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Formation of tin(IV) adducts by the reactions of tri(*n*-octyl)phosphine oxide with tin(II) halides: a spectral study

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Abstract—The reactions of SnX_2 (X = Cl,Br) with tri(*n*-octyl)phosphine oxide (TOPO) under aerobic conditions yielded the oxidative addition products of the stoichiometry $SnX_4 \cdot 2TOPO$, as inferred by their mass spectra. The ^{31}P NMR and ^{119}Sn NMR of the products indicated the presence of *cis* and *trans* isomers in solution. © 1997 Elsevier Science Ltd

Keywords: Sn^{II} halides; phosphine oxide; oxidative addition; *cis-trans* isomerism; ^{31}P NMR; ^{119}Sn NMR.

Tertiary phosphine oxides are good ligands for many metal ions [1] including tin [2–7]. Tri(*n*-octyl) phosphine oxide (TOPO) is useful for the solvent extraction of metal ions [8]. The TOPO complex of Th^{IV} had been structurally characterized [9]. It was therefore, thought that it would be worthwhile to study the reactivity pattern of TOPO with tin(II) halides under aerobic conditions. Our results are presented in this paper.

EXPERIMENTAL

TOPO (SD Fine Chem Ltd) and tin(II) bromide (Aldrich) were used without further purification. The purity of TOPO has been checked using ^{31}P NMR chemical shift at 47.6 ppm (lit. 48.0 ppm) [3]. Anhydrous tin(II) chloride was prepared from $SnCl_2 \cdot 2H_2O$ by dehydration with acetic anhydride [10]. Benzene was dried using the published procedure [11].

INSTRUMENTATION AND TECHNIQUES

The ^{31}P NMR and ^{119}Sn NMR spectra were recorded on a Bruker AMX 400 MHz spectrometer at the Sophisticated Instrument Facility, Indian Institute of Science, Bangalore. The FAB mass spectra using 3-nitrobenzyl alcohol as matrix were obtained from a Jeol SX 102 at the Regional Sophisticated Instrumentation Centre, Central Drug Research Institute, Lucknow.

Reaction of tin(II) chloride with TOPO

Tin(II) chloride (0.16 g, 0.84 mmol) was added to the solution of TOPO (0.33 g, 0.85 mmol) in 20 cm^3 of benzene. The mixture was stirred well. After 1 h tin(II) chloride went into solution. A viscous oil (**1**) was obtained by the removal of solvent *in vacuo*. The product was found to be soluble in all organic solvents.

Reaction of tin(II) bromide with TOPO

Tin(II) bromide (0.27 g, 0.97 mmol) was added to the solution of TOPO (0.37 g, 0.96 mmol) in 20 cm^3 of benzene. The mixture was stirred well for 1 h. A viscous oil (**2**) resulted upon removal of the solvent *in vacuo*.

RESULTS AND DISCUSSION

The ^{31}P NMR spectra of both the products (Fig. 1, Table 1) exhibit two triplets of unequal intensities with the tin satellites in the expected intensity ratio of 1 : 21 : 1 corresponding to the natural abundance of ^{119}Sn (8.6%). The ^{119}Sn NMR (Fig. 1) of the products

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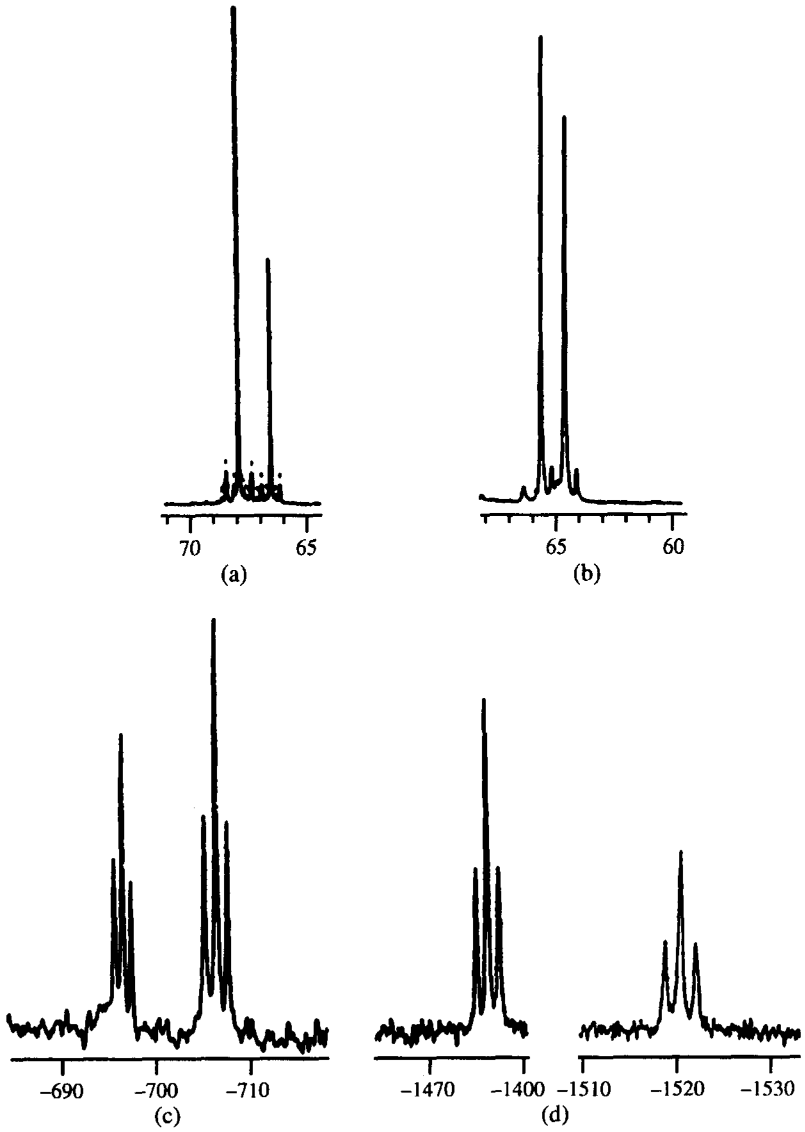

Fig. 1. (a) ^{31}P NMR of **1**; (b) ^{31}P NMR of **2**; (c) ^{119}Sn NMR of **1**; (d) ^{119}Sn NMR of **2**.

also consist of two triplets of unequal intensities with different $^{2}J_{Sn-P}$ values. Based on the ^{31}P and ^{119}Sn NMR spectral data we conclude that **1** is a mixture of *cis* and *trans* isomers of $SnCl_4 \cdot 2TOPO$. This conclusion is supported by the near equality of ^{119}Sn chemical shifts reported for the analogous compounds, *cis*-$SnCl_4 \cdot 2TBPO$ (-707 ppm) and *trans*-$SnCl_4 \cdot 2TBPO$ (-700 ppm) [12] (TBPO = tri(*n*-butyl)phosphine oxide). Similarly **2** is formulated to be the mixture of *cis* and *trans* isomers of $SnBr_4 \cdot 2TOPO$, as proved by the position of ^{119}Sn chemical shifts (-1473 and -1521 ppm). This is in the same range of -1479 ppm reported for *trans*-$SnBr_4 \cdot 2TBPO$ [12]. By comparison with *cis*-$SnCl_4 \cdot 2TBPO$, we assign the upfield ^{119}Sn signals at -706.3 ppm in **1** and -1521.0 ppm in **2** to the *cis* isomers while the other pair of signals are attributed to the *trans* isomers. The signals at 67.9 and 65.8 ppm in the ^{31}P NMR of **1** and **2** respectively are assigned to the *cis* isomers based upon the similarity of $^{2}J_{Sn-P}$ values derived from both ^{119}Sn and ^{31}P NMR signals (Table 1). The other ^{31}P signals correspond to the *trans* isomers (Table 1). In the mass spectra of both **1** and **2** the peaks due to the parent ions are absent. The base peaks in both appear at *m/z* 387 which corresponds to the ligand (TOPO). The peaks due to $SnCl_3 \cdot 2TOPO$ and $SnCl_3 \cdot TOPO$ ions in **1** appear at *m/z* values 997(30%) and 611(74%) respectively. Similarly, the peaks at 1130(24%) and 744(66%) in **2** are assigned to the ions, $SnBr_3 \cdot 2TOPO$ and $SnBr_3 \cdot TOPO$ respectively. The above assignments are also confirmed by the characteristic isotopic distribution in the peaks due to tin–halogen species.

The formation of Sn^{IV} derivatives from Sn^{II} halides is not uncommon. Thus, the reaction of $SnCl_2$ with ligands such as pyridine, tetrahydrofuran [13] and

Table 1. ^{31}P and ^{119}Sn chemical shifts for **1** and **2**

Compound	Possible assignments	^{31}P NMR ($^2J_{Sn-P}$ Hz)	^{119}Sn NMR ($^2J_{Sn-P}$ Hz)
1	*cis*	67.9(t) (176)	−706.3(t) (179)
	trans	66.5(t) (134)	−696.5(t) (134)
2	*cis*	65.8(t) (250)	−1521(t) (248)
	trans	64.7(t) (181)	−1476(t) (186)

^{31}P and ^{119}Sn NMR chemical shifts recorded using $CDCl_3$ as solvent are referenced against external 85% phosphoric acid and tetramethyltin respectively.

acetylacetone [14] in the presence of air had been reported to produce Sn^{IV} complexes. Similarly, the reaction of SnX_2 (X = Cl, Br, I) with sodium diethyldithiocarbamate to form Sn^{IV} complexes were previously proved by our work [15,16]. The oxidative addition of TOPO with $SnCl_2$ in the presence of air is in contrast to the formation of $SnCl_2 \cdot 2TPPO$ [4] (TPPO = triphenylphosphine oxide) whose structure has been confirmed by X-ray crystallography [17].

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