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# The Preparation and Kinetics of the Sterically Hindered Gold (III) Complex, $[\text{Au}(1,1,4\text{-Me}_3\text{dien})\text{Cl}](\text{PF}_6)_2$

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UNION COLLEGE - GRADUATE STUDIES

Schenectady, New York

THE PREPARATION AND KINETICS  
OF THE STERICALLY HINDERED  
GOLD (III) COMPLEX,  $[\text{Au}(1,1,4 - \text{Me}_3\text{dien})\text{Cl}](\text{PF}_6)_2$

This thesis is submitted to the Committee of Graduate Studies and the Department of Chemistry of Union College, Schenectady, New York, in partial fulfillment of the requirements for the degree of Master of Science in Chemistry.

by James S. Jackowski

By James S. Jackowski

Approved Charles F. Wick  
Thesis Advisor

Approved Baron Stewart  
Committee on Graduate Studies

Date 3 June 1980

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1980

DEDICATION

This thesis is dedicated to my wife Linda and my daughters Stacey and Colleen for their spiritual support of my educational endeavors. A special thanks goes out to my parents for making it all possible.

ACKNOWLEDGEMENT

I am especially grateful to my thesis advisor Dr. Charles Weick for his constant counseling and guidance in completing this work.

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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 <sub>-H</sub>	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 <sub>-H</sub>	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- triamine $(\text{C}_2\text{H}_5)_2\text{NCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{N}(\text{C}_2\text{H}_5)_2$
Et <sub>4</sub> dien <sub>-H</sub>	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 <sub>-H</sub>	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- triamine $(\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$
Me <sub>4</sub> dien <sub>-H</sub>	the conjugate base of Me <sub>4</sub> dien $(\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2^-$

LIST OF ABBREVIATIONS (cont'd)

<u>Abbreviation</u>	<u>Name &amp; Formula</u>
Me <sub>2</sub> dien	1,1 - dimethyldiethylenetriamine $(\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}_2$
Me <sub>2</sub> dien <sub>-H</sub>	the conjugate base of Me <sub>2</sub> dien $(\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{N}^-\text{CH}_2\text{CH}_2\text{NH}_2$
MeEt <sub>4</sub> dien	4- methyl- 1,1,7,7 - tetraethyl- diethylenetriamine $(\text{C}_2\text{H}_5)_2\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{N}(\text{C}_2\text{H}_5)_2$
Me <sub>5</sub> dien	1,1,4,7,7 - pentamethyldiethyle- netriamine $(\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$
1,4,7 - Me <sub>3</sub> dien	1,4,7 - trimethyldiethylenetriamine $(\text{CH}_3)\text{NHCH}_2\text{CH}_2\text{N}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{NH}(\text{CH}_3)$
1,4,7 - Me <sub>3</sub> dien <sub>-H</sub>	the conjugate base of Me <sub>3</sub> dien $(\text{CH}_3)\text{NHCH}_2\text{CH}_2\text{N}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{N}(\text{CH}_3)^-$
1,1,4 - Me <sub>3</sub> dien	1,1,4 - trimethyldiethylenetriamine $(\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{NH}_2$
1,1,4 - Me <sub>3</sub> dien <sub>-H</sub>	the conjugate base of 1,1,4 - Me <sub>3</sub> dien $(\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{NH}^-$

### ABSTRACT

The N-alkylated gold (III) complex  $[\text{Au}(1,1,4\text{-Me}_3\text{dien})\text{Cl}](\text{PF}_6)_2$  (where 1,1,4-Me<sub>3</sub>dien is  $\text{CH}_3\text{CH}_3\text{NCH}_2\text{CH}_2\text{NCH}_3\text{CH}_2\text{CH}_2\text{NH}_2$ ) has been synthesized. The rate constant ( $k_{\text{Br}}$ ) for the monobromination (nucleophilic  $\text{Br}^-$  substitution) reaction was determined to be  $132 \text{ l mole}^{-1}\text{sec}^{-1}$ . The implications of such a  $k_{\text{Br}}$  value relative to similar non N-alkylated and other N-alkylated complexes are discussed.

The enthalpy of activation ( $\Delta H^\ddagger$ ) and the entropy of activation ( $\Delta S^\ddagger$ ) for the monobromination reaction were determined to be  $9.4 \text{ kcal mole}^{-1}$  and  $-24 \text{ cal deg}^{-1} \text{ mole}^{-1}$  respectively. The ( $\Delta S^\ddagger$ ) obtained is directly related to the steric hindrance of the three methyl groups on the ligand nitrogen atoms.

## INTRODUCTION

"Square-planar metal complexes generally undergo substitution at rates that are reagent dependent. In particular such dependence has been observed for substitution by monodentate ligands in diethylenetriamine complexes of Pt(II),<sup>1,2</sup> Pd(II),<sup>2,3</sup> and Au(III)<sup>4</sup>. However, certain N-alkyl-substituted diethylenetriamine complexes of these metals react at rates that are almost independent of the concentration of the entering reagent.<sup>5-8</sup> Such complexes have alkyl groups occupying regions above and below the plane of the ion which are thought to inhibit reagent attack."<sup>9</sup>

The steric hindrance effects of the above mentioned N-alkyl groups seem to influence substitution reaction rates more than the concentration of the incoming ligand.

Certain square planar Au(III) complexes, which are isoelectronic and isostructural with Pt(II) complexes exhibit halide substitution reaction rates that are dependent on the extent of N-alkylation. For example, the substitution of Br<sup>-</sup> for Cl<sup>-</sup> in [Au(dien)Cl]<sup>+2</sup> and [Au(dien<sub>-H</sub>)Cl]<sup>+</sup> show a strong rate dependency on the concentration of Br<sup>-</sup>.<sup>4</sup> However, [Au(Me<sub>5</sub>dien)Cl]<sup>+2</sup>, [Au(Et<sub>4</sub>dien<sub>-H</sub>)Cl]<sup>+</sup> and [Au(MeEt<sub>4</sub>dien)Cl]<sup>+2</sup> undergo Br<sup>-</sup> substitution at rates which are slightly dependent on the concentration of bromide ion.<sup>10</sup>

The intent of this work was to synthesize the Au(III) complex  $[\text{Au}(1,1,4 - \text{Me}_3\text{dien})\text{Cl}] (\text{PF}_6)_2$  and to study the kinetics of its monobromo-substitution reaction.

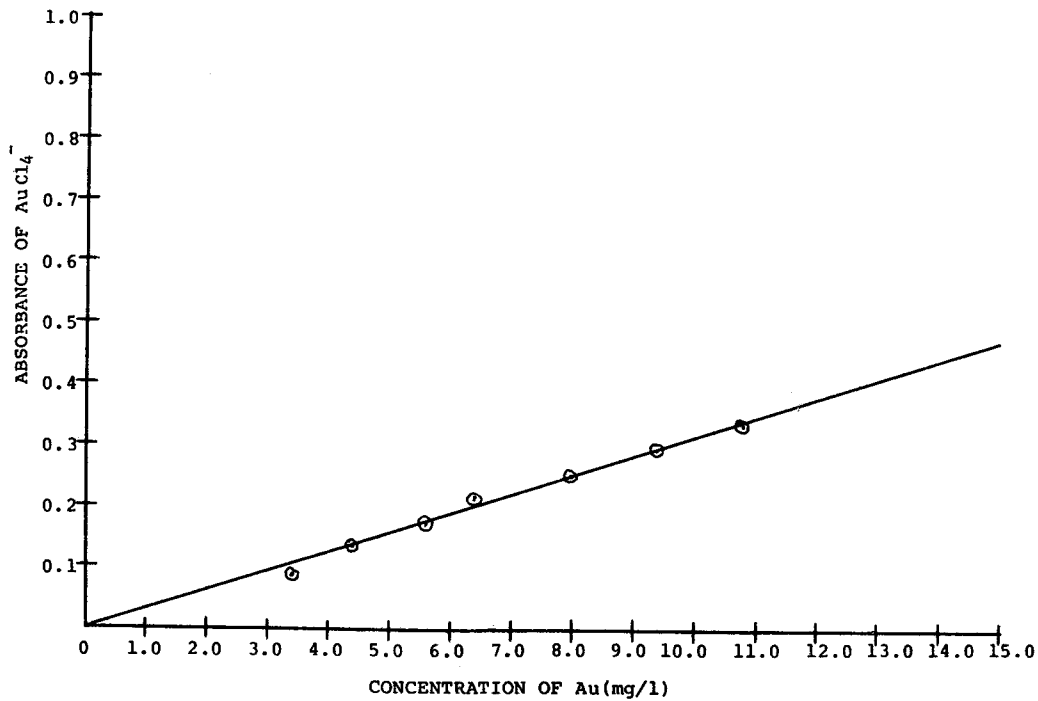
### EXPERIMENTAL

Materials: The gold powder (purity 99.9%) and ammonium hexafluorophosphate (purity 96%) were obtained from Alfa Inorganics. The 1,1,4 - trimethyldiethylenetriamine was purchased from Ames Laboratories and used without further purification. All other chemicals used were reagent grade.

Analyses: A standard curve (Beer's Law Plot) of Absorbance versus Concentration Au was prepared for use in the analysis of all synthesis products for Au content. (See Figure I) All analyses were performed in at least triplicate. The pure gold samples used in preparation of the curve and the synthesis product samples were treated in the same manner. Samples of 4-10 mg were dissolved in 5-6 ml of aqua regia in 10 ml beakers and covered. The resulting solutions were placed on a hot plate and treated for removal of nitrate ion. This was accomplished by gently boiling each solution down to 2-3 ml three to four times followed by the dropwise addition of 2-3 ml concentrated HCl after each volume reduction until all nitrate ion was removed.

When pre-treatment was complete the solutions were each evaporated to 2-3 ml volumes and removed from the hot plate. The yellow-orange  $\text{HAuCl}_4 \cdot \text{XH}_2\text{O}$  crystalline pastes that formed were dissolved in 1.0 M  $\text{NH}_4\text{Cl}$  and the solutions transferred to 100 ml volumetric flasks and diluted to volume with 1.0N HCl.

FIGURE I



The absorbance of each solution was measured at 313 nm on a Beckman DU Spectrophotomer. Removal of nitrate ion is essential since at 313 nm the presence of nitrate ion shifts the characteristic absorption peak of  $\text{AuCl}_4^-$  significantly from 313 nm. Absorption scans of the solutions from 270-350 nm on a Cary 118 spectrophotometer confirmed that all nitrate ion had been removed. The Au content of each sample was then determined using the standard curve in Figure I. The chloride content of each sample was determined by titration with mercuric nitrate ( $\text{Hg}(\text{NO}_3)_2$ ) using diphenyl carbazide as an indicator.<sup>11</sup>

Synthesis of Complex:  $\text{HAuCl}_4 \cdot x\text{H}_2\text{O}$  (Prepared as described in the preceding section on analysis) containing 1.0 gram Au (5 mmoles) was dissolved in 100 ml of distilled  $\text{H}_2\text{O}$  with stirring and cooling to 5°C. Five grams of LiCl were added to the solution to prevent hydrolysis and the temperature was reduced to 0°C. To this solution was added, dropwise from a buret, 30.5 ml of 0.249 mmole/ml of 1,1,4-trimethyldiethylenetriamine. The reaction mixture was constantly cooled and stirred by a combination cooling plate-magnetic stirrer device. The addition of the chelating agent was done slowly enough to prevent exceeding a pH of 5.2 thereby preventing hydrolysis of the reaction mixture. After the addition of 1,1,4- $\text{Me}_3\text{dien}$  was complete the mixture was stirred for an additional 15 minutes. Approximately



5.5 ml of 1M LiOH were then added to the reaction vessel. Again the pH of the reaction contents was not allowed to exceed 5.2. After the addition of LiOH was complete the solution was filtered under vacuum and the yellow-beige filtrate saved for recovery of the complex. This filtrate was transferred to a 250 ml round bottom flask and mixed with 4.0g of ammonium hexafluorophosphate. This mixture was frozen to liquid N<sub>2</sub> temperature and then placed on a rotary evaporator for removal of excess solvent. During removal of solvent light brown crystals appeared. When the volume in the flask was approximately 10 ml the contents of the flask were filtered under vacuum. A dark beige precipitate was collected, washed with ether and saved for recrystallization. The dark beige crystals were dissolved in 0.001M HCl. The crystals did not appear to dissolve completely so acetone was added dropwise until all crystals went into solution. This solution was frozen to an ice and then placed on a rotary evaporator for removal of excess solvent. When volume was reduced to 10 ml the solution was filtered and the light beige crystals collected were washed with ether and saved for further characterization. Based on a starting amount of 1.0g Au the yield for this synthesis was 45%. Calculated for [Au(1,1,4-Me<sub>3</sub>dien)Cl](PF<sub>6</sub>)<sub>2</sub>; Au 29.50%, Cl 5.31%. Found: Au 28.18%, Cl 7.47%.

Spectrophotometric Studies: Absorption data in the visible and ultraviolet energy ranges were obtained with a Cary 118 spectrophotometer.

Kinetic Studies: The kinetics of the following nucleophilic substitution reaction were studied at 25°C:

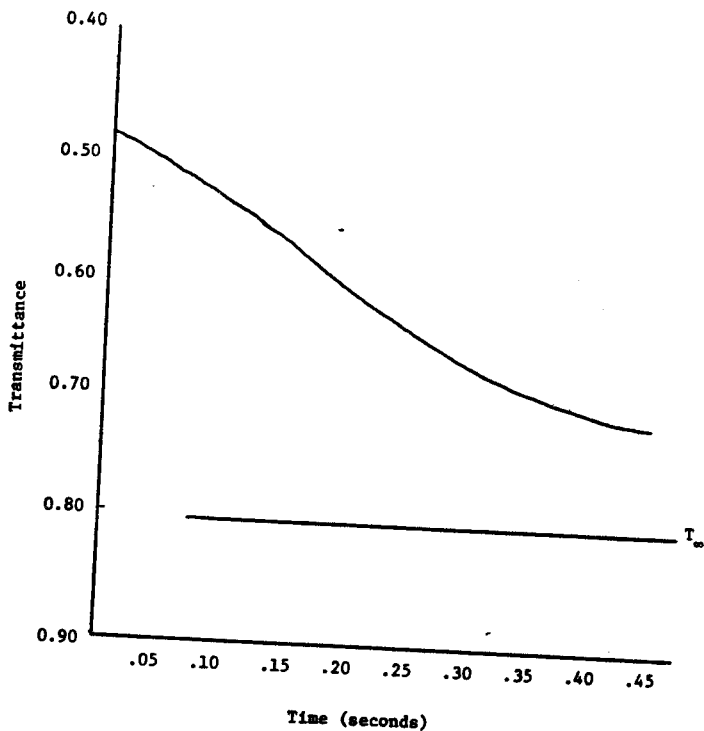
$$[\text{Au}(1,1,4\text{-Me}_3\text{dien})\text{Cl}]^{+2} + \text{Br}^- \xrightarrow[\text{pH } 1.3]{\text{H}^+} [\text{Au}(1,1,4\text{-Me}_3\text{dien})\text{Br}]^{+2} + \text{Cl}^- \quad (R_1)$$

Preliminary spectroscopic studies indicated that this reaction should be studied at low pH to prevent the hydrolysis of terminal H atoms on the ligand and/or replacement of  $\text{Cl}^-$  by  $\text{OH}^-$ .

In this study volumes of  $8.27 \times 10^{-4} \text{M}$   $[\text{Au}(1,1,4\text{-Me}_3\text{dien})\text{Cl}](\text{PF}_6)_2$  in  $0.1\text{M HClO}_4$  were reacted with equal volumes of  $0.02, 0.04, 0.06, 0.08$  and  $0.10\text{M NaBr}$  in  $\text{NaClO}_4$ . For each reaction the ionic strength ( $\mu$ ) was  $0.15$  after mixing and pH was  $1.3$ .

An Aminco Morrow Stopped Flow Spectrophotometer equipped with a monochromator from a Beckman DU Spectrophotometer was used to follow the progress of these reactions at  $315 \text{ nm}$ . The output of the photomultiplier tube was coupled through an Aminco-Morrow High Performance Kinetic Photometer to a Tektronix 3A1 Storage Oscilloscope. The trace of Percent Transmittance versus Time for each reaction was photographed with a Polaroid Oscilloscope Camera. A typical trace of Transmittance as a function of Time is shown in Figure II.

FIGURE II



Typical trace of Transmittance vs. Time for reaction of  $8.27 \times 10^{-4} M$  complex in  $0.1 M HClO_4$  with equal volumes of 0.02, 0.04, 0.06, 0.08 and 0.10M Na Br.  $\mu=0.15$ ,  $pH=1.3$ ,  $T=25^\circ C$ .

The transmittance readings were converted to absorbance values and a plot of  $\ln[(A_t - A_\infty)/A_o - A_\infty]$  vs. time produced a straight line for each of the five reactions. The straight line obtained in each case fits the equation:

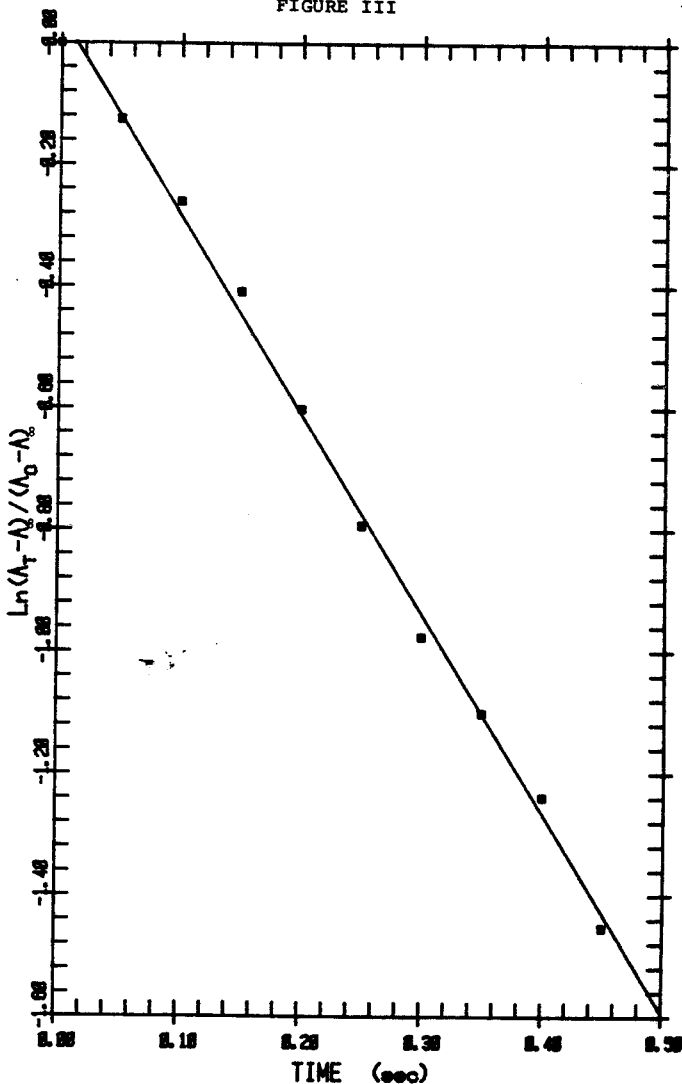
$$k_{\text{obs}} t = -\ln \left[ \frac{(A_t - A_\infty)}{(A_o - A_\infty)} \right]$$

where  $k_{\text{obs}}$  = pseudo first order rate constant reaction  $R_1$ .

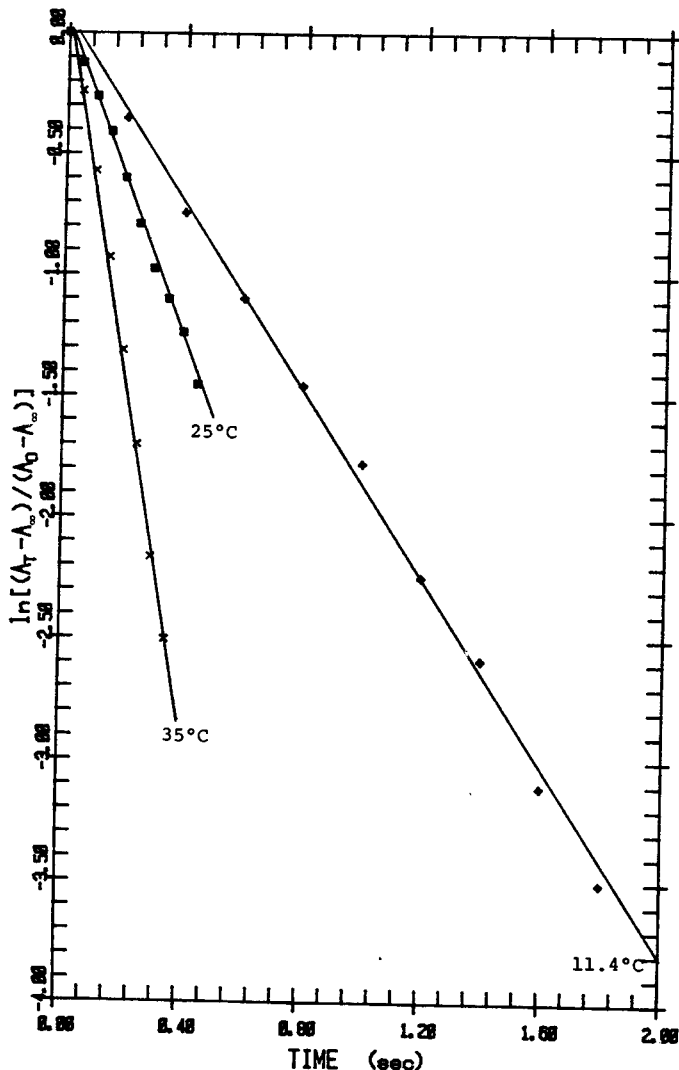
A typical plot is shown in Figure III.

Another study was undertaken to determine the enthalpy of activation ( $\Delta H^\ddagger$ ) and the entropy of activation ( $\Delta S^\ddagger$ ) for reaction  $R_1$ ;  $[\text{Au}(1,1,4\text{-Me}_3\text{dien})\text{Cl}]^{+2} + \text{Br}^- \xrightarrow[\text{pH } 1.3]{\text{H}^+} [\text{Au}(1,1,4\text{-Me}_3\text{dien})\text{Br}]^{+2} + \text{Cl}^-$ . The  $k_{\text{observed}}$  values for this reaction were determined at 11.4°C, 25°C (already noted in text) and 35°C by reacting equal volumes of solutions of (0.06M NaBr + 0.14M NaClO<sub>4</sub>) and  $8.27 \times 10^{-4}$ M complex (55.2 mg complex/100 ml 0.1N HClO<sub>4</sub>). After mixing  $\mu=0.15$ , and pH=1.3. Plots of  $\ln[(A_t - A_\infty)/A_o - A_\infty]$  vs. time for these reactions are represented in Figure IV.

**Results:** The pseudo first order rate constants determined from graphs such as that in Figure III for reaction  $R_1$  are presented in Table I. Each value represents the average of four or more measurements and the standard deviation of the mean is listed.



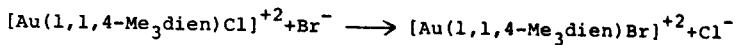
Plot of  $\ln[(A_T - A_\infty)/(A_0 - A_\infty)]$  vs. Time for reaction of  $8.27 \times 10^{-4} M$  complex in  $0.1 M HClO_4$  with equal volumes of 0.02, 0.04, 0.06, 0.08 and 0.10M NaBr in  $NaClO_4$ .  $\mu=0.15$ ,  $pH=1.3$ ,  $T=25^\circ C$



Plot of  $\ln[(A_T - A_\infty)/(A_0 - A_\infty)]$  vs. Time for the reaction of equal volumes of (0.06M NaBr + 0.14M NaClO<sub>4</sub>) + 55.2mg complex/100ml 0.1M HClO<sub>4</sub>, at 11.4°C, 25°C, and 35°C, pH=1.3,  $\mu=0.15$ .

TABLE I

Pseudo First Order Rate Constants For the Reaction:



$T = 25^\circ\text{C}$

$\mu = 0.15$  with  $\text{NaClO}_4$

$\text{pH} = 1.3$

$\text{Br}^-$ Concentration (Mole $\ell^{-1}$ )	$\bar{k}_{\text{observed}}$ ( $\text{sec}^{-1}$ )
0.05	$3.51 \pm 0.24$
0.04	$5.17 \pm 0.54$
0.03	$3.39 \pm 0.18$
0.02	$2.55 \pm 0.03$
0.01	$1.03 \pm 0.11$

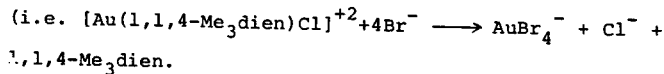
Figure V is a plot of  $k_{\text{obs}}$  vs. concentration of  $\text{Br}^-$ . This straight line fits the equation:

$$k_{\text{obs}} = k_{\text{Br}}[\text{Br}^-] + k_{\text{s}}$$

where  $k_{\text{Br}}$  represents the overall rate constant for the bromide path reaction and  $k_{\text{s}}$  is the rate constant for the solvent path reaction. From the slope it was determined that  $k_{\text{Br}}$  is  $132 \text{ l mole}^{-1} \text{ sec}^{-1}$  and  $k_{\text{s}} = -0.28 \text{ sec}^{-1}$  which is essentially negligible. The fact that a plot of  $k_{\text{obs}}$  vs.  $[\text{Br}^-]$  produced a straight line shows that the nucleophilic substitution reaction ( $R_1$ ) has a first order dependence on  $\text{Br}^-$  concentration while the reaction is second order overall according to the expression:

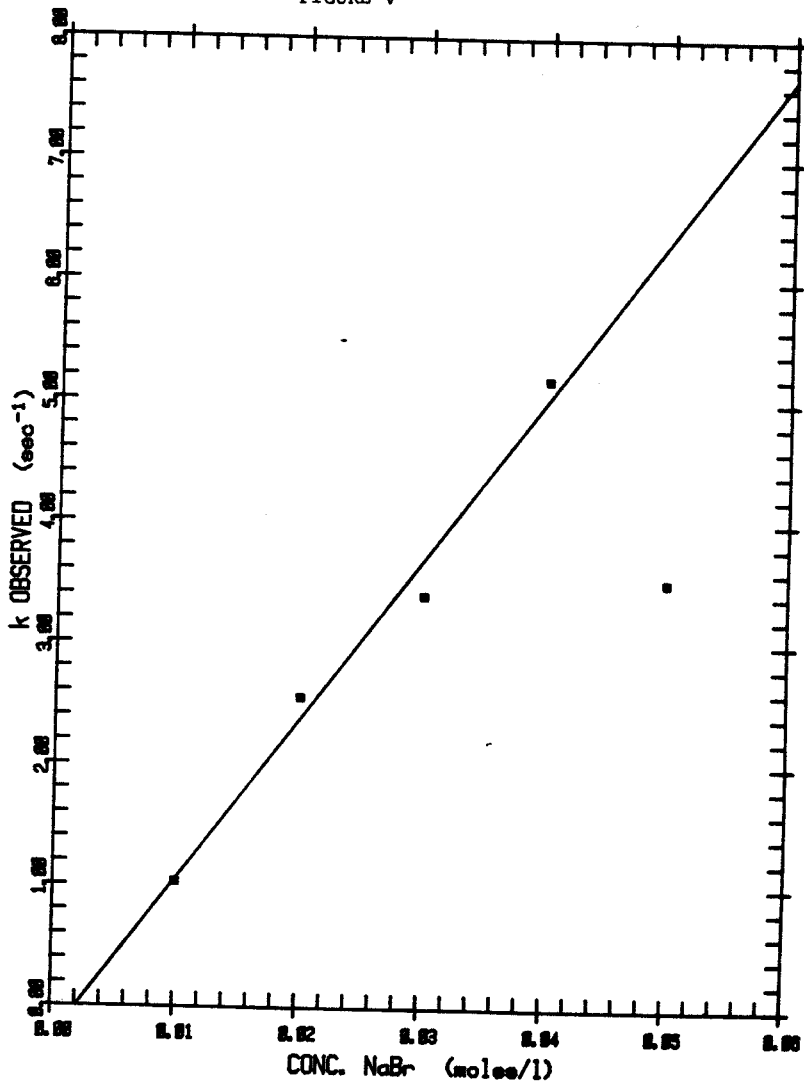
$$\frac{d[\text{Au}(1,1,4\text{-Me}_3\text{dien})\text{Br}]^{+2}}{dt} = (k_{\text{Br}}[\text{Br}^-] + k_{\text{s}})[\text{Au}(1,1,4\text{-Me}_3\text{dien})\text{Cl}]^{+2}$$

In Figure V it is obvious that the data point at  $[\text{NaBr}] = 0.05\text{M}$  does not coincide with the other four data points. This could be due to a malfunction of the Stopped-Flow Spectrophotometer or the effects of a subsequent reaction.



As stated earlier values of  $k_{\text{observed}}$  for reaction  $R_1$  at  $11.4^\circ\text{C}$ ,  $25^\circ\text{C}$  and  $35^\circ\text{C}$  were determined from the slopes of the plots in Figure IV. Table II shows the results obtained.

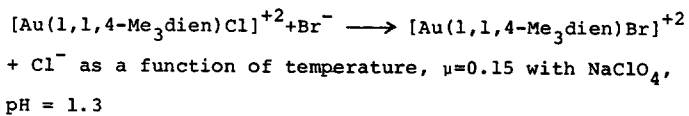




Plot of  $k_{obs}$  vs. Time for the reaction of  $8.27 \times 10^{-4} M$  complex in  $0.1M HClO_4$  with equal volumes of 0.02, 0.04, 0.06, 0.08 and 0.10M NaBr.  $\mu=0.15$ ,  $pH=1.3$ ,  $T=25^\circ C$ .

TABLE II

Pseudo first order rate constants for the reaction:



T°C	$k_{\text{obs}}$ (sec <sup>-1</sup> )	1/T°K
11.4	1.95	$3.514 \times 10^{-3}$
25	3.39	$3.35 \times 10^{-3}$
35	7.69	$3.25 \times 10^{-3}$

Figure VI is a graphical representation of  $\ln(k_{\text{obs}}/T)$  vs.  $1/T^{\circ}\text{K}$ . The values of the slope and y intercept of this line were used to calculate the enthalpy of activation ( $\Delta H^{\ddagger}$ ) and the entropy of activation ( $\Delta S^{\ddagger}$ ) for reaction  $R_1$  through use of the equation;

$$k_{\text{obs}} = (kT/h)e^{\Delta S^{\ddagger}/R} \cdot e^{-\Delta H^{\ddagger}/RT} \quad 12$$

$k_{\text{obs}}$  = pseudo first order rate constant ( $\text{sec}^{-1}$ )

$k$  = Boltzman constant,  $1.38 \times 10^{-16}$  erg deg $^{-1}$

$T$  =  $^{\circ}\text{Kelvin}$ , 298.15

$h$  = Planck's constant,  $6.63 \times 10^{-27}$  erg sec

$\Delta H^{\ddagger}$  = Enthalpy of activation

$\Delta S^{\ddagger}$  = Entropy of activation

$R$  = Gas constant,  $1.987$  cal $^{\circ}\text{K}$ mole $^{-1}$

Upon rearranging;

$$\ln(k_{\text{obs}}/T) = \ln(k/he^{\Delta S^{\ddagger}/R}) - \frac{\Delta H^{\ddagger}}{RT}$$

From graph:

$$\text{slope} = -4.717 \times 10^3$$

$$\text{y intercept} = 11.52$$

Solving for  $\Delta H^{\ddagger}$ ;

$$\text{Slope} = -\Delta H^{\ddagger}/R$$

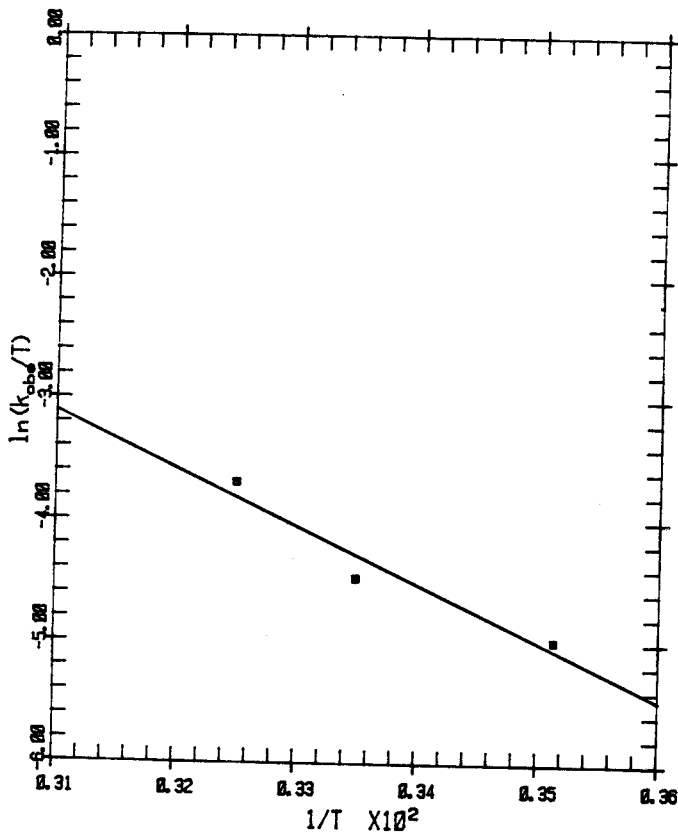
$$[\Delta H^{\ddagger} = 9.37 \text{ kcal mole}^{-1}]$$

Solving for  $\Delta S^{\ddagger}$ ;

$$\text{y intercept} - \ln(k/h) = \Delta S^{\ddagger}/R$$

$$[\Delta S^{\ddagger} = -24.32 \text{ cal deg}^{-1} \text{mole}^{-1}]$$

FIGURE VI



Plot of  $\ln(k_{\text{obs}}/T)$  vs.  $1/T^\circ\text{K}$  for reaction of equal volumes of (0.06M NaBr + 0.14M NaClO<sub>4</sub>) + 55.2mg complex/100 ml 0.1M HClO<sub>4</sub> at 284.5°K, 298.15°K and 308.15°K, pH=1.3,  $\mu=0.15$ .

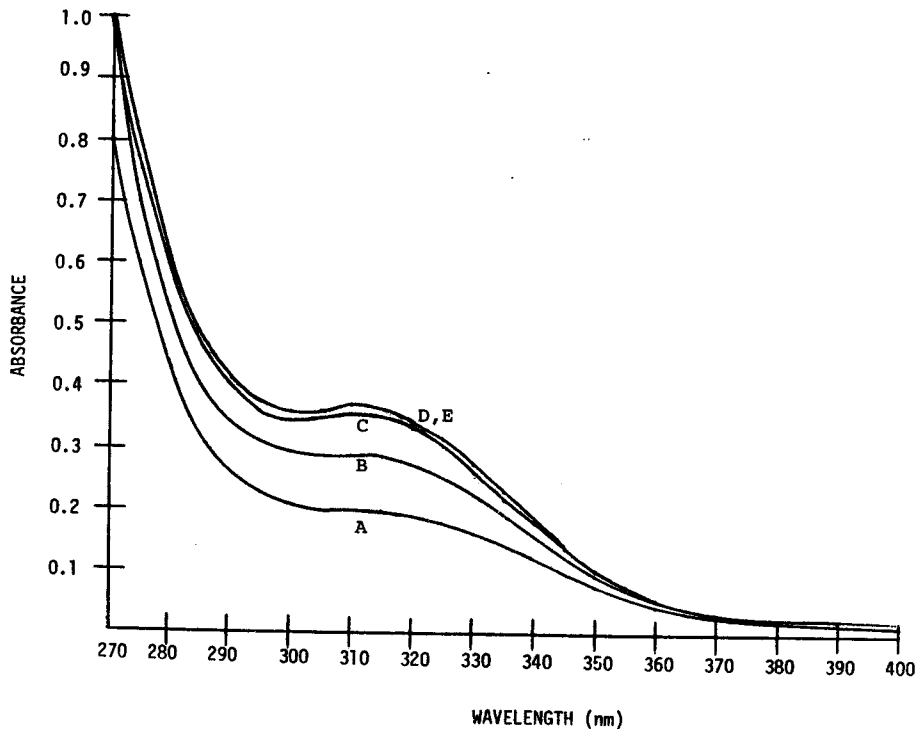
This large negative  $\Delta S^\ddagger$  value is much more negative than the  $\Delta S^\ddagger$  of  $-4 \text{ cal deg}^{-1} \text{ mole}^{-1}$  determined for the monobromination of the non-N-alkylated  $[\text{Au}(\text{dien})\text{Cl}]^{+2}$  complex by Baddley and Basolo under similar conditions of  $\text{pH}=2.3$  and  $\mu=0.2$ .<sup>4</sup> The result is very similar to the  $\Delta S^\ddagger$  of  $-24 \text{ cal deg}^{-1} \text{ mole}^{-1}$  determined by Weick and Basolo for the reaction:  $[\text{Au}(\text{Et}_4\text{dien})\text{Cl}^*]^{+2} + \text{Cl}^- \longrightarrow [\text{Au}(\text{Et}_4\text{dien})\text{Cl}]^{+2} + \text{*Cl}^-$  in their isotopic exchange studies.<sup>7</sup> Such a large negative  $\Delta S^\ddagger$  for the 1,1,4 complex is indicative of the more highly ordered transition state and slower reaction rate ( $k_{\text{BR}}$ ) caused by the steric hindrance of the three methyl groups in the N-alkylated complex relative to the non-N-alkylated complex.

Discussion: Annibale, Natile and Cattalino have reported that the complexes  $[\text{Au}(\text{dien})\text{Cl}]^{+2}$  and  $[\text{Au}(4\text{-Medien})\text{Cl}]^{+2}$  convert to dichloro, bidentate forms in HCl solution below  $\text{pH}=3$ .<sup>13</sup> To determine if this type of reaction occurs with  $[\text{Au}(1,1,4\text{-Me}_3\text{dien})\text{Cl}]^{+2}$  the following study was carried out.

A  $55 \text{ mg}$  ( $8.24 \times 10^{-2}$  mmoles) sample of complex was dissolved in 60 ml of de-ionized  $\text{H}_2\text{O}$ , adjusted to  $\text{pH} 10$  with  $1 \text{M}$  NaOH and passed through an anion exchange column in the  $\text{OH}^-$  form to convert all complex to  $[\text{Au}(1,1,4\text{-Me}_3\text{dien-H})\text{OH}]^{+2}$ . Next the sample was diluted to 200 ml and the pH readjusted to 10. Successive absorption spectra were taken with a Cary 118

spectrophotometer in the range 270 nm - 400 nm at 25°C as the pH was reduced from 10 to 2.3 by the dropwise addition of 0.1M HClO<sub>4</sub>. When the pH of the stirred solution reached 2.3 the dropwise addition of 0.0141M NaCl was initiated. See Figure VII. Curves A,B,C,D and E are curves obtained after the addition of 0, 4.23x10<sup>-2</sup>, 6.35x10<sup>-2</sup>, 7.75x10<sup>-2</sup> and 8.25x10<sup>-2</sup> mmoles Cl<sup>-</sup> respectively. Curve A represents the spectra of [Au(1,1,4-Me<sub>3</sub>dien)H<sub>2</sub>O]<sup>+3</sup>. Curve B is the curve obtained as [Au(1,1,4-Me<sub>3</sub>dien)H<sub>2</sub>O]<sup>+3</sup> is converted to [Au(1,1,4-Me<sub>3</sub>dien)Cl]<sup>+2</sup>. That no isosbestic points are noticed between curves A,B,C,D, and E indicates that the molar absorptivity of the chloro species is much greater than that of the aquo species. Note that curves D and E corresponding to the addition of 7.75x10<sup>-2</sup> and 8.25x10<sup>-2</sup> mmoles Cl<sup>-</sup> coincide which suggests that the reaction of Cl<sup>-</sup> with complex ion is complete. As more Cl<sup>-</sup> was added to the reaction solution no further absorption changes occurred indicating that reaction was complete with the addition of 8.25x10<sup>-2</sup> mmoles Cl<sup>-</sup>. These results indicate a reaction product with a 1:1 Cl<sup>-</sup> to Au ratio. (i.e. [Au(1,1,4-Me<sub>3</sub>dien)Cl]<sup>+2</sup>) If at this point a bidentate species were present then two coordination sites would be available to the Cl<sup>-</sup>. Under such conditions mixtures of diaquo, aquochloro, and dichloro forms would be present and further reaction or addition of more chloride ion could be expected. Similar results were obtained when 0.01M NaBr was used instead of NaCl.

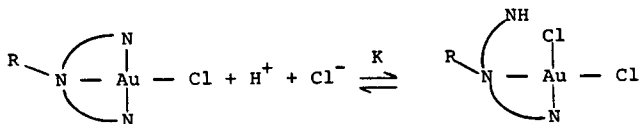
FIGURE VII



Curves A, B, C, D, E are the curves obtained after reacting a solution containing  $8.23 \times 10^{-2}$  mmoles of complex as  $[\text{Au}(1,1,4\text{-Me}_3\text{dien})\text{H}_2\text{O}]^{+3}$  with 0,  $4.23 \times 10^{-2}$ ,  $6.35 \times 10^{-2}$ ,  $7.75 \times 10^{-2}$ , and  $8.25 \times 10^{-2}$  mmoles  $\text{Cl}^-$  respectively.

These results do not agree with those of Annibale, Natile and Cattalino who report a reaction product with a Cl to Au ratio greater than 1:1 for such a reaction under similar conditions.<sup>13</sup>

As shown in Table III  $k_{Br}$  rates for  $[Au(1,4,7-Me_3dien)Cl]^+2$  and  $[Au(1,1,4-Me_3dien)Cl]^+2$  are slower than for  $[Au(dien)Cl]^+2$  and faster than for  $[Au(1,4,7-Et_3dien)Cl]^+2$ . This suggests that alkyl groups sterically hinder  $Br^-$  attack. It seems that methylation of the central nitrogen probably hinders  $Br^-$  attack to a much greater extent than indicated by models. No concrete explanation for this is currently available but results of Annibale, Natile and Cattalini support this idea.<sup>13</sup> They report equilibrium constants for reactions of the type:



For the reaction of  $[Au(dien)Cl]^+2$   $K=10^4$  but for  $[Au(4-Medien)Cl]^+2$  a value of  $K=3 \times 10^3$  was found.<sup>13</sup> This information suggests that the methyl group on the central nitrogen makes ligand detachment and entry of a second halide ion less favored by a factor of approximately one-third.

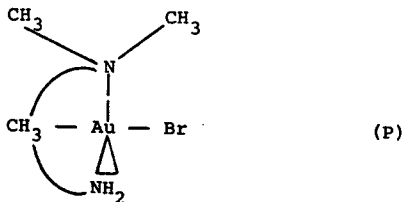
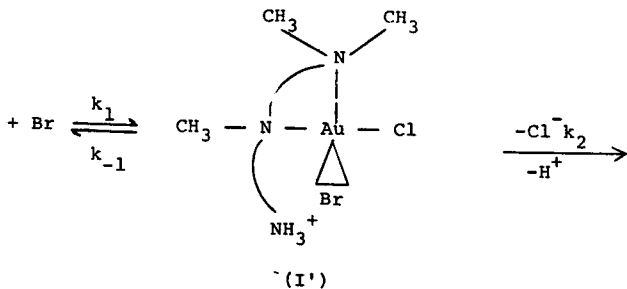
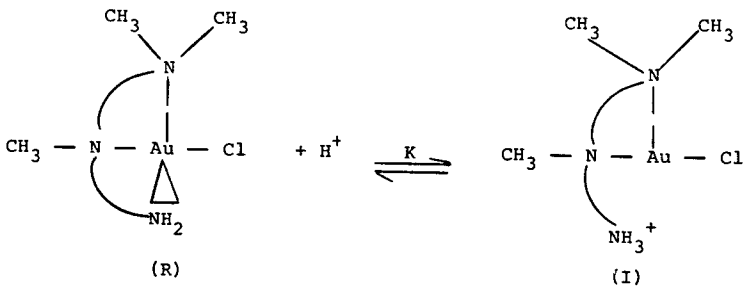


TABLE III

Rate constants for the reaction:  
 $[\text{Au}(\text{amine})\text{Cl}]^{+2} + \text{Br}^- \longrightarrow [\text{Au}(\text{amine})\text{Br}]^{+2} + \text{Cl}^-$   
 at 25°C in strong acid.

<u>Complex</u>	<u>pH</u>	<u><math>k_{\phi}</math></u>	<u><math>k_{\text{Br}} \text{ l mole}^{-1} \text{ sec}^{-1}</math></u>	<u>Reference</u>
$[\text{Au}(1,1,4\text{-Me}_3\text{dien})\text{Cl}]^{+2}$	1.0	-0.28	132	This work
$[\text{Au}(1,4,7\text{-Me}_3\text{dien})\text{Cl}]^{+2}$	1.0	0.2	170	10
$[\text{Au}(\text{dien})\text{Cl}]^{+2}$	2.0	0.0	380	4
$[\text{Au}(1,4,7\text{-Et}_3\text{dien})\text{Cl}]^{+2}$	1.0	0.33	36	14

Mechanism: From the first order dependence on  $[\text{Br}^-]$  determined for the monobromination reaction ( $R_1$ ) the following mechanism is proposed:



Based on a steady state approximation the corresponding rate expression for this reaction is  $k_{Br} = \frac{K k_1 k_2 [H^+]}{k_{-1} + k_2}$

derived as follows:

$$\frac{d[I']}{dt} = 0 = k_1 [I][Br^-] - k_{-1} [I'] - k_2 [I']$$

$$k_1 [I][Br^-] = (k_{-1} + k_2) [I']$$

$$[I'] = \frac{k_1 [I][Br^-]}{k_{-1} + k_2}$$

$$K = \frac{[I]}{[R][H^+]}$$

$$[I] = K[R][H^+]$$

$$[I'] = \frac{k_1 K [R][H^+][Br^-]}{k_{-1} + k_2}$$

$$\frac{dP}{dt} = k_2 [I']$$

$$\frac{dP}{dt} = \frac{k_1 k_2 K [R][H^+][Br^-]}{k_{-1} + k_2}$$

Therefore:

$$K \frac{k_1 k_2 [Br^-][H^+][R]}{k_{-1} + k_2} = k_{Br} [Br^-][R]$$

$$k_{Br} = \frac{K k_1 k_2 [H^+]}{k_{-1} + k_2}$$

The mechanism proposed is consistent with the mechanism proposed by Golden for the monobromination of [Au(1,4,7-Me<sub>3</sub>dien)Cl]<sup>2+</sup>.<sup>10</sup> Golden proposed a dangling ligand end intermediate

species for formation of the monobromo species and the complete conversion of  $[\text{Au}(1,4,7\text{-Me}_3\text{dien})\text{Cl}]^{2+}$  to  $\text{AuBr}_4^-$  at pH 1 in the presence of excess  $\text{Cl}^-$ . 10

A di-halo intermediate similar to (I') is also supported by Annibale, Natile and Cattalani for the nucleophilic substitution reaction of  $[\text{Au}(4\text{-Medien})\text{Cl}]^{+2}$ ,  $\xrightarrow{[\text{H}^+][\text{Cl}^-]}$   $\text{AuCl}_4^-$ . 13

SUPPLEMENT

Figure VIII represents the ultraviolet spectra of  $[\text{Au}(1,1,4\text{-Me}_3\text{dien})\text{Cl}]^{2+}$  and  $[\text{Au}(1,1,4\text{-Me}_3\text{dien})\text{Br}]^{2+}$  in acid solution at  $\text{pH} = 2.3$ . The large difference between the absorbance of each species at  $\lambda = 315\text{nm}$  indicates that  $315\text{nm}$  is an optimum wavelength for following reaction

$R_1$ :

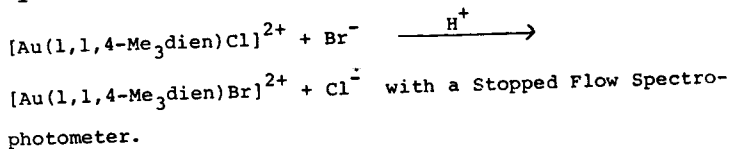
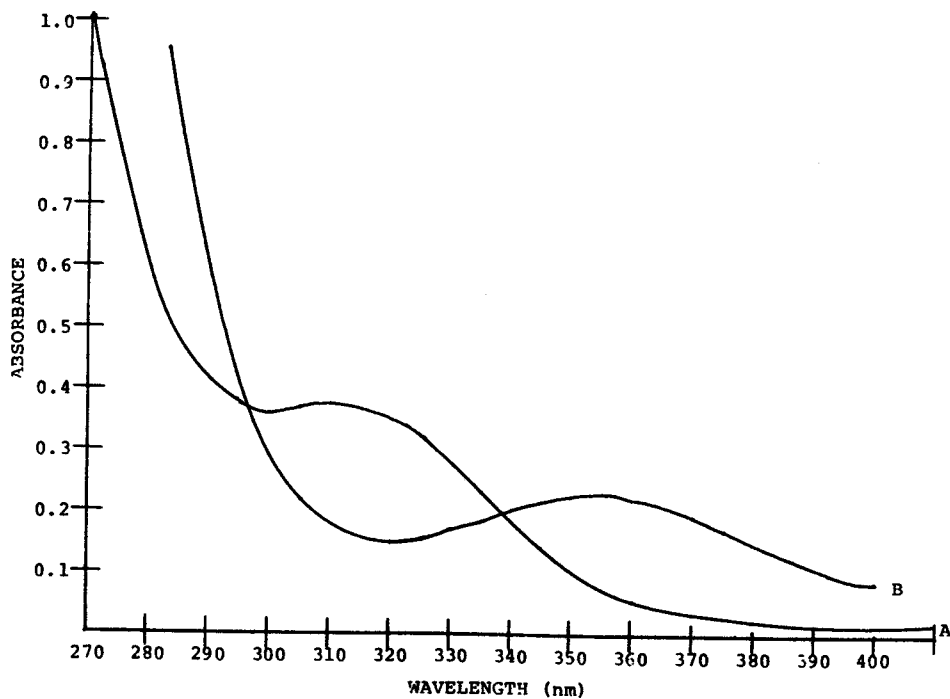


FIGURE VIII



Curves A and B are the spectra of  $[\text{Au}(\text{1,1,4-Me}_3\text{dien})\text{Cl}]^{2+}$  and  $[\text{Au}(\text{1,1,4-Me}_3\text{dien})\text{Br}]^{2+}$  respectively in acid solution with pH adjusted to 2.3 with 1.0M  $\text{HClO}_4$ .

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