resulting spectra. Thus we have shown that the simple recording of the chemical shifts permits a correct stereochemical assignment in the case of disilylated derivatives. In all of the cases considered, a simple visual examination of the spectral multiplicity allows the determination of the molecule's geometry. In addition, measurement of the coupling constants has led us to demonstrate the existence of both a Karplus-type relationship for ^3J (Si–H), and steric hindrance between the silicon in the endo position and the large ring. This steric hindrance is reflected directly by the sigificant variations in the values of ^3J and $^2J'$.

This work is the first example of a stereochemical study invoking ^{29}Si NMR. The heightened selectivity of SPI permits the assignments of the $SiMe_3$ signals in ^{1}H NMR. SPI is thus found to be a particularly effective technique in the structural analysis of organosilicon compounds. The use of SPI calculation and simulation gives results in good agreement with the experimental spectra. Access to SPI requires only the most basic equipment, that is, a spectrometer operating in the pulsed Fourier transform mode and fitted with a decoupler capable of being set within about 1 Hz of a required frequency, with fine low level power control. SPI is thus the method of choice in the analysis of organosilicon synthons whose use by organic chemists is ever increasing.

Experimental Section

Spectra were recorded on a Bruker WH-90 spectrometer (17.87 MHz for ^{29}Si) equipped with a Nicolet BNC 12 computer.

All samples were 80% solutions in C_6D_6 (10-mm tubes). Chemical shifts are given downfield (δ) from Me_4Si as internal standard.

For the decoupled ^{29}Si spectra, the experiments were performed by using the "gated decoupling pulse modulated interrupted proton band decoupling" technique[8] in order to cancel the negative nuclear Overhauser effect. The following parameters were used: time pulse 5.5 μs ($\alpha = 45°$) and recycle delay = 30 s.

For the SPI spectra, the experiments were performed by using the technique previously described in the literature.[3] The following parameters were used: time for SPI π pulse = 0.1 s, time ^{29}Si pulse = 11 μs ($\alpha = 90°$), and recycle delay = 5 s.

In all cases, a resolution enhancement was performed by using the RE technique.[7]

The theoretical spectra were calculated on a HP 85 microcomputer and were drawn on a 4662 Tektronix digital plotter.

Registry No. *exo*-**1**, 75311-61-4; *endo*-**1**, 75311-62-5; **1′**, 79054-31-2; *exo*-**2**, 18178-57-9; *endo*-**2**, 18178-58-0; **2′**, 56431-99-3; *exo*-**3**, 88270-79-5; *endo*-**3**, 88270-80-8; **3′**, 88230-22-2.

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[8] Freeman, R.; Hill, H. D. W.; Kaptein, R. *J. Magn. Reson.* **1972**, *7*, 327.

Reactions of Organosilicon Anionic Species with Nitrous Oxide

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The flowing afterglow technique has been used to study the chemistry of several anionic organosilicon species. In particular, silyl anions, silicon-stabilized carbanions, and pentacovalent silicon anions have been investigated. Because certain of the species studied were isomeric and indistinguishable by our mass spectroscopic detection system, chemical methods were developed to determine the structure of these isomeric anions. This was commonly accomplished by using reaction with nitrous oxide as detailed in full in this account.

Organosilicon chemistry has drawn a great deal of recent attention because of its central role in the development of numerous synthetic methods,[1] and this has given added impetus to mechanistic studies of this element. Our approach has been to study ionic reactions of silicon in the gas phase. For these studies we use a flowing afterglow (FA) apparatus or the closely related selected ion flow tube (SIFT). In a FA, highly reactive ions (HO^-, H_2N^-, F^-) are generated by electron impact in a rapidly flowing helium stream contained in a meter long stainless-steel tube. These ions are rapidly cooled (thermalized) by collisions with the helium buffer gas. Neutral reagents are then added through various ports along the flow tube; thus, multistep reaction sequences can be performed. The ionic species in the gases are sampled at the end of the tube by a quadrupole mass filter. Reaction rate constants and product branching ratios can be readily measured. In the SIFT variation, ions are produced in a separate ion source and those with the desired mass/charge (m/z) ratio are injected into the flow tube in the absence of their neutral precursors, ions of other masses, photons, and electrons.

With use of these techniques, we have carried out a number of studies of simple reactions of organosilicon compounds. We showed, for example, how organosilicon compounds can be used as precursors of carbanions in the gas phase, as they are in solution,[2] uncovered some unusual reactions of cyclic silanes,[3] and carried out a comparative kinetic investigation of nucleophilic substitution reactions

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[1] Weber, W. P. "Silicon Reagents for Organic Synthesis"; Springer-Verlag: Berlin, 1983.

[2] DePuy, C. H.; Bierbaum, V. M.; Flippin, L. A.; Grabowski, J. J.; King, G. K.; Schmitt, R. J.; Sullivan, S. A. *J. Am. Chem. Soc.* **1983**, *102*, 5012.

[3] Sullivan, S. A.; DePuy, C. H.; Damrauer, R. *J. Am. Chem. Soc.* **1981**, *103*, 480.

0276-7333/84/2303-0362$01.50/0

of silicon and carbon halides.[4] We also demonstrated that pentacovalent silicon anions can be generated in the gas phase and that the relative fluoride affinity of neutral silicon compounds can be determined.[3] Our results to date indicate that the methods of gas-phase ion–molecule chemistry are extremely promising for the exploration of reaction pathways in organosilicon chemistry.

A potential difficulty of these techniques, one common to all mass spectrometric methods, is that only the mass of an ion is determined. Its structure, if there is any possible ambiguity, must be elucidated by other methods. Because all of our silicon work to date has involved anionic species and because anionic rearrangements of silicon species are fairly common,[5] one of our goals is to examine the possible occurrence of such reactions. We were, therefore, anxious to develop methods that could be used to distinguish among various isomeric structures of anions containing silicon. One urgent problem was to distinguish between an anion on and adjacent to a silicon atom. Both silyl anions and silicon-stabilized carbanions (α-silyl carbanions) are known to be intermediates in many reactions.[1] While such isomeric species (e.g., $Me_3SiCH_2^-$ and $Me_2Si^-CH_2CH_3$) are known to have independent existence in solution, where they can be stabilized by solvation and the presence of counterions, their gas-phase chemistry remained to be determined.

Experimental Section

All experiments were performed at 298 K by using the previously described systems. Typical helium pressure and flow rate were 0.3 torr and 140 STP cm^3/s. Amide, hydroxide, and fluoride ions were prepared by electron impact on NH_3, N_2O and CH_4, and NF_3 respectively. Neutral reagents were obtained from commercial sources. N_2O flow rates were typically 1.5 STP cm^3/s and those of the silanes were <0.5 STP cm^3/s.

Results and Discussion

In previous studies we have found nitrous oxide, N_2O, to be a versatile neutral reagent for ion–molecule studies because it reacts in several different ways depending upon the structure of its anionic reaction partner. For example, basic anions with two hydrogens on the anionic center react to form diazo anions[6] (eq 1). Anions with fewer hydrogens

$$CH_2{=}CH{-}CH_2^- + N_2O \rightarrow CH_2{=}CH{-}CH_2\text{-}N{=}N{-}O^- \rightarrow H_2O + CH_2{=}CH{-}C^-{=}N{=}N \quad (1)$$

form adducts and/or products that have lost a molecule of nitrogen (e.g., adduct minus N_2) (eq 2). In one case,

$$C_6H_5^- + N_2O \rightarrow C_6H_5O^- + N_2$$

$$C_6H_5^- + N_2O \rightarrow C_6H_5N_2O^- \quad (2)$$

even nitrogen atom transfer has been observed[7] (eq 3).

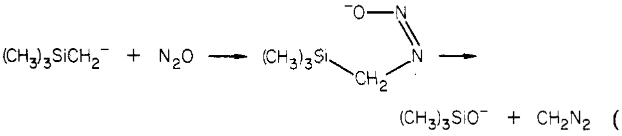
$$CH_2{=}C^{-}\cdot + N_2O \rightarrow {}^-CH_2{-}C{\equiv}N + \cdot NO \quad (3)$$

This chemical versatility of N_2O, as well as the practical advantage that large flows of it can be introduced into the FA, led us to examine its possible utility as a reagent for distinguishing between silyl anions and silicon-stabilized carbanions.

Tetramethylsilane reacts rapidly ($k = 1.5 \times 10^{-9}$ cm^3 $molecule^{-1}$, corresponding to reaction at every collision; measured by SIFT) with hydroxide ion to form $(CH_3)_3SiO^-$ with loss of methane. Amide ion reacts at the same rate giving not only the analogous $(CH_3)_3SiNH^-$ and methane products but also significant amounts of an M − 1 ion. [Since appreciable amounts of HO^- are always present when preparing H_2N^- in the flow tube (from H_2N^- reacting with traces of H_2O), $(CH_3)_3SiO^-$ is also present in this experiment.] We formulate this as the (trimethylsilyl)methyl anion (eq 4). This ion reacts with N_2O as shown

$$(CH_3)_4Si + H_2N^- \rightarrow (CH_3)_3SiNH^- + CH_4$$
$$\rightarrow (CH_3)_3SiCH_2^- + NH_3 \quad (4)$$

in eq 5. In a typical experiment amide ion is produced



(5)

at the electron gun and $(CH_3)_4Si$ is added 30 cm downstream. After an additional 30 cm or more is allowed for the product ions to thermalize, N_2O is added. The M − 1 ion rapidly disappears, and the ion at *m/z* 89 increases by a corresponding amount. The driving force for eq 5 is obviously the formation of the strong silicon–oxygen bond and the conversion of the highly basic carbanion to the more stable oxide ion. Although we do not detect the neutal products of reactions occurring in the flow tube, diazomethane appears to be the only reasonable product based on both mechanistic and thermochemical grounds. In view of the observed loss of a CH_2 group in eq 5, it appears extremely unlikely that a rearrangment to $(CH_3)_2Si^-CH_2CH_3$ has occurred, especially in view of the results reported below for reactions of silyl anions and N_2O.

In order to generate authentic silyl anions, we chose a displacement reaction of silicon (eq 6). Although fluoride

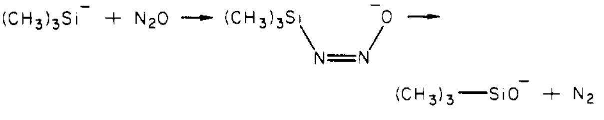
$$(CH_3)_3Si\text{-}Si(CH_3)_3 + H_2N^- \rightarrow \underset{m/z\ 73}{(CH_3)_3Si^-} + (CH_3)_3SiNH_2 \quad (6)$$

ion can also be used for this transformation, we found amide ion to give a cleaner reaction. The anion formed also reacts with N_2O, but this occurs exclusively by oxygen transfer (eq 7) without loss of any substituent. This reaction could in principle occur by direct attack at oxygen with expulsion of N_2. However, we believe this is not the reaction pathway largely because $(CH_3)_2N^-$, which is a stronger base than $(CH_3)_3Si^-$, does not react with N_2O in an analogous fashion (eq 8). Instead, we believe that the

$$(CH_3)_3Si^- + N_2O \rightarrow (CH_3)_3SiO^- + N_2 \quad (7)$$

$$(CH_3)_2N^- + N_2O \nrightarrow (CH_3)_2N\text{-}O^- + N_2 \quad (8)$$

reactions of N_2O are always initiated by nucleophilic attack at the terminal nitrogen atom and that, in this case, the product forms by a variation of the Peterson reaction[8] (eq 9).



(9)

We have used these reactions of N_2O to probe the structures of several silicon-containing anions. A simple

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[4] Damrauer, R.; DePuy, C. H.; Bierbaum, V. M. *Organometallics* **1982**, *1*, 1553.

[5] West, R. In "Advances in Organometallic Chemistry"; Stone, F. G. A., West, R., Eds.; Academic Press: New York, 1977; Vol. 1.

[6] Bierbaum, V. M.; DePuy, C. H.; Shapiro, R. H. *J. Am. Chem. Soc.* **1977**, *99*, 5800.

[7] Dawson, J. H. J.; Nibbering, N. M. M. *J. Am. Chem. Soc.* **1978**, *100*, 1928.

[8] Peterson, D. J. *J. Org. Chem.* **1982**, *33*, 649.

example is the demonstration of the structure of the M − 1 ion resulting when trimethylsilane and H_2N^- react (eq 10). Addition of N_2O to the stream of M − 1 ion lead

$$(CH_3)_3SiH + H_2N^- \nrightarrow \underset{m/z\ 73}{(CH_3)_3Si^-} \overset{N_2O}{\nrightarrow} \underset{m/z\ 89}{(CH_3)_3SiO^-}$$

$$(CH_3)_3SiH + H_2N^- \rightarrow \underset{m/z\ 73}{(CH_3)_2Si(H)CH_2^-} \xrightarrow{N_2O} \underset{m/z\ 75}{(CH_3)_2Si(H)O^-} \quad (10)$$

exclusively to the formation of a *m/z* 75 ion, indicating that proton abstraction has occurred only from the methyl groups. A similar conclusion has been reached earlier by Bowie,[9] who studied the reaction by ion cyclotron resonance spectroscopy using deuterium tracers.

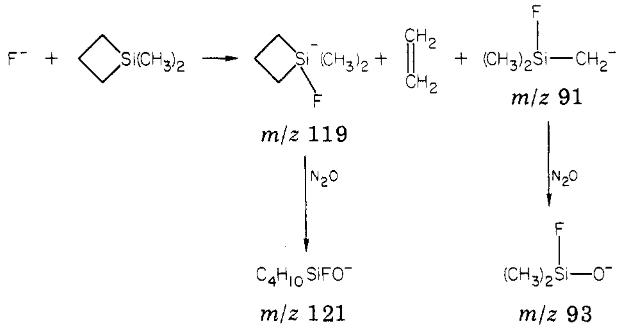
Not only can silyl anions and silicon-stabilized carbanions be distinguished by N_2O, but isomeric silicon-stabilized carbanions can be distinguished from one another. For example, proton abstraction from trimethylvinylsilane could occur either from the vinyl or the methyl group (eq 11). After reaction with N_2O only the *m/z* 101 ion is

$$(CH_3)_3SiCH{=}CH_2 + H_2N^- \rightarrow \underset{m/z\ 99}{(CH_3)_2Si(CH_2^-)CH{=}CH_2} \xrightarrow{N_2O} \underset{m/z\ 101}{(CH_3)_2Si(O^-)CH{=}CH_2} \quad (11)$$

formed, showing that proton abstraction from methyl takes place. In contrast, proton abstraction occurs from both methyl and butyl groups in butyltrimethylsilane (eq 12).

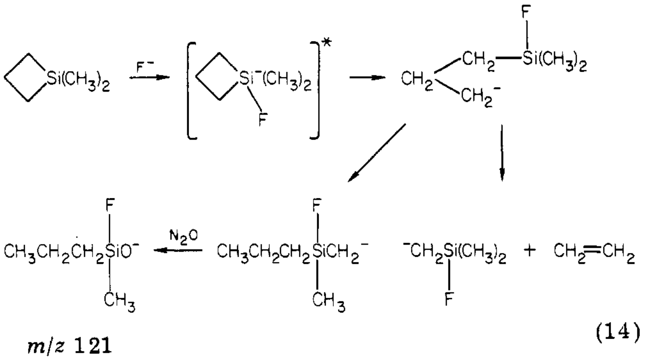
$$(CH_3)_3SiCH_2CH_2CH_2CH_3 + H_2N^- \rightarrow \xrightarrow{N_2O} (CH_3)_3SiO^- + (CH_3)_2Si(O^-)CH_2CH_2CH_2CH_3 \quad (12)$$

We have also used N_2O to probe the structure of the anion obtained by reaction of dimethylsilacyclobutane (DMSCB) and fluoride ion. We have reported earlier[3] that both an adduct (*m/z* 119) and an adduct minus ethylene (*m/z* 91) are formed. These products were formulated as shown in eq 13. In agreement with this equation, the



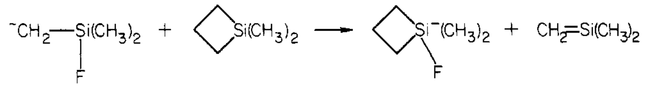
(13)

latter ion (*m/z* 91) indeed reacts with N_2O to form the expected siloxide. To our great surprise, however, some of the former ion, which we though to be exclusively the silacyclobutane adduct, also reacts with N_2O producing an ion with the loss of CH_2N_2. A more detailed investigation revealed that the ratio of *m/z* 119 to *m/z* 91 is dependent on the DMSCB concentration (flow) in the flow tube: at very low flows of DMSCB, very little *m/z* 119 ("adduct") forms, but nearly all that forms reacts with N_2O, while at high flows a large amount of *m/z* 119 forms, but only a relatively small amount of it reacts with N_2O. We believe these facts are accommodated by the reaction pathways shown in eq 14. Addition of F^- to DMSCB is highly



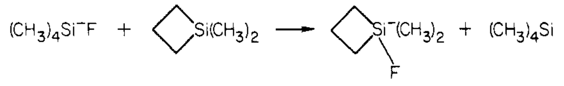
(14)

exothermic[3] leading to an excited adduct that ring cleaves before it can be collisionally cooled by the helium buffer gas. The resultant carbanion decomposes mainly by loss of ethylene, but a small amount undergoes intramolecular proton transfer to form the indicated silicon-stabilized carbanion. At higher neutral flows, there is sufficient DMSCB present for fluoride ion transfer to occur from the *m/z* 91 ion to DMSCB (eq 15). This transfer leads to an



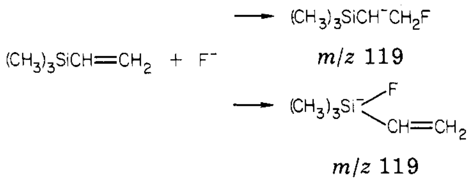
(15)

adduct with much less initial internal energy, one unlikely to fragment. We have independently made this adduct by the much less exothermic transfer of a fluoride ion from the fluorotetramethylsilyl anion (eq 16). When formed in this way, it does not react with N_2O.



(16)

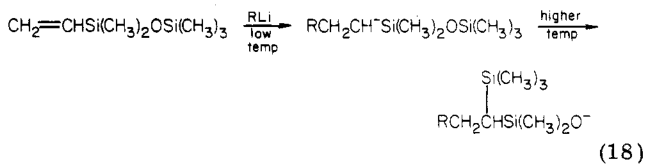
Vinyltrimethylsilane presents another problem that can be probed by N_2O. Two reasonable modes of addition are possible for its reaction with F^- (eq 17), one giving a silicon-stabilized carbanion and the other, a pentacovalent silicon anion. The ion obtained in the FA does not react



(17)

with N_2O, strongly suggesting that the pentacoordination pathway occurs under these conditions.

Finally, we have examined the reaction of H_2N^- and hexamethyldisiloxane in order to study a prototype of the carbanion to siloxide rearrangement studied in solution by West[10] and, more recently, Weber.[11] They found (eq 18) that at low temperature a silicon-stabilized carbanion



(18)

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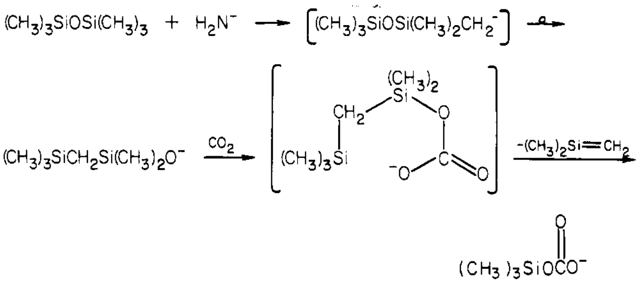
[9] Klass, G.; Trenerry, V. C.; Sheldon, J. C.; Bowie, J. H. *Aust. J. Chem.* **1981**, *34*, 519.

[10] Gornowicz, G. A.; West, R. *J. Am. Chem. Soc.* **1968**, *90*, 4478.

[11] Weber, W. P.; Firgo, H. A. *Organometallics* **1982**, *1*, 649.

Organometallics 1984, 3, 365–369

is formed but rearranges as the temperature is raised. When hexamethyldisiloxane and H_2N^- react in the FA, an M − 1 ion is obtained. It does not react with N_2O, suggesting that rearrangement is facile. To confirm this we reacted the M − 1 ion with the CO_2, a reagent which we have shown reacts with siloxides (CO_2 reacts with carbanions giving an adduct, but in this case we have demonstrated that no carbanion is present since no reaction with N_2O takes place.) to give carbonates. In this case, however, the simple carbonate is not obtained; rather $(CH_3)_2Si{=}CH_2$ is extruded as formulated in eq 19.



(19)

In summary, we have shown how N_2O can be used to distinguish among various anionic structures of silicon. In particular, silyl anions themselves react with N_2O for form siloxides by oxygen atom transfer, silicon-stabilized carbanions also react to form siloxides, but with loss of carbon, and pentacoordinate silicon anions do not react.

Acknowledgment. We wish to thank the Council on Research and Creative work of the University of Colorado graduate school and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of the work. Also we acknowledge the experimental help given by J. J. Grabowski.

Registry No. $(CH_3)_4Si$, 75-76-3; $(CH_3)_3SiO^-$, 41866-81-3; $(CH_3)_3SiNH^-$, 88035-99-8; $(CH_3)_3SiCH_2^-$, 88036-00-4; N_2O, 10024-97-2; $(CH_3)_3Si{-}Si(CH_3)_3$, 1450-14-2; $(CH_3)_3Si$, 54711-92-1; $(CH_3)_3Si{-}H$, 993-07-7; $(CH_3)_2SiHO^-$, 43641-64-1; $(CH_3)_3SiCH{=}CH_2$, 754-05-2; $(CH_3)_2Si(CH_2^-)CH{=}CH_2$, 88036-01-5; $(CH_3)_2Si(O^-)CH{=}CH_2$, 88036-02-6; $(CH_3)_3SiCH_2CH_2CH_2CH_3$, 1000-49-3; $(CH_3)_2Si(O^-)CH_2CH_2CH_2CH_3$, 88036-03-7; $(CH_3)_3SiOSi(CH_3)_3$, 107-46-0; $(CH_3)_2Si{=}CH_2$, 4112-23-6; DMSCB, 2295-12-7; 1,1-dimethyl-1-fluoro-1-silacyclobutaneanion, 76346-24-2; trimethylfluorosilane anion, 76350-68-0; dimethylfluorosilanol anion, 88036-04-8; fluorotrimethylvinylsilane anion, 88036-05-9.

A Tin Four- to Five-Coordinate Reaction Path. Molecular Structures of the Cyclic Stannanes (t-Bu)$_2$Sn(OCH$_2$CH$_2$)$_2$NMe and Me$_2$Sn(SCH$_2$CH$_2$)$_2$NMe[1,2]

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Received June 13, 1983

The molecular structures of *N*-methyl-5,5-di-*tert*-butyldiptychoxazstannolidine (**4**, (t-Bu)$_2$Sn(OCH$_2$CH$_2$)$_2$NMe) and *N*-methyl-5,5-dimethyldiptychthiaazstannolidine (**5**, Me$_2$Sn(SCH$_2$CH$_2$)$_2$NMe) were determined by X-ray analysis. As a result, the two trigonal-bipyramidal forms **1** and **2** postulated to equilibrate in a fast intramolecular exchange by NMR were isolated for the first time. **4** crystallizes in the monoclinic space group $P2_1/c$ ($Z = 12$) with $a = 22.655$ (5) Å, $b = 25.990$ (4) Å, $c = 9.036$ (2) Å, and $\beta = 106.97$ (2)°. The structure refined to $R = 0.074$ and $R_w = 0.098$. Three independent molecules are present per unit cell. **5** crystallizes in the orthorhombic space group $P2_12_12_1$ ($Z = 4$) with $a = 8.844$ (2) Å, $b = 9.253$ (3) Å, and $c = 14.309$ (12) Å. The structure refined to $R = 0.038$ and $R_w = 0.073$. Pentacoordination is achieved by N→Sn dative bonding in both compounds. For **4**, the most electronegative atoms, the ring oxygens, are located in apical positions. For **5**, the less electronegative ring sulfur atoms are situated equatorially leaving a methyl group and the N→Sn bond in apical positions. The N–Sn dative bond formed in an equatorial position for **4** is the first example of this type. The N→Sn dative bond in **4** (2.32 (2) Å average) is the shortest and the one in **5** (2.58 (1) Å) is the longest so far reported. The tin atom lies on the equatorial plane in **4**, whereas, for **5**, the tin atom is displaced 0.37 Å out of the equatorial plane toward the apical methyl group. In a series of related five-coordinated cyclic tin(IV) acid–base adducts that are shown to follow a tetrahedral to trigonal-bipyramidal coordinate and serve as a model for nucleophilic substitution of Sn(IV) tetracoordinate compounds, **5** has the most tetrahedral character. It is reasoned that intramolecular ligand exchange occurring by way of a Berry pseudorotation route at low temperatures and a dissociation–inversion route at higher temperatures is plausible. However, as the five-coordinated tin structures become more trigonal bipyramidal, a greater preference for intramolecular ligand exchange via the pseudorotation route is expected.

Introduction

Diptychstannolidines are examples of nonrigid pentacoordinated tin compounds that contain an intramolecular N→Sn dative bond. Most have been formed by the reaction of diorganotin(IV) derivatives with either diethanolamines or diethanthiolamines.[3] NMR data[4,5] support the two basic configurations, **1** and **2**, the particular one assumed depends on the nature of the groups

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[1] (a) Pentacoordinated Molecules. 49. Presented at the 182nd American Chemical Society National Meeting, New York, Aug 1981; American Chemical Society: Washington, DC, 1981; Abstract No. INOR 144. Previous paper in the series: Day, R. O.; Schmidpeter, A.; Holmes, R. R. *Inorg. Chem.* **1983**, *22*, 3696.

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[5] (a) Zschunke, A.; Tzschach, A.; Jurkschat, K. *J. Organomet. Chem.* **1976**, *112*, 273. (b) Jurkschat, K.; Mügge, C.; Tzschach, A.; Zschunke, A.; Larin, M. F.; Pestunovich, V. A.; Voronkov, M. G. *Ibid.* **1977**, 139, 279. (c) Mügge, C.; Jurkschat, K.; Tzschach, A.; Zschunke, A. *Ibid.* **1979**, *164*, 135.

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