Inorganica Chimica Acta, 102 (1985) L17–L18

Observation of Slow Berry Pseudorotation for a Pentacoordinated Tin(IV) System

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Received March 9, 1985

Whereas many examples of isomerisation of pentacoordinated phosphorus structures via a Berry pseudorotation [1] are known [2] and somewhat fewer for silicon compounds [3], there appear to be no reported examples for tin in which intramolecular structural fluxionality can be slowed for a pentacoordinate tin(IV) complex with monodentate ligands. Intramolecular mobility of pentacoordinate tin(IV) has been observed for diptychoxazostannolidines, which contain a tridentate ligand, where a dissociation-isomerisation process is involved [4]. In this paper we report the first observation of an intramolecular exchange involving monodentate ligands on five coordinate tin(IV) which can be slowed to allow detection of the individual isomers.

During the continuation of our investigations involving ^{31}P and ^{119}Sn NMR to study the Lewis acidity of tin(IV) compounds [5, 6] we prepared, *in situ*, the 1:1 adducts $Ph_2SnCl_2 \cdot Bu_3P{=}O$ and $Ph_2SnBr_2 \cdot Bu_3P{=}O$. Intermolecular exchange of $Bu_3P{=}O$ within either compound is rapid at room temperature but is slowed sufficiently at −60 °C to permit observation of ^2J(Sn–P). At −60 °C the ^{119}Sn NMR spectra of dichloromethane solutions containing equimolar quantities of either Ph_2SnCl_2 or Ph_2SnBr_2 with $Bu_3P{=}O$ are doublets with tin-119 chemical shifts consistent [7, 8] with the formation of pentacoordinated tin species. NMR data for all complexes discussed in this paper are given in Table I.

TABLE I. NMR Parameters for 1:1 Adducts Between Tributylphosphine-oxide, L, and Diphenyltindihalides in Dichloromethane Solution.

Compound	$\delta(^{31}P)^a$ (ppm)	$\delta(^{119}Sn)^a$ (ppm)	^2J(Sn–P) (Hz)	Temp. (°C)
Ph_2SnCl_2L	62.8	−276	156	−80
Ph_2SnBr_2L	62.6	−319	166	−80
$Ph_2SnClBrL^b$		−282	156	−100
		−312	163	−100

[a] ^{31}P Spectra referenced against 85% aqueous phosphoric acid; ^{119}Sn spectra referenced against $SnMe_4$, high frequency positive convention. [b] Observed in a mixture of $Ph_2SnCl_2/Ph_2SnBr_2/Bu_3P{=}O$ 1:1:2.

The analogous compound $Ph_2SnCl_2 \cdot Ph_3P{=}O$, which is not sufficiently soluble for tin NMR studies, has been isolated and studied by Mössbauer and IR spectroscopy and by dipole measurements with the conclusion that it has a trigonal bipyramidal structure (**1**) both in the solid state and in solution [9]. Several other 1:1 adducts between Ph_2SnCl_2 and monodentate oxygen donor ligands also have the same structure [10] and it seems reasonable to suggest this structure for the 1:1 adducts containing $Bu_3P{=}O$.

At −60 °C the tin-119 NMR spectrum of a dichloromethane solution containing Ph_2SnCl_2, Ph_2SnBr_2 and $Bu_3P{=}O$ in the molar ratio 1:1:2 shows doublets due to each of the adducts $Ph_2SnCl_2 \cdot Bu_3P{=}O$ and $Ph_2SnBr_2 \cdot Bu_3P{=}O$ as well as an extremely broad resonance ($w_{1/2}$ approx. 500 Hz) between these doublets (Fig. 1). Cooling to −75 °C causes the broad resonance to disappear but the other two doublets remain and sharpen. At −85 °C two additional broad resonances appear and at −100 °C each of these is resolved into a doublet. The integrated intensities of the four doublets are equal.

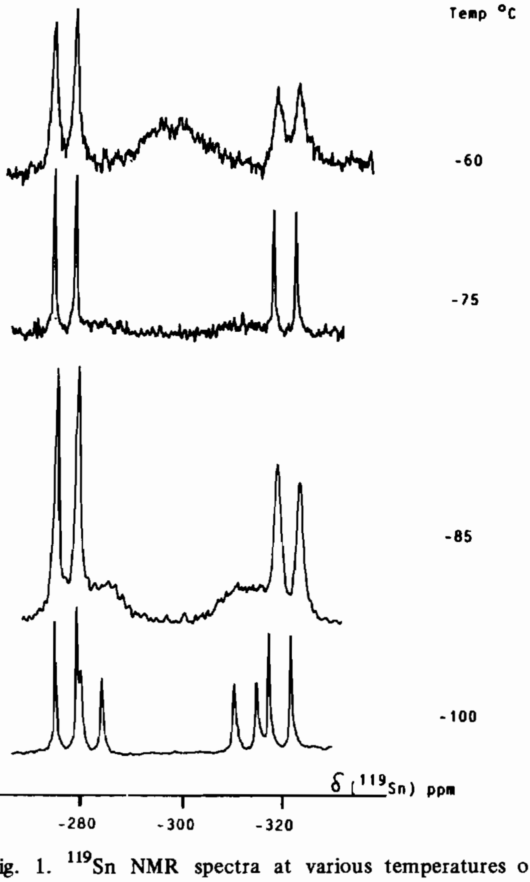

Fig. 1. ^{119}Sn NMR spectra at various temperatures of a mixture of $Ph_2SnCl_2/Ph_2SnBr_2/Bu_3P{=}O$ = 1:1:2.

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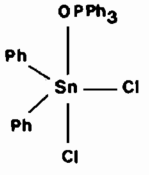
These results confirm that the 1:1 adducts also have the structure (1) and furthermore indicate the presence of the two possible isomers (2) and (3) of the mixed halogen species. These two isomers apparently undergo rapid Berry pseudorotation above approximately -75 °C to give an average NMR signal, whereas intramolecular exchange of the halogen atoms in either $Ph_2SnCl_2 \cdot Bu_3P{=}O$ or $Ph_2SnBr_2 \cdot Bu_3P{=}O$ does not change the structure of the adducts so sharp signals are observed at higher temperatures. In addition, the presence of these signals also rules out the possibility of either $Bu_3P{=}O$ or halide dissociation being the mechanism of exchange in the mixed ligand complex. Using a coalescence temperature of -75 °C, the calculated barrier to pseudorotation, $\Delta G^{\ddagger}$, for $Ph_2SnClBr \cdot Bu_3P{=}O$ is 35 KJ mol^{-1}.



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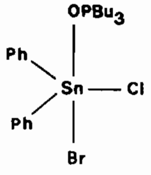

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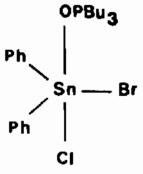

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Pentacoordinate tin(IV) complexes are thought to involve a secondary hybridisation such that the percentage of s character can be considered to concentrate in the orbitals of the trigonal plane giving them sp^2 character [11–14]. Under these circumstances, for a trigonal bipyramidal structure, the isomer with the more electron donating group in the equatorial plane, *i.e.* isomer (3), would give rise to the tin resonance at lower frequency.

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