

Cis-Trans Isomerization of Dimeric  $[\text{Me}_2\text{Al}(\mu\text{-NH}^t\text{Bu})_2]$ 

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The *trans* (**2a**)-*cis* (**2b**) isomerization of  $[\text{Me}_2\text{Al}(\mu\text{-NH}^t\text{Bu})_2]$  (**2**) has been studied by  $^1\text{H}$  NMR spectroscopy. The equilibrium has been observed to follow reversible first order kinetics with  $\Delta H^\circ = 2.22 \pm 0.07 \text{ kJmol}^{-1}$  and  $\Delta S^\circ = 2.85 \pm 0.07 \text{ JK}^{-1}\text{mol}^{-1}$ . The activation parameters for the conversion **2a**  $\rightarrow$  **2b** are  $\Delta H_1^\ddagger = 49.7 \pm 2.3 \text{ kJmol}^{-1}$  and  $\Delta S_1^\ddagger = -126.3 \pm 0.2 \text{ JK}^{-1}\text{mol}^{-1}$  and for the reverse reaction **2b**  $\rightarrow$  **2a** are  $\Delta H_{-1}^\ddagger = 47.5 \pm 2.3 \text{ kJmol}^{-1}$  and  $\Delta S_{-1}^\ddagger = -129.1 \pm 0.5 \text{ JK}^{-1}\text{mol}^{-1}$ . The isomerization is markedly accelerated in the presence of Lewis bases. A crossover experiment indicates that the isomer interconversion is a unimolecular process. The large negative entropies of activation suggest either the existence of a sterically congested intermediate or the participation of solvent in the isomerization process.

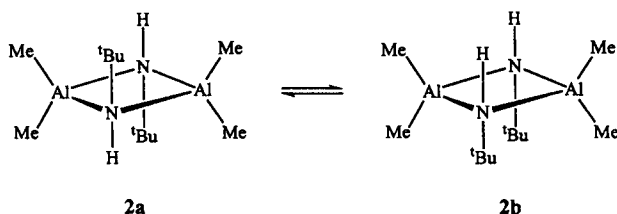
## Introduction

In recent years there has been a renewed interest in dimeric  $\mu$ -amido complexes,  $[\text{R}_2\text{M}(\mu\text{-NR}^t\text{R}^t)]_2$  (M: group 13 element), due to their potential application as single-source precursors for the preparation of group 13 nitride thin films, employing organometallic chemical vapor deposition (OM-CVD).<sup>1</sup> In previous work,<sup>2</sup> we have reported the synthesis and crystal structure of dimeric amidogallane  $[\text{Me}_2\text{Ga}(\mu\text{-NH}^t\text{Bu})_2]$  (**1**) together with kinetic and thermodynamic studies of the dissociative *cis-trans* isomerization of **1**. For further exploration of our work on the *cis-trans* isomerization with respect to the four-membered (M-N)<sub>2</sub> ring of the dimeric  $\mu$ -amido complexes, an analogous isomerization study of a dimeric amidoaluminum  $[\text{Me}_2\text{Al}(\mu\text{-NH}^t\text{Bu})_2]$  (**2**) has been carried out. Compound **2** has been previously reported to exist only as the *trans* isomer in solution up to 190 °C.<sup>3</sup> We, however, report herein a facile *cis-trans* isomerization of **2** with thermodynamic and kinetic results for the process.

## Experimental Section

**General Comments.** All experiments were performed under nitrogen either in a Vacuum Atmospheres drybox or with standard Schlenk techniques. Compounds **2**<sup>3</sup> and  $[\text{Et}_2\text{Al}(\mu\text{-NH}^t\text{Bu})_2]$ <sup>4</sup> were prepared by the procedures reported previously. Slow recrystallization of **2** in toluene at  $-10$  °C gave pure *trans* isomer **2a**.  $^1\text{H}$  NMR (300 MHz) spectra were recorded on a Bruker AM-300 spectrometer.

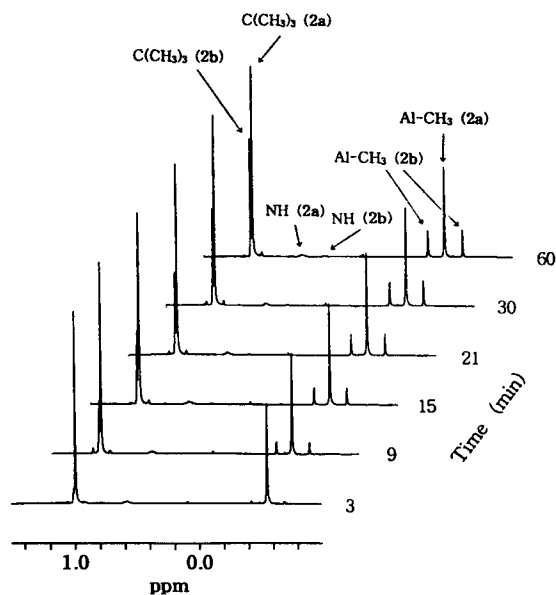
**$^1\text{H}$  NMR Study of Isomerization of *trans* **2a** to *cis* **2b**.** Crystals of **2a** (ca. 5 mg) were transferred to four 5 mm NMR tubes, and toluene- $d_8$  (0.6 mL) was added to each NMR tube under an atmosphere of nitrogen. The tubes were sealed and then heated in an NMR probe at 25, 35, 45, and 55 °C, respectively, while the resonances due to the methyl



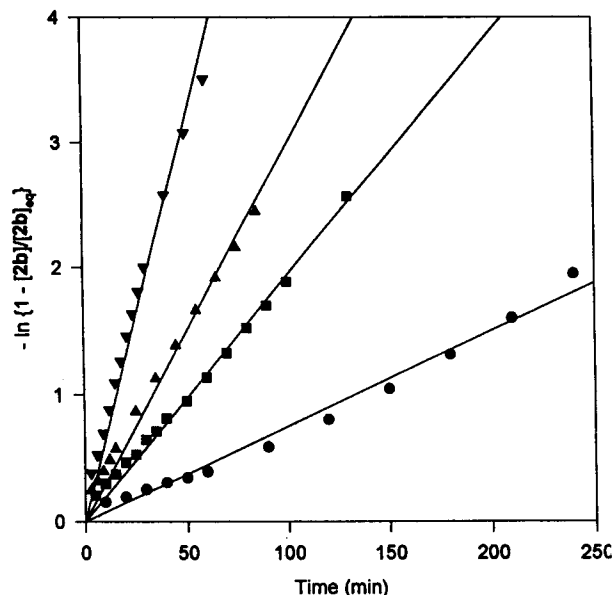
groups on the aluminum atoms, at  $\delta -0.56$  for **2a** and at  $\delta -0.70$  and  $-0.43$  for **2b**, were monitored periodically by  $^1\text{H}$  NMR spectroscopy. The isomerization reactions followed reversible first-order kinetics and showed excellent fits of data to a common plot of  $-\ln\{1 - [\mathbf{2b}]/[\mathbf{2b}]_{eq}\}$  vs time. Equilibrium constants at the four temperatures were measured similarly by  $^1\text{H}$  NMR after heating four NMR tubes in heated oil baths at controlled ( $\pm 0.5$  °C) temperatures, respectively. After equilibrium was reached, each NMR tube was quickly removed from the oil bath and placed into an ice bath to quench isomerization.

## Results and Discussion

Slow recrystallization of a *cis-trans* mixture of **2** affords crystals of only the *trans* isomer **2a**. The *trans* (**2a**)  $\rightarrow$  *cis* (**2b**) isomerization reaction was studied by  $^1\text{H}$  NMR spectroscopy. Typical time-resolved  $^1\text{H}$  NMR spectra of **2a** in toluene- $d_8$  at 55 °C are shown in Figure 1. As the intensities



**Figure 1.** Time-resolved  $^1\text{H}$  NMR spectra (300 MHz, toluene- $d_8$ ) of **2a** and **2b** at 55 °C.



**Figure 2.** Kinetics plots of the isomerization of **2a** to **2b** in toluene- $d_6$  at 25 (●), 35 (■), 45 (▲), and 55 (▼) °C.

**Table 1.** Kinetic and Thermodynamic Data in Toluene- $d_6$

$t, ^\circ\text{C}$	$K_{eq}$	$10^3 k_{obs}, \text{min}^{-1}$	$10^3 k_1, \text{min}^{-1}$	$10^3 k_{-1}, \text{min}^{-1}$
25	$0.576 \pm 0.002$	$0.760 \pm 0.053$	$0.278 \pm 0.019$	$0.482 \pm 0.034$
35	$0.588 \pm 0.001$	$1.886 \pm 0.039$	$0.698 \pm 0.014$	$1.188 \pm 0.025$
45	$0.608 \pm 0.002$	$2.676 \pm 0.037$	$1.012 \pm 0.014$	$1.664 \pm 0.023$
55	$0.625 \pm 0.002$	$5.685 \pm 0.164$	$2.187 \pm 0.139$	$3.498 \pm 0.101$

of the resonances of **2a** decrease, the resonances corresponding to  $t\text{Bu}$  and  $\text{Al-CH}_3$  of **2b** increase in intensity. Relative concentrations of the two isomers were measured by integration of the peaks due to  $\text{Al-CH}_3$  at  $\delta -0.56$  for **2a** and at  $\delta -0.70$  and  $-0.43$  for **2b**. Analyses according to reversible first-order kinetics give excellent fits of experimental data, as is shown in Figure 2. The kinetic and thermodynamic data are listed in Table 1. The equilibrium constants,  $K_{eq} = [\mathbf{2b}]/[\mathbf{2a}]$ , measured for the isomerization range from  $0.576 \pm 0.002$  at 25 °C to  $0.625 \pm 0.002$  at 55 °C, indicating that **2a** is favored in this equilibrium. The plot of  $\ln K_{eq}$  vs  $1/T$  yields  $\Delta H^\circ = 2.22 \pm 0.07 \text{ kJmol}^{-1}$  and  $\Delta S^\circ = 2.85 \pm 0.07 \text{ JK}^{-1}\text{mol}^{-1}$  for the process, **2a**  $\rightarrow$  **2b**. The *trans* isomer is thermodynamically more stable, but the positive entropy change favors the *cis* isomer. The  $T\Delta S$  term is apparently responsible for the conversion of **2a** to **2b**. This may be due to the descent in symmetry from **2a** to **2b**. Activation parameters derived from the Eyring plots of  $\ln(k/T)$  vs  $1/T$  and  $\ln(k_{-1}/T)$  vs  $1/T$  (cor-

relation coefficient, 0.9771 and 0.9736, respectively) are  $\Delta H_1 = 49.7 \pm 2.3 \text{ kJmol}^{-1}$  and  $\Delta S_1 = -126.3 \pm 0.2 \text{ JK}^{-1}\text{mol}^{-1}$  for the forward isomerization **2a**  $\rightarrow$  **2b** and  $\Delta H_{-1} = 47.5 \pm 2.3 \text{ kJmol}^{-1}$  and  $\Delta S_{-1} = -129.1 \pm 0.5 \text{ JK}^{-1}\text{mol}^{-1}$  for the reverse isomerization **2b**  $\rightarrow$  **2a**. The net enthalpy and entropy changes for **2a**  $\rightarrow$  **2b** from the thermodynamic data are in good agreement with those obtained from the kinetic data,  $\Delta H_1 - \Delta H_{-1} = \Delta H^\circ$  and  $\Delta S_1 - \Delta S_{-1} = \Delta S^\circ$ , within experimental error.

The two most obvious pathways of the isomer interconversion of **2** are (1) initial breaking of a  $\text{Al-N}$  bond, followed by rotation about the nonbridged  $\text{Al-N}$  bond and rebridging or (2) complete dissociation of the dimer and reassociation of the monomers. The isomerization of **2** is markedly accelerated in the presence of Lewis bases such as pyridine and 4-methylpyridine. No evidence for the formation of  $\text{Me}_2\text{Al}(\mu\text{-NH}^t\text{Bu})_2\text{AlEt}_2$  was observed from the crossover reaction of  $[\text{Me}_2\text{Al}(\mu\text{-NH}^t\text{Bu})]_2$  and  $[\text{Et}_2\text{Al}(\mu\text{-NH}^t\text{Bu})]_2$ , implying an intramolecular pathway. These results appear to support the pathway (1) for the isomerization as was previously proposed in **1**<sup>2</sup> and  $[\text{Me}_2\text{Al}(\mu\text{-NMePh})]_2$ .<sup>5</sup> The large negative values of  $\Delta S_1$  and  $\Delta S_{-1}$  for **2**, however, suggest that the transition state is considerably more ordered than **2a** and **2b**. The kinetic and thermodynamic data of **1** and **2** are compared in Table 2. The activation enthalpies of both  $\Delta H_1$  and  $\Delta H_{-1}$  for **2** are much smaller than those of **1**. The Lewis acidities of species  $\text{R}_3\text{M}$  are known to decrease for the heavier homologues of group 13 atoms ( $\text{Me}_3\text{Al} > \text{Me}_3\text{Ga}$ ), based on dissociation enthalpies for the adducts  $\text{R}_3\text{M}:\text{NMe}_3$ .<sup>6</sup> Both the activation entropies and enthalpies for **2**, therefore, are not consistent with the dissociative pathway (1). Our efforts to detect an intermediate for the isomerization have not been successful as of yet. Nevertheless, our kinetic data of **2** suggest either the existence of a sterically congested intermediate or the participation of solvent, which is distinctly different from the isomerization pathway (1) of compound **1**. The large negative entropies of activation for the intramolecular *cis-trans* isomerization have been previously reported in  $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Fe}_2(\text{CO})_3(\mu\text{-SiHTol})$ <sup>7</sup> ( $\text{Tol} = p\text{-C}_6\text{H}_4\text{Me}$ ) and  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_2(\mu\text{-CO})(\mu\text{-CH}_2)$ <sup>8</sup> complexes.

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**Table 2.** Comparison of Kinetic and Thermodynamic Data of **1** and **2** in Toluene- $d_6$

Compound	$\Delta H^\circ, \text{kJmol}^{-1}$	$\Delta S^\circ, \text{JK}^{-1}\text{mol}^{-1}$	$\Delta H_1, \Delta H_{-1}, \text{kJmol}^{-1}$	$\Delta S_1, \Delta S_{-1}, \text{JK}^{-1}\text{mol}^{-1}$	ref.
<b>1</b>	$3.12 \pm 0.04$	$4.56 \pm 0.06$	$120.8 \pm 7.4$	$41.4 \pm 2.6$	2
			$117.8 \pm 7.9$	$37.3 \pm 2.5$	
<b>2</b>	$2.22 \pm 0.07$	$2.85 \pm 0.07$	$49.7 \pm 2.3$	$-126.3 \pm 0.2$	this work
			$47.5 \pm 2.3$	$-129.1 \pm 0.5$	

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## Molecular Orbital Study of Bonding and Stability on Rh(I)-Alkyne Isomers

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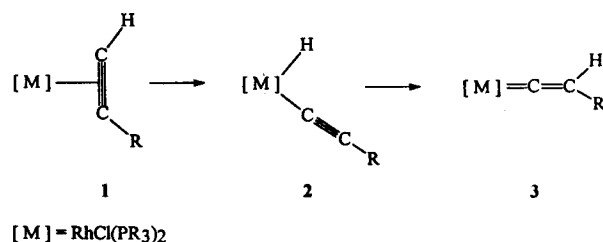
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*Ab initio* and extended Hückel calculations were carried out on the isomers of *trans*-RhCl( $\eta^2$ -C<sub>2</sub>H<sub>2</sub>)(PH<sub>3</sub>)<sub>2</sub> (1). Due to  $\pi$ -back donation in 1 complex, the rotational energy barrier of alkyne ligand is computed to be in the range of 18.6-25.2 kcal/mol at MP4 levels. The optimized hydrido-alkynyl complex (2) at *ab initio* level has the distorted trigonal bipyramidal structure. Vinylidene complex (3) is computed to be more stable than 1 complex by 17.1 kcal/mol at MP4//MP2 level. The stabilities of isomers show similar trend at the various level calculations, that is, EHT, MP4//HF, and MP4//MP2 levels. The optimized geometries at *ab initio* level are in reasonable agreement with experimental data. A detailed account of the bonding in each isomers (1-3) have been carried out in terms of orbital analyses.

### Introduction

The chemistry of alkynes with transition metals has attracted much attention in recent years,<sup>1</sup> due to the usefulness for the reactions of polymerization, cyclization, hydrogenation, and oxidative addition. With various experimental and theoretical approaches, many studies have been carried out to investigate the basic principles of the transformation of alkyne complexes to vinylidene complexes.<sup>2</sup> R. Hoffmann<sup>3</sup> examined the electronic and structural features of the isomerization of various metal alkynes into vinylidene complexes *via* a 1,2-hydrogen shift. For the d<sup>6</sup>-ML<sub>5</sub> fragment, the alternative pathway for the isomerization involving hydrido-alkynyl complex requires much higher energy. However, recent experimental works<sup>2(b),c)</sup> support that the rearrangement of alkyne to vinylidene occurs stepwise through the C-H activated intermediates (Scheme 1).

Reactions of alkynes with RhCl(PR<sub>3</sub>)<sub>2</sub> moiety produce *trans*-RhCl( $\eta^2$ -HCCR)(PR<sub>3</sub>)<sub>2</sub> (1), then slowly equilibrate with intermediates (2) in benzene or THF at room temperature. The  $\eta^2$ -alkyne complexes can be quantitatively transformed to vinylidene complexes (3) on heating in hexane solvent.<sup>4</sup> Recently, the formation of the intermediate hydrido-alkynyl complexes (2) has been observed in various systems.<sup>5</sup> In the present paper, we will report the computational results of *ab initio* and extended Hückel molecular orbital methods on Rh(I)-alkyne isomers related to the hydrogen migration



Scheme 1.

reaction.

### Computational Methods

Calculations were carried out at two levels. For qualitative analysis, the extended Hückel method with the modified Wolfsberg-Helmholz formula<sup>6</sup> were performed. The atomic parameters for H, C, P, Cl, and Rh were taken from previous work.<sup>7</sup> The *ab initio* calculations used the GAUSSIAN 92 and 94 programs<sup>8</sup> on a Cray Y-MP C916 and Indigo 2 workstation. A relativistic effective core potential was used for the core electrons in Rh (up to 4p),<sup>9</sup> P and Cl (up to 2p).<sup>10</sup> The basis sets used were double- $\zeta$  for the valence region with the contraction scheme (21/21/31) for Rh and (21/21) for P and Cl. The 3-21G basis<sup>11</sup> was used for the alkyne ligand and STO-3G<sup>12</sup> for the hydrogens on the PH<sub>3</sub> groups. A full