Journal of Organometallic Chemistry
Elsevier Publishing Company Amsterdam
Printed in The Netherlands

SHORT COMMUNICATION

Preparation and far infrared spectrum of tetramethylammonium dichlorotriphenylstannate(IV)*

Recently the stereochemistry of some pentacoordinate compounds of tin has been established[1], *e.g.*, $[\text{Sn}(\text{CH}_3)_3\text{F}]_n$, $[\text{Sn}(\text{CH}_3)_3(\text{OH})]_2$, $\text{Sn}(\text{C}_5\text{H}_5\text{N})(\text{CH}_3)_3\text{Cl}$, etc. Here the preparation of a compound of pentacoordinate tin, *viz.*, tetramethylammonium dichlorotriphenylstannate(IV), is reported and its stereochemistry is established by far infrared spectroscopy as trigonal bipyramidal with the three phenyl groups occupying equatorial positions and the two chlorine atoms occupying apical positions.

The infrared spectrum was taken from 4000 cm^{-1} to 70 cm^{-1} and the instruments used have been described elsewhere[2]. The observed vibrational modes of the SnC_3Cl_2 skeleton are 460, 450, 190, 150, and 135 cm^{-1}. If the $\text{Ph}_3\text{SnCl}_2{}^-$ anion is considered to be monomeric, the tin atom must be pentacoordinate and various structures based on the trigonal bipyramid and the square based pyramid are possible. According to selection rules, the infrared spectrum of all the structures except D_{3h} would be expected to exhibit eleven (C_{2v}) or twelve (C_s) fundamental bands. Thus the observed bands cannot be in accord with C_{2v} or C_s symmetry. A dimeric structure of this compound in which molecules are connected by chlorine bridges would have lower symmetry, and again the observed bands are not in accord with this structure. By contrast the D_{3h} structure has only five allowed fundamentals in the infrared region $(2a_2''+3e')$ and the observed spectrum can be interpreted in terms of this symmetry. Thus the band at 460 cm^{-1} is assigned to SnC_3 anti-symmetrical stretch. The splitting of SnC_3 antisymmetrical stretch into two bands, *i.e.* 460 cm^{-1} and 450 cm^{-1}, may be due to a "solid state" effect. The band at 190 cm^{-1} may be assigned to SnCl_2 antisymmetrical stretch. The bands at 150 cm^{-1} and 135 cm^{-1} may be due to SnC_3 out of plane bending and SnC_3 in plane bending. The SnCl_2 bending was not observed above 70 cm^{-1} and therefore it is not possible to assign it. Thus D_{3h} symmetry is favoured in which three phenyl groups occupy the equatorial positions and two chlorine atoms occupy the apical positions.

If the spectrum of the SnC_3Cl_2 skeleton is compared with the spectrum of the SnC_3Cl skeleton in triphenyltin chloride, two important features emerge. The Sn–C stretch (449 cm^{-1})[4] in SnC_3Cl skeleton is slightly at lower position than the SnC_2 antisymmetrical stretch in SnC_3Cl_2 skeleton, although the coordination number of latter compound is five. Thus there may be a slight strengthening of the C–Sn bond in SnC_3Cl_2 skeleton as compared to the Sn–C bond in SnC_3Cl skeleton. By contrast, the Sn–Cl bond in the SnC_3Cl_2 skeleton is weakened as compared to the Sn–Cl bond in the SnC_3Cl skeleton, because the position of the SnCl_2 antisymmetrical stretch at 190 cm^{-1}, is much lower than the Sn–Cl stretch (332 cm^{-1})[4] of the SnC_3Cl skeleton. It appears that the tin atom in the $\text{Sn}(\text{C}_6\text{H}_5)_3\text{Cl}_2^-$ anion may be using sp^2 hybrid

---

* This work was done at the University of Newcastle Upon Tyne.

orbitals in forming the three equatorial bonds with the phenyl groups. The tin atom could then use its remaining *p* orbital to form two three-centre four-electron bonds[5] with the two apical chlorine atoms. The Sn–Cl bonds would then possess individual bond orders of roughly $\frac{1}{2}$, thereby ensuring that the Sn–Cl bond in $Sn(C_6H_5)_3Cl_2^-$ will be weaker than in triphenyltin chloride.

A recent X-ray analysis[1] of the $Sn(CH_3)_2Cl_3^-$ anion shows that the apical Sn–Cl bond (2.54 Å) is longer than the equatorial Sn–Cl bond (2.35 Å). In addition the anion is distorted from a regular trigonal bipyramid. The longer apical Sn–Cl bonds can be interpreted on the Rundle's formulation which neglects *d* orbitals. However the possibility of some π-bonding or *d* orbital participation in the Cl–Sn–Cl bonds is not excluded. This simple picture of the bonding does not explain the distortion of molecule from ideal geometry which may be due to secondary effects[5]. By applying VSEPR theory[6] to the $Sn(CH_3)_2Cl_3^-$ anion the distortion of this molecule from a regular trigonal bipyramid may be qualitatively understood.

Tetramethylammonium dichloro/triphenylstannate(IV) was prepared by dissolving triphenyltin chloride (1 mole) in hot n-propanol in a round bottom flask fitted with a condenser and P_2O_5 guard tube. Tetramethylammonium chloride (1 mole) dissolved in hot n-propanol was then added and a white solid was precipitated. This was filtered off after digestion on a water bath for 0.5 h, washed several times with hot n-propanol and finally with petroleum ether (boiling range 40–60°). The compound was dried in vacuum at 60°. It is soluble in nitromethane. The compound was characterized by elemental analysis for tin, nitrogen and chloride. (Found: Cl, 14.6; N, 2.9; Sn, 24.3. $C_{22}H_{27}Cl_2NSn$ calcd.: Cl, 14.32; N, 2.83; Sn, 23.97%.)

Acknowledgements

I thank Prof. N. N. GREENWOOD for providing laboratory facilities during my stay at the University of Newcastle Upon Tyne (from 1962–65) and Dr. G. S. RAO and Mr. V. B. KARTHA of B.A.R.C. for helpful discussions.

Chemistry Division,
Bhabha Atomic Research Centre,
Bombay-74 (India)

T. S. SRIVASTAVA

1 E. L. MUETTERTIES AND R. A. SCHUNN, *Quart. Rev.*, 20 (1966) 245.
2 N. N. GREENWOOD, T. S. SRIVASTAVA AND B. P. STRAUGHAN, *J. Chem. Soc., A*, (1966) 699.
3 G. W. FRASER, N. N. GREENWOOD AND B. P. STRAUGHAN, *J. Chem. Soc.*, (1963) 698.
4 T. S. SRIVASTAVA, *J. Organometal. Chem.*, 10 (1967) 373.
5 P. C. VAN DER VOORN AND R. S. DRAGO, *J. Am. Chem. Soc.*, 88 (1966) 3255.
6 R. J. GILLESPIE, *J. Chem. Educ.*, 40 (1963) 298.

Received March 21st, 1967