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Dynamic NMR as a Nondestructive Method for the Determination of Rates of Dissociation. IX. Rates of Dissociative Reactions of the Coordinated Form of [o-(Diethylaminomethyl)-phenyl]halodimethyl(or diphenyl)stannanes[1,2]

Michinori Ōki* and Manabu Ohira
Department of Chemistry, Faculty of Science, The University of Tokyo,
Bunkyo-ku, Tokyo 113

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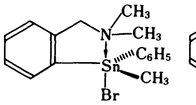
The coordinated form of [o-(diethylaminomethyl)phenyl]halodimethyl(or diphenyl)stannanes was found to exhibit dynamic behaviors in their ^{1}H NMR spectra. Examination of a series of halogen compounds by total line shape analysis of the diastereotopic methylene proton signals revealed that, at 10 °C, the rates of dissociation were 11.7, 22.9, 28.6, and 73.3 s^{-1} for fluoro, chloro, bromo, and iodo compounds, respectively: The results are in conformity with the expectation from the electronegativity of halogens. The relatively small differences in the activation parameters in the whole series may include contribution by solvation energies. The diphenyl compound exhibited fast exchange rates relative to the corresponding dimethyl compound. This was attributed to the steric factor rather than the pπ-dπ interaction.

The ligand exchange is one of the fundamental reactions in coordination chemistry. The dissociative reactions are often found in the ligand exchange and have been the target of many investigations.[3] As to the methodology for the determination of the rates of exchange, not only classical chemical reactions but also the dynamic NMR technique played an important role, because the latter affords data which are too fast for the ordinary laboratory time scale. Among many others we can pick up following examples which dealt with the coordination chemistry of amine ligands by dynamic NMR in the literature.

After the pioneering work by Mole,[4] various groups of investigators studied the exchange reactions of trivalent aluminium-amine complexes.[5,6] This technique was extended to boron-amine[7] and gallium-amine[8] complexes. An amine-sulfur dioxide complex was also studied.[9] These classic literatures use excess of substrates, usually the base, to observe coalescence of complexed and uncomplexed signals. Thus it may be said that these techniques determine the rates of exchange, either dissociative or associative, in the presence of excess of other reagents than the solvent concerned.

Observation of the dissociative processes in the absence of foreign materials is important, since it affords information about the "intrinsic" dissociative nature of the complex concerned. This is, on one hand, possible by observing the spin-spin coupling between the central metal atom in a complex and the atom, which has non-zero nuclear spin, in the ligand because the coupling disappears on dissociation. This technique has been reviewed.[10] Although the most of ligands contain atoms, which have non-zero nuclear spin, such as hydrogen, the central atom is not necessarily NMR-active. Therefore, the observation of spin-spin couplings has limitation in this respect.

Since we have been able to show that dissociation rates of a type of ammonium salts could be followed by the dynamic NMR method,[11] we are interested in applying this method to the problem in coordination chemistry. The necessary conditions for detection by this procedure are that 1) the compound in question has a pair of diastereotopic NMR-active nuclei, 2) the diastereotopic nuclei exchange their sites by dissociation, and 3) preferably the ligand which dissociates is singular. Literature search revealed that there were some examples which are similar but not exactly the same with our topomerization technique. van Koten and associates found that spin-exchange between the diastereotopic methyl protons in the coordinated form of bromo[o-(dimethylaminomethyl)phenyl]methylphenylstannane (**1**) was observed by the dynamic NMR technique.[12] They further elaborated to show that a diastereomer of bromo[o-[1-(dimethylamino)ethyl]-phenyl]methylphenylstannane (**2**) isomerized to another slowly at a low temperature.[13] These phenomena can be explained by dissociation of the amine ligand followed by internal rotation, inversion of amine and religation (or alternatively the chiral center of tin racemizes after dissociation of the ligand). Corriu *et al.* reported the similar phenomenon in the corresponding silicon compounds (**3**),[14] although they postulated that coordinated and decoordinated forms were observed. We believe our explanation of dissociation-topomerization is more likely than the postulate by Corriu *et al.*



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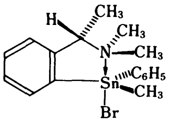

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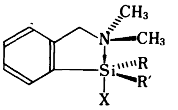
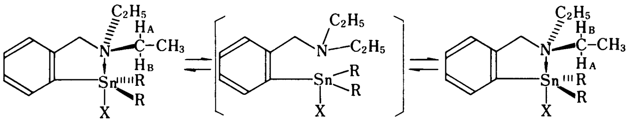


3

van Koten *et al.* extended their work further to more complicated tin compounds in which a 6-membered ring was formed by ligation.[15] Deeming and Rothwell were able to show dynamic nature of an amine ligand in a similar situation in palladium complexes, although they postulated that the mechanism of the exchange is different from that discussed here.[16]

The works cited above were possible because the metal atom was a chiral center. However, the diastereotopic nature does not require the presence of a chiral center. Therefore, by designing a proper molecule, we should be able to observe topomerization by dissociation in a compound which has no chiral center. This will broaden the scope of the technique and is worthwhile to be tried. We designed bromo[*o*-(diethylaminomethyl)phenyl]dimethylstannane (**4**: R=CH_3, X=Br) because the methylene protons in the ethyl group should be diastereotopic when the amine coordinates but it topomerizes when the ligand dissociates, internal rotation takes place, the amine inverts, and then the ligand recoordinates (Scheme 1).



4

Scheme 1.

This paper reports successful observation of topomerization in **4** and discusses the effect of the substituents on the rates of topomerization.

Experimental

N,*N*-Diethylbenzylamine (**5**) was prepared by adding 20 g of diethylamine in 30 mL of acetone to 25.0 g of benzyl chloride and 30 g of potassium carbonate in 50 mL of water and 100 mL of acetone and heating the mixture for 5 h. The yield was 54%. Colorless oil, bp 60—62 °C/3.5 mmHg (lit,[17] bp 211—212 °C). ^{1}H NMR ($CDCl_3$, δ): 1.01 (6H, t, J=7 Hz), 2.49 (4H, q, J=7 Hz), 3.53 (2H, s), 7.1—7.4 (5H, br s).

Bromo[o-(diethylaminomethyl)phenyl]dimethylstannane (4: R=CH_3, X=Br). To a mixture of 20 mL of dry ether and 5 mL of 1.5 M butyllithium (1M=1 mol dm^{-3}) in hexane, 1.2 g (7.4 mmol) of *N*,*N*-diethylbenzylamine was added with stirring. The mixture was stirred at room temperature under a nitrogen atmosphere until the Gilman color test II[18] became negative. This required 7—10 d. The solution of *o*-lithio-*N*,*N*-diethylbenzylamine was added to a solution of 2.4 g (7.8 mmol) of dibromodimethylstannane in 20 mL of dry ether during the course of 1 h with stirring. The stirring was continued for further 3 h and the solvents were evaporated. The residue was taken up in benzene and evaporated. Recrystallization of the product from benzene-hexane gave 0.5 g (17%) of the desired compound, mp 145—146 °C. Found: C, 40.01; H, 6.00; N, 3.48; Br, 20.66%. Calcd for $C_{13}H_{22}BrNSn$: C, 39.94; H, 5.67; N, 3.58; Br, 20.44%. ^{1}H NMR ($CDCl_3$, δ): 0.92 (6H, s), 0.99 (6H, t, J=7 Hz), 2.65 (4H, q, J=7 Hz), 3.65 (2H, s), 6.9—7.4 (3H, m), 8.23 (1H, m). ^{1}H NMR (toluene-d_8, δ): 0.43 (6H, t, J=7 Hz), 0.73 (6H, s), 2.03 (4H, q, J=7 Hz), 3.03 (2H, s), 6.5—7.4 (3H, m), 8.62 (1H, m).

Chloro[o-(diethylaminomethyl)phenyl]dimethylstannane (4: R=CH_3, X=Cl), mp 150—151 °C, was similarly prepared in 30% yield. Found: C, 44.92; H, 6.65; N, 3.87; Cl, 10.70%. Calcd for $C_{13}H_{22}ClNSn$: C, 45.07; H, 6.40, N, 4.04; Cl, 10.23%. ^{1}H NMR ($CDCl_3$, δ): 0.80 (6H, s), 0.99 (6H, t, J=7 Hz), 2.64 (4H, q, J=7 Hz), 3.64 (2H, s), 6.9—7.5 (3H, m), 8.18 (1H, m).

Chloro[o-(diethylaminomethyl)phenyl]diphenylstannane (4: R=C_6H_5, X=Cl), mp 135—136 °C, was similarly prepared in 9% yield. Found: C, 58.49; H, 5.62; N, 3.10; Cl, 7.67%. Calcd for $C_{23}H_{26}ClNSn$: C, 58.70; H, 5.57; N, 2.98; Cl, 7.53%. ^{1}H NMR ($CDCl_3$, δ); 0.70 (6H, t, J=7 Hz), 2.24 (4H, q, J=7 Hz), 3.59 (2H, s), 7.1—7.9 (13H, m), 8.47 (1H, m).

Iodo[o-(diethylaminomethyl)phenyl]dimethylstannane (4: R=CH_3, X=I). To a solution of 0.30 g (0.87 mmol) of compound **4** (R=CH_3, X=Cl) in 20 mL of ethyl acetate was added 0.13 g (0.87 mmol) of sodium iodide in 20 mL of ethyl acetate. The precipitate of sodium chloride was filtered off and the filtrate was concentrated. The residue was purified by recrystallization from dichloromethane-pentane to give 0.34 g (90%) of the desired compound, mp 140—141 °C. Found: C, 35.60; H, 5.45; N, 3.16; I, 28.42%. Calcd for $C_{13}H_{22}INSn$: C, 35.66; H, 5.06; N, 3.20; I, 28.98%. ^{1}H NMR ($CDCl_3$, δ): 1.01 (6H, t, J=7 Hz), 1.12 (6H, s), 2.68 (4H, q, J=7 Hz), 3.68 (2H, s), 6.9—7.5 (3H, m), 8.32 (1H, m).

Fluoro[o-(diethylaminomethyl)phenyl]dimethylstannane (4: R=CH_3, X=F). A solution of 0.28 g of **4** (R=CH_3, X=I) in 20 mL of methanol was mixed with 0.10 g of potassium fluoride in 5 mL of water and the whole was refluxed for 3 h. The solvents were evaporated and the residue was taken up in benzene. The benzene solution was evaporated and the residue was recrystallized from ether-hexane to afford the desired compound, mp 74—77 °C, in 80% yield. Found: C, 47.10; H, 6.75; N, 4.28%. Calcd for $C_{13}H_{22}FNSn$: C, 47.31; H, 6.71; N, 4.24%. ^{1}H NMR ($CDCl_3$, δ): 0.62 (6H, d, J_{HF}=4.2 Hz), 1.00 (6H, t, J=7 Hz), 2.66 (4H, q, J=7 Hz), 3.64 (2H, s), 7.0—7.5 (3H, m), 7.99 (1H, m).

Dynamic NMR Measurement. The measurement was carried out on a JEOL FX-400 NMR spectrometer which operates at 400 MHz for protons. The samples were dissolved in chloroform-*d* to make up *ca.* 100 mmol/L solutions. The data were accumulated for 200 times. Temperature was calibrated by the chemical shift differences of methanol protons. The chemical shift differences of the AB protons and the coupling constants at *ca.* −50 °C are summarized in Table 1. J_{AX} and J_{BX} were constant at 7.2—7.3 Hz for all the compounds examined.

Total Line Shape Analysis and Kinetic Parameters. The line shapes were analyzed by computer simulation with the use of the modified Binsch program.[19] The spectra were analyzed as an AB part of an ABX_3 system. The coupling constants were constant throughout the temperature range examined but the chemical shift differences drifted as temperature changed but one case, compound **4** (R=CH_3, X=I). Thus for those which gave drifts in chemical shift differences, the chemical shift differences were checked at several temperatures where the rates of exchange were negligibly small. The chemical shift change was found to be linearly correlated with temperature and the following equations gave chemical shift differences at a given temperature. T_2 was estimated from the

4: $R=C_6H_5$, X=Cl

$$\Delta\nu_{AB} = -0.409T + 62.66 \quad (r=0.996)$$

4: $R=CH_3$, X=Cl

$$\Delta\nu_{AB} = -0.0336T + 25.37 \quad (r=0.999_5)$$

4: $R=CH_3$, X=F

$$\Delta\nu_{AB} = -0.0582T + 16.35 \quad (r=0.991_5)$$

4: $R=CH_3$, X=Br

$$\Delta\nu_{AB} = -0.0170T + 26.74 \quad (r=1.000)$$

Table 1. Chemical shift differences of the methylene protons in ethyl groups and coupling constants at *ca.* −50 °C at 400 MHz

R	X	$\Delta\nu_{AB}$/Hz	J_{AB}/Hz
CH_3	F	19.3	−13.7
CH_3	Cl	27.0	−13.7
CH_3	Br	27.6	−13.7
CH_3	I	27.8	−13.7
C_6H_5	Cl	82.8	−13.9

line widths of benzyl protons and was assumed to be constant at 0.16 s. The calculated spectra and the observed ones were matched by the visual method. The agreement of the both spectra were excellent. The following rate constants were obtained (k/s^{-1} and T/°C in parentheses are given). For **4** (R=C_6H_5, X=Cl), see Fig. 1.

4 (R=CH_3, X=F): 6.1 (5.1), 12.0 (10.5), 27.0 (16.2), 35.0 (18.1), 47.0 (20.7), 58.0 (22.6).

4 (R=CH_3, X=Cl): 7.0 (1.9), 11.5 (5.0), 22.0 (9.2), 42.0 (14.5), 75.0 (18.7), 98.0 (21.5), 120.0 (22.8).

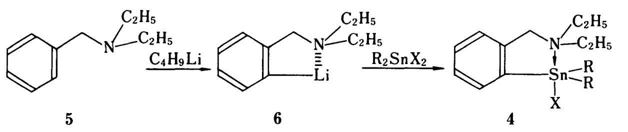
4 (R=CH_3, X=Br): 7.5 (1.3), 16.0 (6.6), 25.0 (9.0), 33.0 (10.9), 45.0 (12.7), 62.0 (21.5), 118.0 (20.0).

4 (R=CH_3, X=I): 4.0 (−8.4), 8.0 (−4.5), 18.0 (0.7), 36.0 (5.1), 78.0 (10.5), 90.0 (11.3), 175.0 (16.2).

The rate constants thus obtained were put into the Eyring equation to obtain the activation parameters. The rate constants and free energies of activation at a given temperature were calculated with the use of these activation parameters.

Results and Discussion

The first point which we wish to raise is the steric effect in the synthesis of the compounds which was performed as is shown in Scheme 2. Although lithiation of *N*,*N*-dimethylbenzylamine with butyllithium proceeded smoothly and the Gilman color test II became negataive after a day or so at room temperature,[20] the same lithiation of *N*,*N*-diethylbenzylamine (**5**) required 7—10 d to give the negative Gliman test II. We were not able to lithiate completely the ortho position of *N*,*N*-diisopropylbenzylamine. It seems that the steric effect in the coordinated form (**6**) which stabilizes the lithiated compound is severely affected by the bulkiness of the substituent on the nitrogen.



Scheme 2.

The ^1H NMR spectra of **4** at 60 or 90 MHz gave a simple A_2X_3 quartet for the methylene protons of the ethyl groups. This could mean either the rate of exchange was large on the NMR time scale or the chemical shift differences were too small to detect, although the exchange rate was small. A ^1H NMR spectrum at 60 MHz at −50 °C showed essentially no change from that at room temperature. Summing up this result and the data reported by van Koten *et al.*,[12] we concluded that the chemical shift differences of the AB protons were too small for a spectrometer operating at 60 MHz. Then we shifted to a spectrometer operating at 400 MHz.

The AB part of the spectrum of **4** (R=CH_3, X=Br) at 400 MHz showed a barely resolved signal at room temperature but it became a distinct AB part of the ABX_3 system when the spectrum was determined at lower temperatures. The other compounds showed the similar trend. Since the spectral change due to temperature for **4** (R=CH_3, X=Br) is given in a preliminary note,[2] the temperature dependent spectra of **4** (R=C_6H_5, X=Cl) are shown in Fig. 1 together with the calculated spectra. Activation parameters obtained from the rate constants and temperatures are summarized in Table 2 together with $\Delta G^{\neq}$'s and k's at 10 °C, which were obtained by calculation, for comparison. The correlation coefficients were very close to 1 and we may discuss the effect of substituents with the use of these data.

The first point we wish to discuss is that argument, saying that the results by van Koten *et al.*[12,13] and

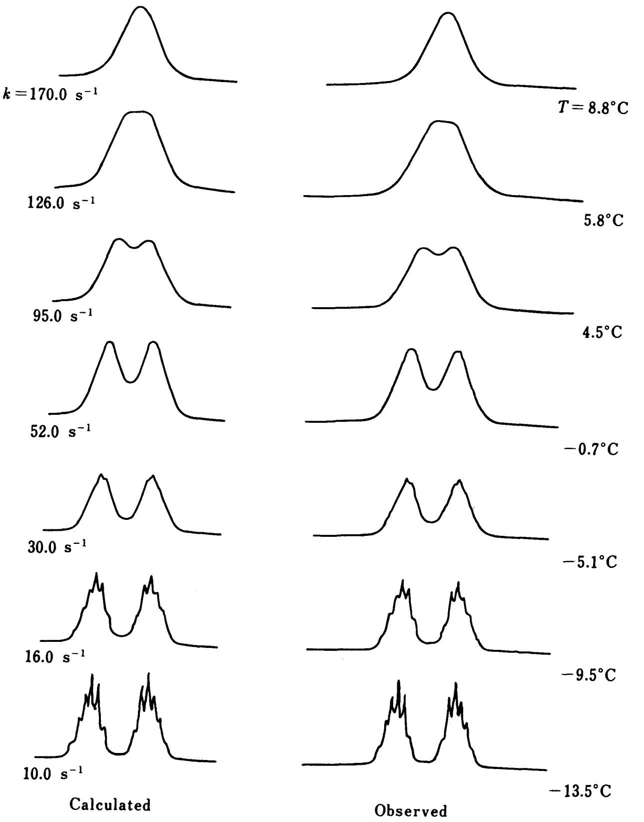


Fig. 1. Calculated and observed spectra of the AB part of ABX_3 patterns in **4** (R=C_6H_5, X=Cl) at various temperatures.

TABLE 2. ACTIVATION PARAMETERS FOR TOPOMERIZATION OF **4** IN CHLOROFORM-*d* AND PERTINENT DATA

R	CH_3	CH_3	CH_3	CH_3	C_6H_5
X	F	Cl	Br	I	Cl
Correlation Coeff.	0.9994	0.9991	0.9990	0.9998	0.9991
$\Delta H^{\neq}$/kcal mol^{-1} [a)]	21.0±0.7	21.1±0.8	23.4±0.9	22.8±0.3	18.2±0.7
$\Delta S^{\neq}$/e. u.	20.5±2.5	22.3±2.7	30.9±1.1	30.5±1.1	16.2±2.5
$\Delta G^{\neq}_{283}$/kcal mol^{-1}	15.2	14.8	14.7	14.1	13.7
k_{283}/s^{-1}	11.7	22.9	28.6	73.3	195

a) 1 cal=4.184 J

Corriu *et al.*[14] could be caused by the fluxional behavior of the complexes, can be denied by the present results. The X-ray crystallography of compound **1** was carried out and concluded that nitrogen and bromine occupy the apical positions.[21] Although electronegative groups favor to be in the apical positions in trigonal bipyramid complexes, this general trend cannot rule out the possibility that a configuration in which nitrogen or bromine occupies the basal position is present in solution. However, in our cases, if it were the fluxional behavior of the complexes, the coalescence of the AB proton signals could not have been observed for the following reasons. The AB protons at a site (that is either apical or basal) give their own chemical shifts but they are still diastereotopic in another site unless they dissociate and inversion of nitrogen takes place. Therefore, the fluxional behavior could explain the change in the chemical shift differences due to temperature but not the coalescence of the diastereotopic proton signals. Topomerization by dissociation is the process we observe.

The common feature of the activation parameters for compound **4** is that large positive entropies of activation are observed. The feature of the entropy of activation gives suggestions in diagnosing the rate-determining step of the observed topomerization processes. As stated earlier, there are four steps involved in the observation: Dissociation of the amine ligand, rotation about the NCH_2–phenyl bond, inversion of amine, and religation. Inversion of the amine is easily rejected, because the free energy of activation for the observed process is 14—15 kcal/mol at 283 K, whereas that for nitrogen inversion in dibenzylmethylamine is 6.6 kcal/mol at 132 K[22] and that for diethylmethylamine is 7.9 kcal/mol at 160 K.[23] Ruling out the NCH_2–phenyl rotation from being the possible rate-determining step is difficult: *o,o′*-disubstituted neopentylbenzenes are known to show a barrier to rotation about the C_{CH_2}–C_{Ar} bond of 13—15 kcal/mol[24] but the effect of removing one *o*-substituent is not known, in addition to the fact that the effect of the stannyl substituent on the barrier is unknown. However, it scarcely happens that the internal rotation of a molecule shows a large positive entropy of activation. Therefore, being a rate-determining step for the NCH_2–phenyl rotation is less likely. The third possibility, that the religation is the rate-determining step, can also be ruled out because we observe only the ligated form: We should have been able to observe the dissociated form, if the barrier to religation were high relative to that for dissociation of the ligand. Then the most probable rate-determining step for the observed topomerization is the dissociation of the ligand.

The same trend, a large positive entropy of activation, was also observed for the dissociation of anilinium ions.[11] The increase in the entropy in the transition state of a reaction seems to be a commonly observed feature when we go from an ionic ground state to a less ionic transition state. This has been attributed to the increase in the freedom of motion of solvent molecules.[25]

When we descend the periodic table from fluorine to chlorine, to bromine, and then to iodine, the free energy of activation at 10 °C decreases and consequently the rates of topomerization increase in this order. This is reasonable in the sense that a more electronegative halogen causes a stronger N–Sn bond than a less electronegative halogen. However, when we see the $\Delta H^{\neq}$'s and $\Delta S^{\neq}$'s which are obtained by division of the free energies of activation at various temperatures, we notice that things are not so simple as are expected from the electronegativity. As far as numericals concern, the fluoro compound gives a rather small enthalpy of activation and the bromo and iodo compounds give large enthalpies of activation. The increase in entropy seems to be large in the bromo and iodo compounds relative to the fluoro compound. Since the division of free energy of activation into enthalpy and entropy terms may include errors, we may not be able to get further into insight. However, it is tempting to consider that solvent molecules and/or the stages of the transition state play important roles in determining the activation parameters.

In view of the fact that topomerization by dissociation of an amine ligand in coordination compounds involves a large positive entropy of activation, it is dangerous to compare free energies at different temperatures. In our examples, the fluoro compound gave the smallest $\Delta\nu_{AB}$ (Table 1) among the compounds examined. This will necessarily make the coalescence temperature low. Since the free energy of activation calculated by the coalescence method is a function of T, the low temperature tends to give a small free energy of activation. The smallest free energy of activation in the fluoro compound in a series of silicon compounds[14] may have the origin in this area. Reexamination is awaited.

The data for **4** ($R=C_6H_5$, $X=Cl$) suggest that topomerization in this compound is much faster than others: The enthalpy of activation is definitely smaller and the increase in entropy in the transition state seems to be smaller than others. It may be possible to attribute the small $\Delta H^{\neq}$ to the decrease in acidity of the tin atom due to pπ-dπ interactions but out choice is the steric effect. Firstly, the d orbital which interacts with the 2p orbital of the phenyl group is 5d. This will make the overlap of the orbitals less effective. Secondly, the phenyl group is large. This will make the steric repulsion significant when the coordination bond is formed. The small entropy of activation seems to support the idea, together with the small enthalpy of activation. The steric interactions will make the Sn–N bond long, thus making the Sn–N bond less ionic. The latter factor should contribute to lessen the entropy of activation, because the freedom of motion of solvent molecules in the ground state will be large, relative to a strongly ionic case, if the ionic nature of a bond is weak.

Finally we wish to discuss the steric effects of the alkyl groups on the nitrogen atom. From the chemical shift differences of diastereotopic methyl protons in **1** and coalescence temperature (30 °C), the free energy of activation for topomerization of **1** is calculated as 15.4 kcal/mol. If we calculate the free energy of activation for topomerization of **4** ($R=CH_3$, $X=Br$) at the same temperature, we obtain 14.0 kcal/mol which is much less than the value for **1**. One would argue on the basis of various factors, but we believe this is due to the steric effects (or entropic effects) of the ethyl group. One of the bases on which we postulate the steric effect is a preliminary study on the rates of topomerization of a compound in which one of the ethyl groups in **4** ($R=CH_3$, $X=Br$) is replaced by a methyl group. This compound gave free energy of activation of 15.2 kcal/mol at 33.5 °C by the coalescence method. Thus replacing the ethyl group by a small methyl group caused the raise of the activation energy.

So far we have discussed on the dissociation of amine ligands. Although this technique cannot be applied to phosphines and arsines due to their slow inversion rates, there is a possibility that this affords information on the dissociation of sulfur or oxygen ligands. Exchange of oxygen ligands in borane–ether complexes is reported,[26] by looking at the coalescence of ^{19}F signals due to $(CH_3)_2O\cdot BF_3$ and $(C_2H_5)_2O\cdot BF_3$. It might be possible to study the dissociation of their complexes without foreign materials by this technique. There is one point which should be kept in mind, however, when we apply the topomerization technique to the dissociation of oxygen or sulfur ligands. That is to distinguish dissociation from inversion. It is clear that the postulate by Brownstein that he observed inversion of pyramidal oxygen and sulfur[27] should be reexamined. We now plan to extend the technique to these areas.

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References

1) Part VIII: M. Ōki and M. Ohira, *Bull. Chem. Soc. Jpn.*, **57**, 3025 (1984).

2) A preliminary note has been published: M. Ōki and M. Ohira, *Chem. Lett.*, **1982**, 1267.

3) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions—A Study of Metal Complexes in Solution," John Wiley, New York (1967).

4) T. Mole, *Aust. J. Chem.*, **16**, 801 (1963).

5) C. A. Smith and M. G. H. Wallbridge, *J. Chem. Soc., A*, **1967**, 7.

6) a) Z. Buczkowski, A. Gryff-Keller, and P. Szczeciński, *Tetrahedron Lett.*, **1971**, 607; b) *Idem., Roczniki Chem.*, **46**, 195 (1972); *Chem. Abstr.*, **76**, 152777r (1972).

7) A. H. Cowley and J. L. Mills, *J. Am. Chem. Soc.*, **91**, 2911 (1969).

8) J. B. DeRoos and J. P. Oliver, *Inorg. Chem.*, **4**, 1741 (1965).

9) R. K. Harris and R. A. Spragg, *Org. Magn. Reson.*, **1**, 329 (1969).

10) J. P. Jensen and E. L. Muetterties, "Dynamic Molecular Process in Inorganic and Organometallic Compounds," in "Dynamic Nuclear Magnetic Resonance Spectroscopy," ed by L. M. Jackman and F. A. Cotton, Academic Press, New York (1975), pp. 253—316.

11) M. Ōki, Y. Yoshioka, H. Kihara, and N. Nakamura, *Chem. Lett.*, **1980**, 1625; M. Ōki, M. Ohira, Y. Yoshioka, T. Morita, H. Kihara, and N. Nakamura, *Bull. Chem. Soc. Jpn.*, **57**, 2224 (1984).

12) G. van Koten and J. B. Noltes, *J. Am. Chem. Soc.*, **98**, 5393 (1976).

13) G. van Koten, J. T. B. H. Jastrzebski, J. G. Noltes, W. M. G. F. Potenagel, J. Kroon, and A. L. Spek, *J. Am. Chem. Soc.*, **100**, 5021 (1978).

14) R. J. P. Corriu, J. Royo, and A. de Saxcè, *J. Chem. Soc., Chem. Commun.*, **1980**, 892.

15) G. van Koten, J. T. B. H. Jastrzebski, J. G. Noltes, G. V. Verhoeckx, A. L. Spek, and J. Kroon, *J. Chem. Soc., Dalton Trans.*, **1980**, 1352.

16) A. J. Deeming and I. P. Rothwell, *J. Chem. Soc., Dalton Trans.*, **1978**, 1497.

17) V. Meyer, *Ber.*, **10**, 309 (1877).

18) H. Gilman and J. Swiss, *J. Am. Chem. Soc.*, **62**, 1847 (1940).

19) G. Binsch, *Top. Stereochem.*, **3**, 97 (1968).

20) G. van Koten, C. A. Schaap, and J. G. Noltes, *J. Organomet. Chem.*, **99**, 157 (1975).

21) G. van Koten, J. G. Noltes, and A. L. Spek, *J. Organomet. Chem.*, **119**, 183 (1976).

22) C. H. Bushweller, J. W. O' Neil, and H. S. Bilofsky, *Tetrahedron*, **28**, 2697 (1972).

23) C. H. Bushweller, S. H. Fleischman, G. L. Grady, P. McGoff, C. D. Rithner, M. R. Whalon, J. G. Brennan, R. P. Marcantonio, and R. P. Domingue, *J. Am. Chem. Soc.*, **104**, 6224 (1982).

24) A. J. M. Reuvers, A. Sinnema, Th. J. Nieuwstad, F. van Rantwijk, and H. van Bekkum, *Tetrahedron*, **27**, 3713 (1971).

25) J. W. Moore and R. G. Pearson, "Kinetics and Mechnism," John Wiley, New York (1981), p. 256.

26) A. C. Rutenberg, A. A. Palko, and J. S. Drury, *J. Am. Chem. Soc.*, **85**, 2702 (1963).

27) S. Brownstein, *J. Am. Chem. Soc.*, **98**, 2663 (1976).