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^{31}P and ^{119}Sn NMR Spectra of Complexes of Diphenyltin(IV)dichloride with Tri(n-octyl)phosphine Oxide

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Abstract

The ^{31}P and ^{119}Sn NMR spectra of the system diphenyltin(IV)–dichloride–tri(n-octyl)phosphine oxide, deuteriochloroform, were studied. The existence of the compound $Ph_2SnCl_2 \cdot L$ ($L = (n\text{-}C_8H_{17})_3PO$) and five isomers of the compound $Ph_2SnCl_2 \cdot 2L$ was revealed.

Introduction

During the study of ^{119}Sn NMR spectra of 1:1 adducts of Ph_2SnX_2 ($X = Cl$ or Br) with Bu_3PO in dichloromethane solutions, Colton and Dakternieks [1] observed only simple signals due to a rapid intermolecular exchange at room temperature. But at temperatures below −60 °C this intermolecular exchange of Bu_3PO is sufficiently slowed, and thus in both the diphenyltin(IV) dihalides it is possible to observe well resolved doublets. This splitting makes it possible to determine coupling constants $^2J(^{119}Sn^{31}P)$ and to identify the composition of the complexes formed in these systems. In the mixture of Ph_2SnCl_2 with Ph_2SnBr_2 and Bu_3PO (1:1:2) at −100 °C there were found both adducts of $Ph_2SnX_2 \cdot Bu_3PO$ and also two isomers of $Ph_2SnClBr \cdot Bu_3PO$. The formation of these isomers was thought to be a result of the Berry pseudorotation of these structurally flexible organotin complexes.

During the continuation of our investigation of organotin(IV) compounds and their complexes we studied the temperature dependences of ^{31}P and ^{119}Sn NMR characteristics of a similar system, *i.e.* diphenyltin(IV) dichloride-tris(n-octyl)phosphine oxide (L) in a solution of the mixture of dichloromethane and dideuteriodichloromethane (70:30 *v*/*v*) using the molar ratio of Ph_2SnCl_2:L equal to 1:1, 1:2 and 1:3, respectively. The parameters obtained for ^{31}P and ^{119}Sn NMR characteristics are given in Table I.

The behaviour of the system with the molar ratio of Ph_2SnCl_2:L = 1:1 is analogous to those described by Colton and Dakternieks [1]. The characteristic pattern of signals in ^{31}P and ^{119}Sn NMR spectra at 300 K gives evidence of a rapid intermolecular exchange of ligands. At 190 K it is possible to observe a well resolved doublet in ^{119}Sn NMR spectra and a

TABLE I. ^{31}P and ^{119}Sn NMR Parameters of $Ph_2SnCl_2 \cdot L$ and $Ph_2SnCl_2 \cdot 2L$

Compound	Temperature (K)	$\delta(^{31}P)^a$ (ppm)	$\delta(^{119}Sn)^b$ (ppm)	$^2J(^{119}Sn^{31}P)^c$ (Hz)
L	300	48.0		
$Ph_2SnCl_2 \cdot L$	300	61.6	-252^d	
	190	63.6	−279	158
$Ph_2SnCl_2 \cdot 2L$	300	58.0	-390^e	
	240	61.0^f		
	190	59.9 (~50%)	−477	170
		62.7 (~40%)	−472	179
		63.8 (~8%)	g	187
		66.0 (~1%)	g	g
		66.8 (~1%)	g	g

$^a\delta(^{31}P)$ referred to external 85% aqueous phosphoric acid. $^b\delta(^{119}Sn)$ referred to external neat $Sn(CH_3)_4$. $^c\pm 1$ Hz. ^{d}Broad signal. ^{e}Very broad signal. $^fw_{1/2} \sim 50$ Hz. ^{g}Not found.

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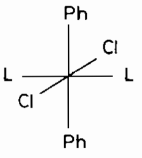
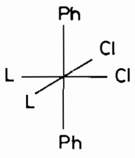
signal with satellites caused by the Sn–P interaction ($^2J(^{119}Sn^{31}P)$ = 158 Hz) in ^{31}P spectra. With decreasing temperature $\delta(^{119}Sn)$ is shifted upfield, while $\delta(^{31}P)$ is shifted downfield. This is in agreement with the idea of the increasing bond interaction $Sn \leftarrow OP$. We assume the splitting of the signal in ^{119}Sn NMR spectra into a doublet to be sufficient evidence for the composition of the complex to be described by the formula $Ph_2SnCl_2 \cdot L$ and for the composition of compounds studied in ref.1 as well.

In ^{31}P NMR spectra of the system with the molar ratio Ph_2SnCl_2:L = 1:2 at room temperature, it is also possible to observe only one signal corresponding to a rapid ligand exchange on the NMR time scale. The signal becomes broader with decreasing temperature and simultaneously the values of $\delta(^{31}P)$ are shifted downfield. At temperatures under 210 K we can observe five signals in ^{31}P NMR spectra (Table I), three of them having the appropriate satellites caused by the Sn–P interaction which makes it possible to determine the values of $^2J(^{119}Sn^{31}P)$ (Fig. 1). We assume that the occurrence of five signals in ^{31}P NMR spectra could be ascribed to the formation of the following five isomers of $Ph_2SnCl_2 \cdot 2L$ (*vide infra*).



A



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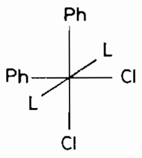

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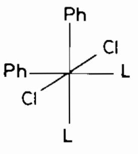

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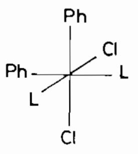

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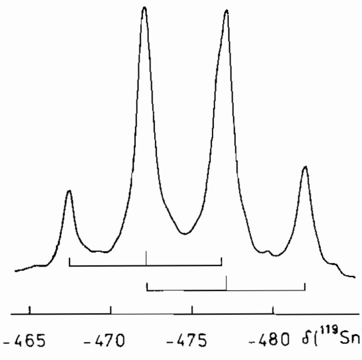

Fig. 1. ^{31}P NMR spectrum of $Ph_2SnCl_2 \cdot 2L$ at 190 K measured at 40.32 MHz.

An unambiguous assignment of the observed signals to the above isomers is not possible in a simple way due to the limited amount of the information obtained. We assume that the most intensive signals can be ascribed to the most probable [2, 3] and most frequent [4–6] *trans*-diorganyltin(IV) isomers (isomers **A** and **B** above). Two observed triplets in ^{119}Sn NMR spectra of this system at 190 K (Fig. 2.) also correspond to these isomers. The splitting of signals in ^{119}Sn NMR spectra into triplets gives evidence of the composition of the $Ph_2SnCl_2 \cdot 2L$ adduct and the values of $\delta(^{119}Sn)$ confirm the octahedral coordination of the central tin atom in the most frequent isomers [7]. Further three expected triplets in ^{119}Sn NMR spectrum were not observed because of low abundance.

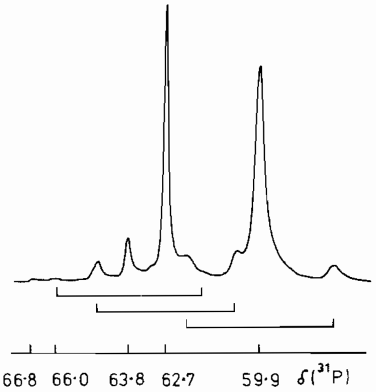

Fig. 2. ^{119}Sn NMR spectrum of $Ph_2CnCl_2 \cdot 2L$ at 190 K measured at 37.14 MHz.

In ^{31}P NMR spectra of the system with molar ratio Ph_2SnCl_2:L = 1:3 at 190 K similar signals as in the previous system with 1:2 molar ratio were found, having (within experimental error), the same $\delta(^{31}P)$ and relative intensities and only one additional signal at 48.1 ppm corresponding to a free ligand L (Table I). This observation is very valuable, indicating that the surplus of ligand L above the molar ratio 1:2 does not affect the composition of adducts in the solution. Simultaneously, it gives evidence for a sufficiently slow exchange of ligands on the NMR time scale at these experimental conditions. It is also evidence that the low-intensity signals in ^{31}P NMR spectra can be ascribed to the presence of a hexacoordinate central tin atom in $Ph_2SnCl_2 \cdot 2L$ adducts.

The determination of multiplicity of signals in ^{119}Sn NMR spectra affords valuable information on the composition and structure of organotin(IV) complexes with ligands containing a phosphorus atom in the neighbourhood of the donor center. On the other hand, the coupling constants $^2J(^{119}Sn^{31}P)$ can be obtained more easily and precisely from the ^{31}P NMR spectra.

References

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