9, and a doublet at 4.26 (J_{HP} = 4.9 Hz), area 2. Small amounts of impurities were also present. Hydrolysis yielded trineopentyl phosphate and neopentyl alcohol as evidenced by ^1H and ^{31}P nmr.

Reaction of Neopentyl Hypochlorite and Trimethyl Phosphite. In a typical experiment, trimethyl phosphite, 0.3117 g (0.0025 mol), was treated at −78° with 68 ml of 0.37 *M* neopentyl hypochlorite solution. The nmr spectrum of the reaction mixture on 100-Hz sweep width indicated neopentyl chloride was not present. When neopentyl chloride was added it could be detected. Other products were those reported before.[4,13]

In another experiment the phosphite, 0.9 g (0.0072 mol), in 5 ml of 1,2-dichloroethane and 10 ml of methylene chloride was added dropwise to a solution of 1.4 g (0.007 mol) of silver fluoroborate and 10 ml of 0.72 *M* neopentyl hypochlorite in 18 ml of 1,2-dichloroethane and 20 ml of methylene chloride maintained between −63 and −70°. The reaction mixture was allowed to warm to room temperature and filtered and the solvent was evaporated to give 1.6 g of oil. The ^1H nmr spectrum in methylene chloride showed a singlet at 1.02, doublet at 4.23 (J_{PH} = 11.5 Hz), and doublet at 4.25 (J_{PH} = 5.5 Hz). These absorptions are assigned to the neopentyl methyls, the methoxy methyls, and the neopentyl methylene, respectively. The salt was not too stable and after 6 days in a refrigerator a new singlet at 0.98 and a doublet at 3.95 (J_{PH} = 11.5 Hz) were noted. These absorptions are probably due to the boron trifluoride complex of dimethyl neopentyl phosphate.

Acknowledgment. Receipt of an FMC Foundation Fellowship by J. H. F. is gratefully acknowledged.

The Determination of the Stereochemical Stability of Organotin Compounds by Nuclear Magnetic Resonance

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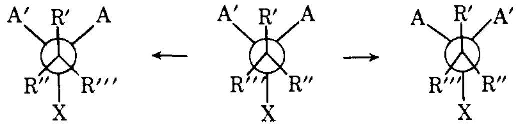
Abstract: The diastereotopic methyl protons in methylneophylphenyltin chloride (**1**) are observably anisochronous in dilute solution in nonpolar solvents. Coalescence of the signals can be produced at a given temperature by addition of a ligand such as DMSO-d_6 or by using a polar solvent such as methylene chloride. The higher the concentration of **1** the lower the temperature required to produce coalescence. Coalescence results from rapid exchange of the diastereotopic nucleii and the observation of a time-averaged signal. The most reasonable mechanism for exchange involves pseudorotation with inversion of configuration at tin. The diastereotopic methyl protons of dimethylphenyl(2-phenylpropyl)tin (**2**) are anisochronous at least up to 222° neat and 160° in the presence of DMSO-d_6–dioxane 1:2. The minimum mean lifetime, at room temperature, for an asymmetric organotin center with four carbon to tin bonds should be greater than 100 days.

In 1900 Pope and Peachey reported the resolution of ethylmethylpropyltin iodide.[1] However subsequent attempts to reproduce this resolution have been unsuccessful.[2,3] In 1928 Kipping attempted unsuccessfully to resolve a number of asymmetric organotin compounds.[4] The recent preparation of optically active, functionally substituted, organosilicon[5] and organogermanium compounds[6] has lead to a resurgence of interest in the resolution of organotin compounds.[3,7] The present study was undertaken to determine if an asymmetric organotin center had sufficient stereochemical stability to allow resolution and to be of use in determining the stereochemistry of substitution at tin.

The method employed was based upon the chemical-shift nonequivalence of diastereotopic nucleii.[8] From the Newman projection formulae of R′R′′R′′′MM′-A_2X it is obvious that inversion of configuration at either M or M′ will lead to an exchange in the magnetic environment of the two diastereotopic A groups. In the absence of exchange A and A′ will be anisochronous. The magnitude of the chemical shift nonequivalence (Δ*AA*′) will depend upon the extent of the difference between the magnetic environment of the two sites. The two sites may be sufficiently similar so that the spectrometer cannot resolve the difference between the two signals. In benzylmethylphenylsilane and in α-bromobenzyldimethylchloromethylsilane diastereotopic nucleii which were unresolved at 60 MHz were resolved at 100 MHz, while in methylneophylphenyltin hydride the diastereotopic nucleii are unresolved even at 100 MHz.[9] Alternatively, the failure to observe chemical-shift nonequivalence may be due to rapid exchange between the two sites with the resultant observation of a time-averaged signal.[8]



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[2] C. N. Naumov and Z. M. Manulkin, *Zh. Obshch. Khim.*, **5**, 281 (1935).

[3] (a) R. W. Bott, C. Eaborn, and G. Redl, unpublished results; (b) G. Redl, Ph.D. Thesis, University of Leicester, 1963.

[4] F. B. Kipping, *J. Chem. Soc.*, 2365 (1928).

[5] L. H. Sommer "Stereochemistry, Mechanism and Silicon," McGraw-Hill Book Co., Inc., New York, N. Y., 1965.

[6] (a) A. G. Brook and G. J. D. Peddle, *J. Amer. Chem. Soc.*, **85**, 1869, 2338 (1963); (b) C. Eaborn, P. Simpson, and I. P. Varma, *J. Chem. Soc.*, *A*, 1133 (1966).

[7] (a) M. LeQuan Minh and M. H. Normant, *Compt. Rend.*, *C*, **266**, 832 (1968); (b) S. Boue, M. Gielen, and J. Nasielski, *Tetrahedron Lett.*, 1047 (1968); (c) M. Gielen, J. Nasielski, and J. Topart, *Rec. Trav. Chim. Pays-Bas*, **87**, 1051 (1968).

[8] K. Mislow and M. Raban in "Topics in Stereochemistry," Vol. 1, N. L. Allinger and E. L. Eliel, Ed., Interscience Publishers, New York, N. Y., 1967 pp 1–38.

[9] G. Redl and G. J. D. Peddle, to be published.

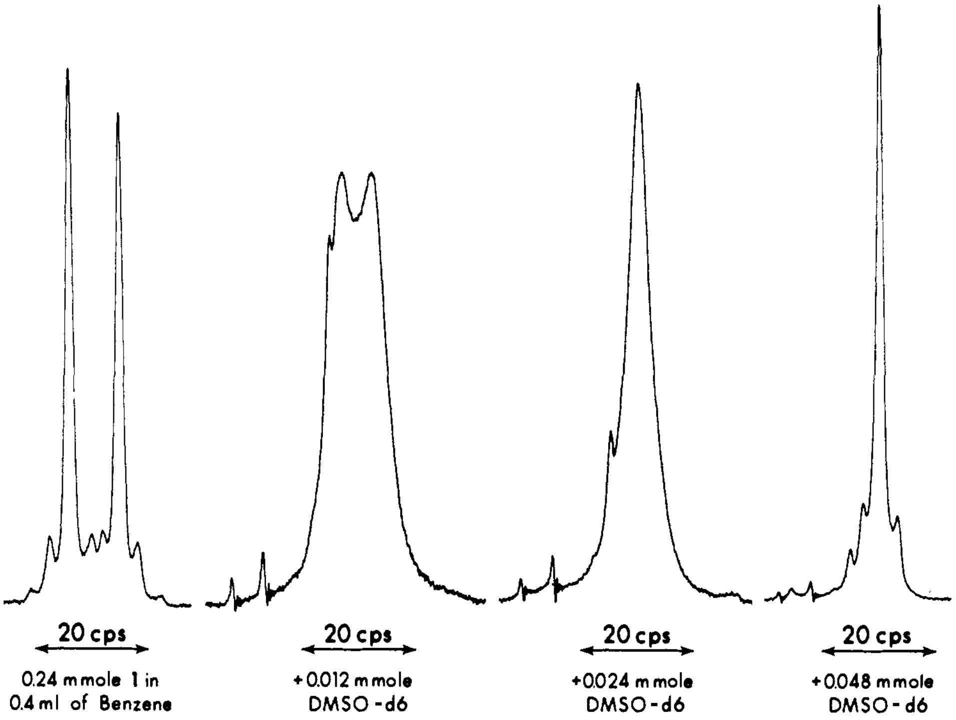


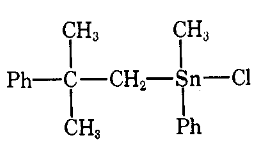
Figure 1. The effect of added DMSO-d_6 on the nmr spectra of the diastereotopic neophyl methyl groups of **1**.

In addition, whether a given pair of diastereotopic nucleii will be observably anisochronous may depend, quite apart from any exchange process, on the relative rotamer populations around the bond or bonds connecting the diastereotopic nucleii to the asymmetric center. Thus the observed chemical shift nonequivalence $\Delta AA'$ can be expressed as the sum of two terms[10]

$$\Delta AA' = \Delta cp + \Delta id$$

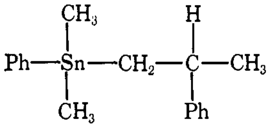
where Δcp is a temperature-dependent contribution due to unequal conformer populations and Δid is a temperature-independent contribution due to intrinsic diastereotopic nonequivalence. As the temperature is raised, the ratio of the conformer populations will approach unity and Δcp will approach zero. As a result the value of $\Delta AA'$ will change to approach a limiting value equivalent to Δid. A clear example for a nonzero Δid value for diastereotopic protons has recently been reported.[11]

For this investigation two related organotin systems were chosen. The first was methylneophylphenyltin chloride, **1**,[12] which was chosen as a representative compound with a good leaving group on tin. The second was dimethylphenyl(2-phenylpropyl)tin in which tin is bonded only to carbon. To investigate the stereochemical stability of an organotin compound with four carbon to tin bonds it was necessary to use **2** since studies of a variety of organosilicon, germanium, and tin compounds had shown that diastereotopic groups attached to asymmetric organometallic centers with four carbon to metal bonds were usually not observably anisochronous.[9,13]



$\mathrm{Ph{-}C(CH_3)_2{-}CH_2{-}Sn(CH_3)(Ph){-}Cl}$

1

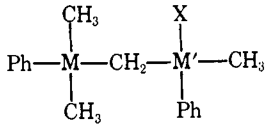


$\mathrm{Ph{-}Sn(CH_3)_2{-}CH_2{-}CH(Ph){-}CH_3}$

2

Methylneophylphenyltin Chloride. Nonequivalence of the neophyl methyl groups (γ protons) was observed in the spectra of dilute solutions of **1** in solvents of low polarity such as benzene, toluene, or carbon tetrachloride (see Figure 1). In contrast to this the methylene protons of **1** were unresolved under all the conditions studied.

Investigation of a number of carbon, silicon, germanium, and tin compounds showed that in each case



$\mathrm{Ph{-}M(CH_3)_2{-}CH_2{-}M'(X)(Ph){-}CH_3}$

M = C, Si, Sn; M′ = C, Si, Ge, Sn; X = Cl, H

the chemical shift difference of the diastereotopic methyl groups was much greater than that of the methylene protons.[9] Examination of Fischer–Hirschfielder–Taylor models of such compounds showed that the diastereotopic methyl groups were in intimate contact with the asymmetric substituents and, as a result, the

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(10) M. Raban, *Tetrahedron Lett.*, 3105 (1966).

(11) G. Redl and G. J. D. Peddle, *J. Phys. Chem.*, 73, 1150 (1969).

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(13) (a) G. J. D. Peddle and G. Redl, Abstracts, 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968, p M149; (b) G. J. D. Peddle and G. Redl, Abstracts, 2nd International Organosilicon Symposium, Bordeaux, France, July 1968, p 149.

differential shielding was presumably much larger than that of the methylene protons.

To demonstrate that the observed chemical shift nonequivalence is due to the diastereotopic nature of the protons we studied the spectra of a variety of other neophyl-substituted silicon, germanium, and tin compounds (*e.g.*, neophyldiphenyltin iodide) but, as expected, chemical shift nonequivalence was only observed for diastereotopic nucleii.[9] Also, the methyl groups are isochronous in tetraneophyltin.[14]

The two side bands on the neophyl methyl signals in the spectra of **1** were assigned to long range coupling with the $Sn^{117/119}$ isotopes. Similar coupling was observed for the neophyl methyl groups in triphenylneophyltin, diphenylneophyltin iodide, diphenylmethylneophyltin, methylphenylneophyltin hydride, and for the γ protons in **2**. The coupling was the same at 60 and 100 MHz and it was absent in analogous carbon, silicon, and germanium compounds. Over the range of temperatures (-30–$+30°$) where the $Sn^{117/119}$–$H\gamma$ coupling was resolvable the coupling of the high field protons decreased (8.5–7.0 cps) while that of the low field protons increased (5.4–6.1 cps) as the temperature was raised.

The nonequivalence of the methyl groups of **1** in nonpolar solvents (Figure 1) provides the first direct evidence for the existence of an asymmetric organotin center. The spectra showed a very marked concentration and solvent dependence. In dilute benzene solution at 38° the chemical-shift difference of the diastereotopic γ protons was 0.086 ± 0.01 ppm and the peak widths at half-heights were 1.55 ± 0.05 cps. No definite change in these parameters could be detected in the concentration region of 0.012–0.2 *M*. As the concentration was increased above 0.2 *M*, peak broadening was observed, followed by coalescence (at $\sim$2.0 *M*), and finally the signal sharpened into a singlet.

The coalescence temperature was concentration dependent. As the concentration of a benzene solution of **1** was decreased from 3.4 to 1.3 *M* the temperature of coalescence increased from 30 to 70°. In 0.7 *M* toluene solution coalescence did not occur up to 130° but the chemical-shift nonequivalence showed the expected[10,11] temperature dependence (the magnitude of the splitting decreased with increasing temperature). At low temperatures ($< -60°$) loss of resolution as a result of viscosity effects and, possibly, of the slowing of rotamer interconversion leads to signal broadening. However, even at $-100°$ in trichlorofluoromethane it was not possible to observe signals attributable to the separate rotamers of **1**.

For a given concentration the coalescence temperature was lower in polar solvents such as methylene chloride than in the less polar solvents such as benzene, toluene, or carbon tetrachloride. Thus while the anisochronous methyl groups in a 0.7 *M* solution of **1** in toluene did not show even a change in line width and were clearly nonequivalent ($\Delta H\gamma H\gamma' = 5.6$ cps) at 130°, for a 0.7 *M* solution in methylene chloride coalescence occurred at $\approx -40°$.

Coalescence could also be produced in nonpolar solvents by the addition of a variety of ligands such as DMSO-d_6, perdeuterioacetone, or hydrogen chloride. The addition of 2 μl (0.02 mmol) of DMSO-d_6 to 0.4 ml of a 0.6 *M* solution (0.24 mmol) of **1** in benzene led to coalescence of the anisochronous neophyl methyl groups (see Figure 1). Under similar conditions 80 μl (1 mmol) of perdeuterioacetone was required to produce coalescence. The effect of hydrogen chloride was observed accidentally when it was found that the neophyl methyl groups of **1** were isochronous in perdeuteriobenzene.[15] The most probable source of the difference in behavior between benzene and perdeuteriobenzene solutions of **1** was possible residual deuterium chloride in the perdeuteriobenzene. It was confirmed that the addition of a small amount of hydrogen chloride to a 0.7 *M* solution of **1** in benzene produced coalescence of the anisochronous methyl groups.

(2-Phenylpropyl)dimethylphenyltin. The diastereotopic methyl groups of **2** were anisochronous (Figure 2) while the diastereotopic methylene protons were unresolved in all the recorded spectra. As in other systems where conformer equilibration is possible[10,11] the magnitude of $\Delta HH'$ was temperature dependent and decreased for a neat[16] **2** from 3.0 cps at 62° to 0.7 cps[17] at 222°. No noticeable line broadening was observed at 160° for a 10% solution of **2** in DMSO-d_6–dioxane (1:2).

Discussion

The observation of chemical-shift nonequivalence for the neophyl methyl groups in **1** proves that asymmetric organotin compounds can exist in enantiomeric pairs and that these enantiomers have finite lifetimes.

The most reasonable explanation for the observed line broadening and the eventual coalescence of the anisochronous peaks that occurs when either the concentration of **1** is increased, or when a good ligand is added to a dilute solution of **1** in nonpolar solvents, is a rapid interchange between the different magnetic environments of the diastereotopic nucleii with the resultant observation of a time-averaged signal. Such an interchange is equivalent to inversion of configuration at the asymmetric organotin center.

Organotin halides undergo facile halogen–halogen exchange[18] and it is probable that the increase in the rate of inversion with increasing concentration of **1** is due to chloride–chloride exchange. The observation of an increase in the rate of inversion upon the addition of trimethyltin chloride to a dilute solution of **1** in benzene provides support for a connection between chloride exchange and inversion. A detailed kinetic study of the rates of halogen exchange and of inversion of configuration is in progress.

The DMSO-induced peak coalescence (see Figure 1) which takes place in dilute solutions suggests that a second inversion mechanism independent of the chloride exchange must be operative. Such an inversion can be explained on the basis of coordination of a ligand to **1** to give a five-coordinate tin complex. It does not matter whether the complex is a trigonal bipyramid or

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(14) H. Zimmer, O. A. Homberg, and M. Jayawant, *J. Org. Chem.*, **31**, 3857 (1966).

(15) Supplied by Merck, Sharp and Dohme of Canada, Ltd.

(16) Approximately 10% 1,3-dimethoxybenzene was added as an internal reference. It is suggested that 1,3-dimethoxybenzene (mp $-55°$; bp 217°) is a useful solvent and internal standard for temperature-dependent pmr studies.

(17) Above 200° partial signal overlap led to low observed value for $\Delta HH'$.

(18) E. V. Van der Berghe, G. P. Van der Kelen, and Z. Eeckhaut, *Bull. Soc. Chim. Belges*, 76, 79 (1967).

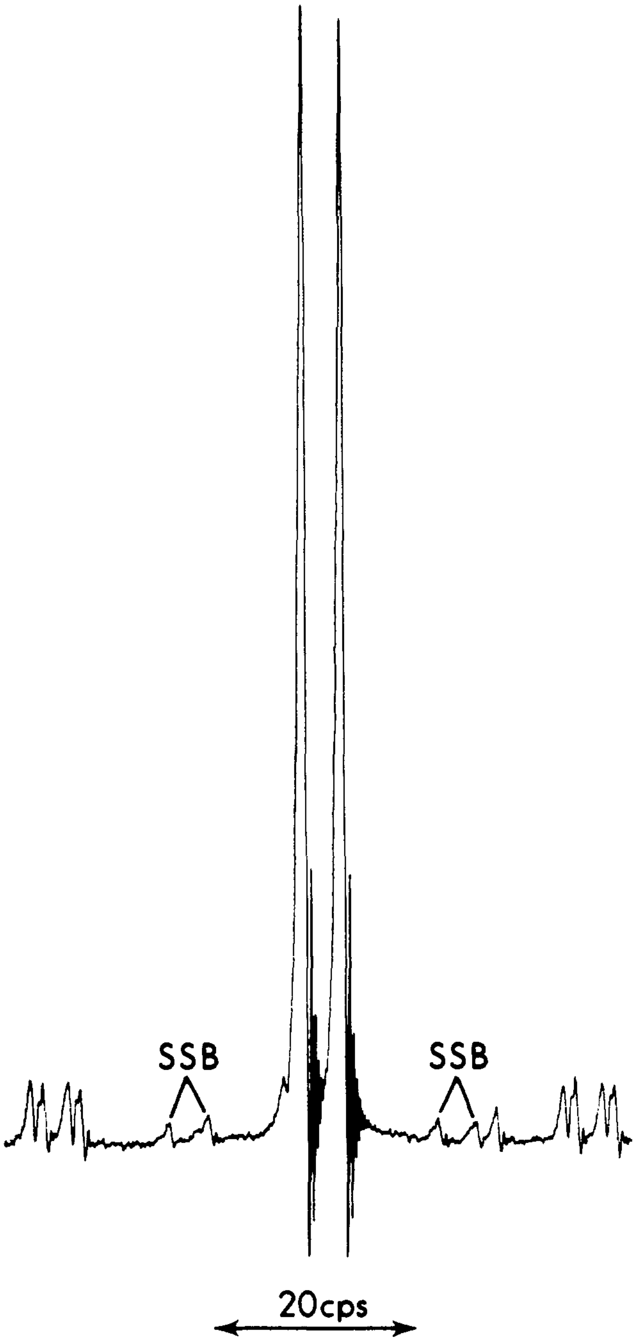

Figure 2. The nmr spectra of the diastereotopic methyl groups of **2**.

a tetragonal pyramid since the interconversion of the two would be expected to be facile,[19] and to result in racemization. Five-coordination complexes of trialkyltin halides with ligands such as DMSO are well known.[20,21] The racemization of α-naphthylphenylmethylfluorosilane[22] and of 1,2-difluoro-1,2-dimethyl-1,2-disilacyclohexane[23] has been proposed to follow a similar course.

Carre, Corrin, and Thomassin have suggested that the racemization of α-naphthylphenylmethylchlorogermane by THF probably involves the coordination of two molecules of solvent to the central atom to give a symmetric octahedral complex.[24] However, since trialkylorganogermanium and -organotin halides show a marked preference for the formation of 1:1 pentacoordinate complexes with ligands,[25] and since racemization can occur *via* tetragonal-pyramid complexes, it is unnecessary to propose the intermediacy of the much less stable octahedral complexes.

The diastereotopic methyl groups of **1** are unresolved in the neat liquid at 38°. As the sample is gradually diluted with benzene the peak broadens until a concentration of $\approx 2\ M$ is reached when two peaks can be seen. The separate peaks then sharpen with increasing dilution and reach a minimum line width at half-height of 1.5 cps at 0.2 *M* concentration. This value does not alter on further dilution to 0.012 *M*. Under the same conditions the line width at half-height for the nonexchanging methyl group on tin was 1.0 cps. We can assign the 0.5-cps difference between the two line widths to exchange broadening ($\delta\nu$) and estimate the mean lifetime (τ) of the inverting species to be $\approx$ 0.6 sec according to the slow exchange approximation.[26]

$$\tau = 1/\pi\delta\nu \qquad (1)$$

The barrier to exchange cannot be calculated directly from the temperature variation of the chemical-shift nonequivalence of the neophyl methyl groups of **1** since, as discussed earlier, the chemical shift difference will be dependent not only on the rate of exchange, but also upon the relative conformer populations.[10,11]

For **2**, in which the tin is bonded only to carbon, no exchange broadening of the diastereotopic methyl groups is observed up to 180°. At higher temperatures, overlap prevents an accurate estimation of line width, but no coalescence of the diastereotopic peaks was observed up to 222°. Since the spectrometer would readily show exchange broadening of greater than 0.1 cps it is possible, using eq 1, to assign a minimum mean lifetime of 3 sec to **2** at 180°. Assuming a unimolecular reaction and 10^{13} for the preexponential term, a lower limit of 28 kcal can be calculated as the Arrhenius activation energy for exchange. Thus at 30° the minimum mean lifetime for **2** is at least 100 days and it follows that an optically active organotin compound with four carbon to tin bonds should be stereochemically stable.

No exchange was observed for **2** even in the presence of a good ligand such as DMSO at 160°. This may be due to the known reluctance of organotin compounds with four carbon to tin bonds to form stable five-coordinate complexes.[27] If a weak association does occur at lower temperatures the complex would likely dissociate upon warming.

Westheimer has reported that alkylfluorophosphoranes do not undergo pseudorotation if an alkyl group

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[19] E. L. Muetterties and R. A. Schunn, *Quart. Rev.* (London), 245 (1966).

[20] H. G. Langer and A. H. Blut, *J. Organometal. Chem.*, **5**, 288 (1966).

[21] W. Kitching, *Tetrahedron Lett.*, 3689 (1966).

[22] L. H. Sommer and P. G. Roderwald, *J. Amer. Chem. Soc.*, **85**, 3898 (1963).

[23] K. Tamao, M. Ishikawa, and M. Kumada, *Chem. Commun.*, 73 (1969).

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[25] F. Rijkens and G. J. M. Van der Kerk, "Organogermanium Chemistry," Germanium Research Committee, Utrecht, Netherlands, 1964, pp 77–92.

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[27] (a) I. R. Beattie, *Quart. Rev.* (London), **17**, 382 (1963); (b) D. Seyferth and S. O. Grim, *J. Amer. Chem. Soc.*, 83, 1610 (1961).

would be forced into an apical position.[28] An analogous explanation could be advanced to explain the failure of any trigonal-bipyramid complex of **2** formed to undergo exchange since pseudorotation would require two alkyl groups to occupy apical positions in a trigonal-bipyramid complex.

Thus while it should be possible to resolve an optically active organotin compound with four carbon–tin bonds, it seems unlikely that such a compound would be very useful in investigating the stereochemistry of substitution at tin.

Experimental Section

The preparation of **1** and **2** will be reported shortly in connection with synthetic studies.[9]

Deuterated solvents were obtained from Merck Sharp and Dohme of Canada, Ltd. Other reagent grade solvents and chemicals were used as received.

Spectra were determined on a Varian Associates HA-100 spectrometer and where it was necessary to check for long-range coupling between the $Sn^{117/119}$-Hγ on a Varian Associates HA-56-60A spectrometer. The 100-MHz spectrometer was equipped with a variable temperature probe standardized against an iron-constantan thermocouple. Line positions were measured directly from calibrated chart paper or by using standard side band techniques.

Samples were degassed and sealed under vacuum prior to study, except in those cases where subsequent ligand addition was desired.

Acknowledgment. We thank the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation for financial support and Mr. D. Gifford for running the HA-100 spectra.

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Stereochemistry of Nucleic Acids and Their Constituents. VIII.[1a] Metal Binding Studies. Crystal Structure of a Guanine–Copper Chloride Complex, a Trigonal-Bipyramidally Coordinated Copper

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Contribution from the Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106. *Received May 16, 1969*

Abstract: The X-ray crystal structure of the complex $(C_5H_6N_5O)CuCl_3 \cdot H_2O$ has been determined using diffractometric single-crystal methods. The crystals are monoclinic, $a = 16.952$, $b = 10.183$, $c = 13.185$ Å, $\beta = 99.968°$, and the space group is C2/c. The structure consists of a binuclear complex with chlorine-bridged copper atoms bound to the N(9) atoms of center-related guanine moieties. Both the N(3) and N(7) sites on the guanine ring are protonated, and these sites participate in hydrogen bonding with neighboring molecules. The combined effect of metal and proton binding severely perturbs the π-electron system of the guanine ring, causing a significant shrinking of the imidazole portion of the ring relative to neutral guanine. The pentacoordinated copper complex displays trigonal-bipyramidal geometry as opposed to the more common square-pyramidal environment. Three chlorine atoms occupy the trigonal plane, while the N(9) atom of guanine and another chlorine take up the axial positions. The axial Cu–Cl bond length is found to be about 0.11 Å shorter than the in-plane Cu–Cl bond length, a feature which may be characteristic of trigonal-bipyramidal coordination of copper.

The importance of metal ions in protein chemistry has long been recognized, and exhaustive studies have been reported in this area. More recently, the related and equally important involvement of metal ions in nucleic acid processes has received considerable attention.[2,3] Model studies with DNA and its constituents have shown that metals bind to various sites of the double helix, bringing about either stabilization (*e.g.*, Mg^{2+}, Na^+, Ni^{2+}) or destabilization (*e.g.*, Cu^{2+}, Cd^{2+}, Pb^{2+}) of the ordered structure. While spectral and potentiometric studies have shed some light on these interactions,[2,3] very few X-ray crystal structures are available to show the precise binding sites of metals to the nucleic acid components.[4,5] We are engaged in an X-ray crystallographic study of pertinent complexes, not only to explain metal binding, but also to provide analog structures which may facilitate work in progress on the structure of transfer RNA. Here we report the crystal structure of a guanine–copper chloride complex showing preferential binding of copper to the N(9) of the imidazole ring, a site normally blocked by the sugar–base glycosidic bond in DNA and RNA.

Yellow-brown crystals of $(C_5H_6N_5O)CuCl_3 \cdot H_2O$ were prepared by treating guanine with an approximate 4:1 molar excess of $CuCl_2 \cdot 2H_2O$ in hot, aqueous HCl. Preliminary oscillation, Weissenberg, and precession photographs showed the space group to be either Cc or C2/c. The successful structure analysis and refinement in the centrosymmetric space group C2/c are taken as confirmation of that choice. Crystal data are: $a = 16.952 \pm 0.001$, $b = 10.183 \pm 0.001$, $c = 13.185 \pm 0.001$ Å; $\beta = 99.968 \pm 0.004°$; $D_m = 2.024$ g cm^{-3},

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[1] (a) Parts VII and VI are in press in "Synthetic Procedures in Nucleic Acid Chemistry," Vol. 2, W. W. Zorbach and R. S. Tipson, Ed., and *Acta Crystallogr.*, respectively; (b) to whom inquiries and reprint requests should be sent at this address: Department of Biochemistry, University of Wisconsin, Madison, Wisconsin 53706.

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