text{dien-H})\text{Cl}]^+$ ,  $[\text{Au}(\text{Me}_4\text{dien-H})\text{Cl}]^+$ ,  $[\text{Au}(\text{Et}_2\text{dien-H})\text{Cl}]^+$  and  $[\text{Au}(\text{Et}_4\text{dien-H})\text{Cl}]^+$ .

As has been stated previously, examination of molecular models indicates that the shielding of the Au(III) by the amine increases in the following order:  $\text{dien-H} < \text{Me}_2\text{dien-H} < \text{Me}_4\text{dien-H} < \text{Et}_2\text{dien-H} < \text{Et}_4\text{dien-H}$ .<sup>6</sup> Examination of the molecular models of Me<sub>5</sub>dien and MeEt<sub>4</sub>dien indicates the Me<sub>5</sub>dien shields the Au(III) slightly more than the Me<sub>4</sub>dien-H and the MeEt<sub>4</sub>dien shields slightly more than the Et<sub>4</sub>dien-H. However, it should be noted that Me<sub>5</sub>dien and MeEt<sub>4</sub>dien complexes are divalent positive ions. Thus the slight shielding



TABLE I

Pseudo First Order Rate Constants at 25°C for:

amine = Me<sub>5</sub>dien

<u>Br<sup>-</sup> concentration</u>	<u>k<sub>obs</sub> x 10<sup>3</sup> at 330 nm</u>
0.10 M	8.3 sec <sup>-1</sup>
0.08 M	7.0
0.05 M	5.0
0.03 M	4.1
0.01 M	3.0
0.005 M	2.5

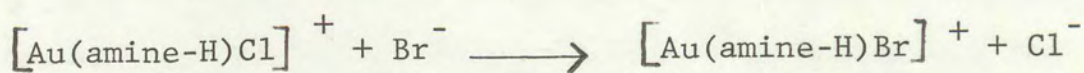
amine = MeEt<sub>4</sub>dien

<u>Br<sup>-</sup> concentration</u>	<u>k<sub>obs</sub> x 10<sup>2</sup> at 340 nm</u>	<u>k<sub>obs</sub> x 10<sup>2</sup> at 380 nm</u>
0.05 M	2.4 sec <sup>-1</sup>	2.4 sec <sup>-1</sup>
0.04 M	2.2	2.2
0.03 M	1.8	1.8
0.02 M	1.6	1.6
0.01 M	1.5	1.5
0.005 M	1.2	1.2

TABLE II

First Order and Second Order

Rate Constants for the Reactions:



and



<u>Complex</u>	<u>k<sub>1</sub> (sec<sup>-1</sup>)</u>	<u>k<sub>2</sub> (M<sup>-1</sup>sec<sup>-1</sup>)</u>	<u>Reference</u>
$[\text{Au}(\text{dien})\text{Cl}]^{2+}$	0	380	5
$[\text{Au}(\text{dien-H})\text{Cl}]^+$	0.6	190	5
$[\text{Au}(\text{Me}_2\text{dien-H})\text{Cl}]^+$	0.20	44	6
$[\text{Au}(\text{Me}_4\text{dien-H})\text{Cl}]^+$	0.062	0.76	6
$[\text{Au}(\text{Me}_5\text{dien})\text{Cl}]^{2+}$	0.002	0.058	this work
$[\text{Au}(\text{Et}_2\text{dien-H})\text{Cl}]^+$	0.023	3.8	6
$[\text{Au}(\text{Et}_4\text{dien-H})\text{Cl}]^+$	0.00012	0.0085	6
$[\text{Au}(\text{MeEt}_4\text{dien})\text{Cl}]^{2+}$	0.01	0.26	this work

The rate constants for the reactions were determined  
at  $25^\circ \pm 0.1^\circ\text{C}$ .



effect of the additional methyl group might be offset by the increased charge of the  $\text{Me}_5\text{dien}$  and the  $\text{MeEt}_4\text{dien}$  complexes.

The data in Table II shows that the bromide substitution of chloride in  $[\text{Au}(\text{Me}_5\text{dien})\text{Cl}]^{2+}$  proceeds via the solvent path 30 times slower and via the bromide path 10 times slower than the same reactions for  $[\text{Au}(\text{Me}_4\text{dien-H})\text{Cl}]^+$ . This decrease in rate can be attributed to the steric blocking of the 5th methyl group. This decrease due to the steric effect would presumably be larger but is offset by the increased charge of the complex. Note that  $\text{H}_2\text{O}$  entry is decreased by a larger factor than  $\text{Br}^-$  entry, because ion-dipole interaction is less than ion-ion interaction. However, the same phenomenon is not observed in the examination of the data in Table II for the  $\text{MeEt}_4\text{dien}$  vs the  $\text{Et}_4\text{dien-H}$  complexes. The bromide substitution of the chloride in  $[\text{Au}(\text{MeEt}_4\text{dien})\text{Cl}]^{2+}$  proceeds via the solvent path approximately 100 times faster and via the bromide path approximately 30 times faster than with  $[\text{Au}(\text{Et}_4\text{dien-H})\text{Cl}]^+$ . Also, by comparison  $[\text{Au}(\text{MeEt}_4\text{dien})\text{Cl}]^{2+}$  reacts two times slower via the solvent path and 15 times slower via the bromide path than  $[\text{Au}(\text{Et}_2\text{dien-H})\text{Cl}]^+$ . While steric hindrance can be invoked to rationalize the slower reaction of  $[\text{Au}(\text{MeEt}_4\text{dien})\text{Cl}]^{2+}$  over  $[\text{Au}(\text{Et}_2\text{dien-H})\text{Cl}]^+$ , such a rationalization is not consistent with the increase in rate observed for  $[\text{Au}(\text{MeEt}_4\text{dien})\text{Cl}]^{2+}$  over  $[\text{Au}(\text{Et}_4\text{dien-H})\text{Cl}]^+$ .



Furthermore, this latter increase cannot be explained in terms of increased charge since this should cause increased  $\text{Br}^-$  entry to a greater extent than  $\text{H}_2\text{O}$  entry as was observed for the methyl substituted complexes. This anomaly can be rationalized in terms of the postulated ring-opening mechanism. Evidence for ring-opening is apparent in the equilibrium studies. The gold(III) complexes of  $\text{Me}_2\text{dien}$  and  $\text{Me}_4\text{dien}$  were found stable in 1 M acidic chloride and bromide solutions. A similar behavior was observed for the gold(III)  $\text{Me}_5\text{dien}$  complex. On the other hand, the complexes of gold(III) containing  $\text{Et}_2\text{dien}$  and  $\text{Et}_4\text{dien}$  broke up in 1 M acidic chloride solutions to yield  $\text{AuCl}_4^-$  and in 1 M acidic bromide solutions to yield  $\text{AuBr}_4^-$ .<sup>6</sup> A similar behavior was also observed for the gold(III)  $\text{MeEt}_4\text{dien}$  complex. Therefore, in the acidic solutions the ethyl groups on the terminal nitrogens of the chelate exert a specific effect leading to ring-opening. Presumably, these complexes are in equilibrium with low concentrations of ions containing the triamine as a bidentate ligand.

Additional evidence for ring-opening, can be seen in the kinetic studies. Spectral changes during the bromide substitution for chloride in  $[\text{Au}(\text{MeEt}_4\text{dien})\text{Cl}]^{2+}$  showed that for a concentration of bromide ion in the range 0.001 M to 0.03 M the substitution product was  $[\text{Au}(\text{MeEt}_4\text{dien})\text{Br}]^{2+}$ . Concentrations greater than 0.03 M  $\text{Br}^-$  showed unwrapping of the ligand to form various substitution products presumably



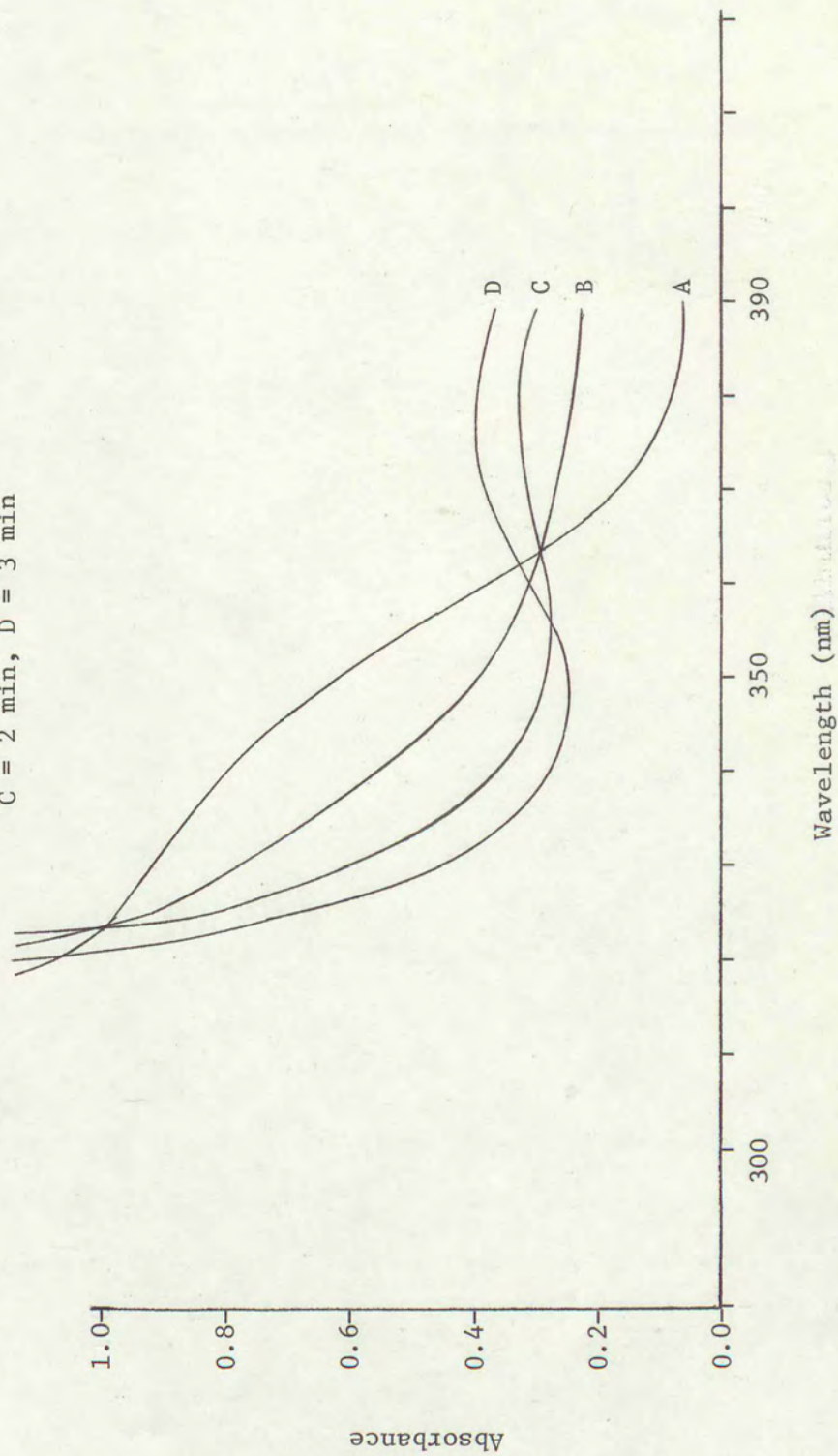
$[\text{AuBr}_4]^-$ ,  $[\text{AuBr}_3\text{OH}]^-$ ,  $[\text{AuBr}_2(\text{OH})_2]^-$ ,  $[\text{AuBr}(\text{OH})_3]^-$  and  $[\text{Au}(\text{OH})_4]^-$ . A typical example of one spectrum obtained is shown in Figure 3.

At 340 nm it was difficult to determine whether decomposition had any effect on the kinetic results since the absorbances of the  $[\text{Au}(\text{MeEt}_4\text{dien})\text{Br}]^{2+}$  and the decomposition products were essentially the same. Therefore, repetitive scans from 320 nm to 390 nm were run on the reaction of  $[\text{Au}(\text{MeEt}_4\text{dien})\text{Cl}]^{2+}$  with 0.05 M  $\text{Br}^-$ . These are shown in Figure 8. As can be seen, the isosbestic points at 323 nm and 367 nm indicate that the formation of  $[\text{Au}(\text{MeEt}_4\text{dien})\text{Br}]^{2+}$  occurred before further unwrapping of the ligand took place. Furthermore, when 0.1 M  $\text{Br}^-$  was added dropwise to the product of the reaction of  $[\text{Au}(\text{MeEt}_4\text{dien})\text{Cl}]^{2+}$  with 0.03 M  $\text{Br}^-$  spectral changes indicated that unwrapping of the ligand took place.

To substantiate the kinetic rate values obtained from the studies at 340 nm kinetic runs with the various concentrations of bromide ion were also carried out at 380 nm. Since the  $[\text{Au}(\text{MeEt}_4\text{dien})\text{Br}]^{2+}$  and the decomposition products have different absorbances at 380 nm, the Guggenheim method was used to calculate rate constants from these runs. The results obtained at 380 nm were essentially the same as those obtained at 340 nm.

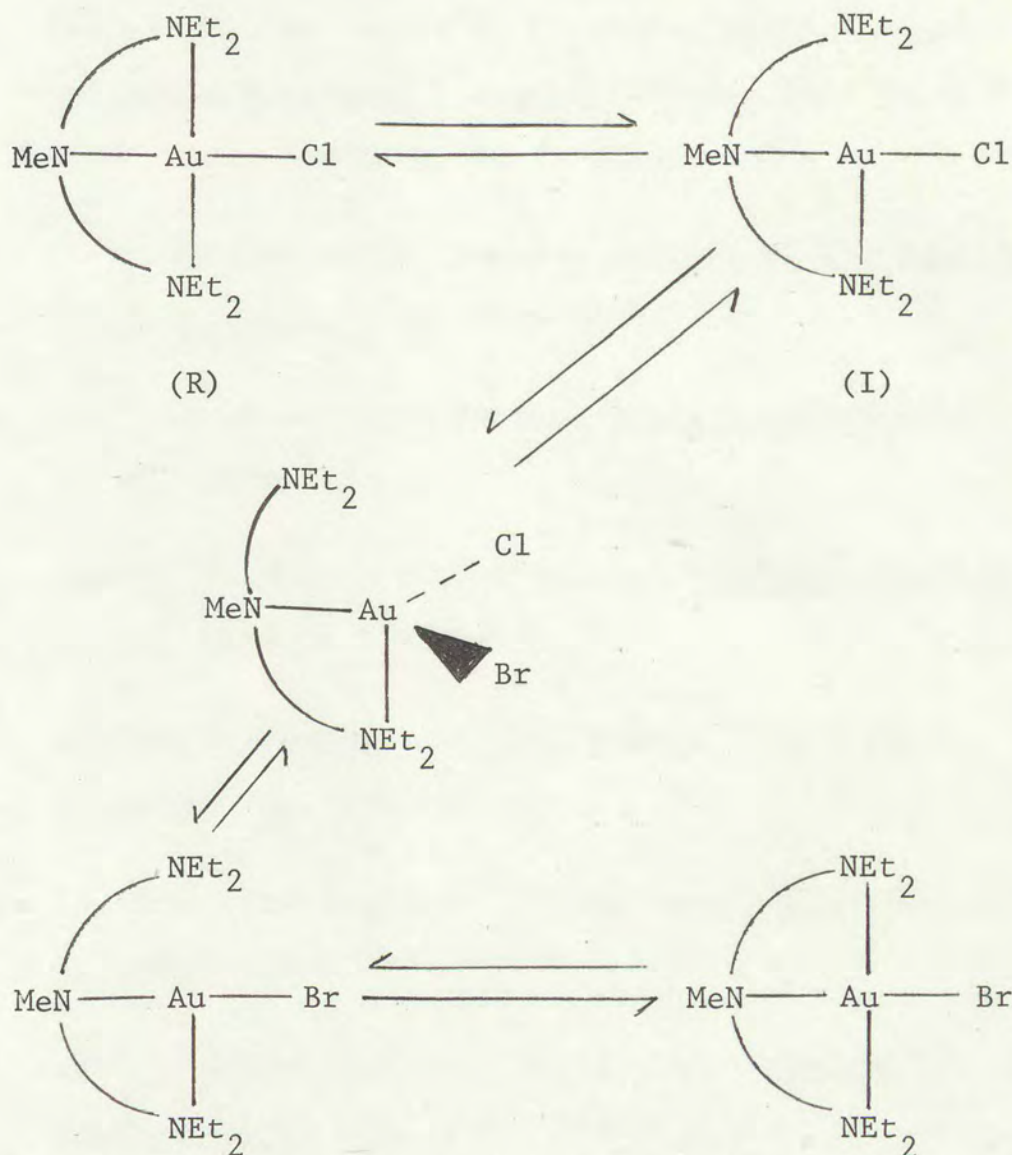
Therefore, the kinetic results for the bromide substitutions for chloride in  $[\text{Au}(\text{MeEt}_4\text{dien})\text{Cl}]^{2+}$  can be rationalized

FIGURE 10  
Reaction of  $[\text{Au}(\text{MeEt}_4\text{dien})\text{Cl}]^{2+}$  with  $0.05 \text{ M Br}^-$   
with respect to time. A = 0 time, B = 1 min,  
C = 2 min, D = 3 min





in terms of the following ring-opening mechanism:



The bidentate species (I) is much more susceptible to bromide ion and solvent attack. Therefore, it is reasonable that bromide ion substitution should occur at a rate greater than observed for  $[\text{Au}(\text{Me}_5\text{dien})\text{Cl}]^{2+}$ . The faster rate observed for  $[\text{Au}(\text{MeEt}_4\text{dien})\text{Cl}]^{2+}$  over  $[\text{Au}(\text{Et}_4\text{dien-H})\text{Cl}]^+$  is presumably the result of the increased charge of the former ion.

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