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SYNTHESIS AND INFRARED CHARACTERIZATION OF SOME NEW POLYNUCLEAR $SnPh_3X$ ADDUCTS (X=Cl,Br,I)

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ABSTRACT. New polynuclear $SnPh_3X$ adducts such as $Et_4NX.2SnPh_3X$ (X=Cl,Br), $SnPh_3X.mSnPh_3Cl$ (X=Br,I; m=1,2,3), $SnPh_3Cl.2SnPh_3I$ and $Et_4(CN)_2SnPh_3Br.2SnPh_3Br$ have been synthesized and discrete structures suggested on the basis of their infrared spectra. The triphenyltin halides act as Lewis acid or base. The basic behaviour of the triphenyltin halides has been reported for the first time in this paper.

INTRODUCTION

Most of the studies carried out on $SnPh_3X$ adducts have dealt with mononuclear adducts, $SnPh_3X$ acting as a Lewis acid [1-7]. Recently Sall and Diop [8,9] have reported the reassignment of the IR spectrum of $SnPh_3Cl$ and the IR characterization of a new dinuclear $SnPh_3Cl$ adduct ($Me_4N.H_2PO_2.2SnPh_3Cl$). To the best of our knowledge no other polynuclear $SnPh_3X$ adduct has been reported in the literature. The aim of this work is the synthesis and the characterization of some new polynuclear $SnPh_3X$ adducts by IR spectroscopy.

EXPERIMENTAL

General. $SnPh_3Cl$ and Et_4NX (X=Cl,Br,I,CN) obtained from Merck Chemicals were used without further purification. $SnPh_3Br$ was obtained by bubbling HBr in absolute ethanolic solution of $SnPh_3OH$ containing ether; $SnPh_3Br_2NEt_4$ was precipitated from a solution containing a mixture of stoichiometric amounts of $SnPh_3Br$ (in ether) and Et_4NBr (in absolute ethanol).

Synthesis and characterization of title adducts. By allowing 2.69 mmol of Et_4NCl to react with 2.69 mmol of $SnPh_3Cl$, both as absolute ethanolic solutions, transparent crystals of $Et_4NCl.2SnPh_3Cl$ were collected by slow evaporation. C: 56.38(56.31); H: 5.34(5.36); N: 1.50(1.53); Cl: 10.94(11.40).

The following adducts were obtained as white precipitates by mixing a 95% ethanolic solution of Et_4NX (X=Cl,CN) with $SnPh_3Br$ in ether; the precipitates were filtered off, washed with ether and dried under vaccum:

$Et_4NCl.2SnPh_3Br$. 2.03 mmol of Et_4NCl and 8.12 mmol of $SnPh_3Br$. Anal. Calc.

(Found): C, 51.55 (51.30); H, 4.87 (4.93); N, 1.36 (1.45); Cl, 3.46 (4.02); Br, 15.61 (16.20).

$Et_4NBr.2SnPh_3Cl$. 4.11 mmol of Et_4NCl and 4.41 mmol of $SnPh_3Br$. Anal. Calc. (Found): C, 53.85 (53.70); H, 5.10 (5.35); N, 1.42 (1.52); Cl, 7.24 (8.01); Br, 8.16 (8.71).

$Et_4N(CN)_2SnPh_3.2SnPh_3Br$. 3.42 mmol of Et_4NCN and 6.84 mmol of $SnPh_3Br$. Anal. Calc. (Found): C, 55.22 (54.95); H, 4.67 (4.90); N, 3.01 (2.88); Br, 11.50 (11.95).

The following adducts were obtained as transparent crystals by slow evaporation of a 95% ethanolic solution containing, the indicated amounts (see below) of a mixture of Et_4NX (X=Br,I) and $SnPh_3Cl$ (the mixture had to be stirred for several hr): $SnPh_3Br.SnPh_3Cl$ (1:1), $SnPh_3Br.2SnPh_3Cl$ (1:2); $SnPh_3Br.3SnPh_3Cl$ (1:4); $SnPh_3I.SnPh_3Cl$ (1:2); $SnPh_3I.2SnPh_3Cl$ (1:3); $SnPh_3I.3SnPh_3Cl$ (1:4); $SnPh_3Cl.2SnPh_3I$ (1:1).

Satisfactory elemental analyses, performed by the "Service Central d'Analyses" C.N.R.S. Vernaison, France were obtained for these adducts. The IR spectra were recorded on a Brucker FTIR model FS113V spectrophotometer as nujol mulls.

RESULTS AND DISCUSSION

Infrared spectra of $SnPh_3Br$ and $SnPh_3Br_2NEt_4$. X-ray structures of $SnPh_3Cl$ and $SnPh_3Br$ were determined by TSE *et al* [10] and Hubert and Preut [11], respectively: they consist of discrete tetrahedral molecules.

The medium band at 338cm^{-1} in the spectrum of $SnPh_3Br$ which is not observed in the spectrum of $SnPh_3Br_2NEt_4$ is assigned to νSnC_3; $\nu SnBr$ is localized at 252cm^{-1} on the IR spectrum of $SnPh_3Br$. The absence or the appearance of the band at 338cm^{-1} for any mono or polynuclear $SnPh_3Cl(Br)$ adduct indicates whether SnC_3 groups are planar or not.

Spectral data of $Et_4NCl.2SnPh_3Cl$ (A), $Et_4NCl.2SnPh_3Br$ (B) and $Et_4NBr.2SnPh_3Cl$ (C). The phenyl and cation bands are omitted. A: $\nu_{as}SnC_3$ 274cm^{-1} (vs); $\nu ClSn_2$ 242cm^{-1} (m). B: $\nu_{as}SnC_3$ 274cm^{-1} (vs); $\nu SnBr$ 230cm^{-1} (s). C: $\nu_{as}SnC_3$ 274cm^{-1} (vs); $\nu SnCl$ 242cm^{-1} (sh); $\nu BrSn_2$ 228cm^{-1} (s). The absence of the band at 338cm^{-1} due to $\nu sSnC_3$, in the IR spectra of A, B, and C indicates planar SnC_3 groups.

From these data, the suggested structures for A, B, and C consist of a central halide shared by two $SnPh_3X$ molecules, the environment of the tin atoms being a trigonal bipyramid. In B and C, the difference of size of the atoms in axial positions does not prevent the SnC_3 groups from being planar as found for $SnPh_3Cl.OPPh_3$ [12]. In A,B, and C, $SnPh_3X$ acts as Lewis acid.

Spectral data of $Et_4N(CN)_2SnPh_3.2SnPh_3Br$. νCN 2160cm^{-1} (m); νSnC_2 301 cm^{-1} (m); νSnN 298cm^{-1} (m); $\nu_{as}SnC_3$:274 cm^{-1} (vs); $\nu SnBr$ 228 cm^{-1} (m). The absence of $\nu sSnC_3$ indicates planar SnC_3 groups, the suggested structure consists of a central triphenyltin IV cation linked to two $SnPh_3Br$ by cyano bridges (for symmetry reasons, the central SnC_3 group is linked to two carbon atoms).

$SnPh_3X.mSnPh_3Cl$ (X=Br,I; m=1,2,3) and $SnPh_3Cl.2SnPh_3I$. During the formation of these adducts, $SnPh_3X$ is produced *in situ* by halogen exchange. Spectral data: $SnPh_3Br.SnPh_3Cl$: ν_sSnC_3 338 cm^{-1} (s); $\nu_{as}SnC_3$ 274 cm^{-1} (vs); $\nu SnBr$ 251 cm^{-1} (m); $SnPh_3I.SnPh_3Cl$: ν_sSnC_3 338 cm^{-1} (s); $\nu_{as}SnC_3$ 274 cm^{-1} (vs); νSnI 239 cm^{-1} (s).

Considering the IR spectra of the two other bromo adducts we notice the presence of these three main bands reported for the 1:1 adduct but the intensity of ν_sSnC_3 becomes stronger as m increases while the intensity of $\nu SnBr$ decreases (these same observations can be made on the spectra of iodo adducts while considering the intensities of ν_sSnC_3 and νSnI).

The band at 338 cm^{-1} indicates the presence of SnC_3 groups of C_{3v} symmetry; the suggested structures for $SnPh_3X.mSnPh_3Cl$ consist of a central $SnPh_3X$ linked respectively to one, two and three molecules of $SnPh_3Cl$ via X ($SnPh_3X$ acts as a Lewis base).

In the case of $SnPh_3X.SnPh_3Cl$ (X=Br,I) one could suggest an infinite chain of $SnPh_3X$ and $SnPh_3Cl$ *via* bridging halides, but in this case, planar SnC_3 groups should be expected as in $Et_4NBr.2SnPh_3Cl$ or $Et_4NCl.2SnPh_3Br$ (in the suggested discrete structure, at least one SnC_3 group is pyramidal). The IR spectrum of $SnPh_3Cl.2SnPh_3I$ shows a medium band at 338 cm^{-1} due to ν_sSnC_3, and a very strong band at 234 cm^{-1} assigned to νSnI. The suggested structure consists of $SnPh_3Cl$ linked to two $SnPh_3I$ *via* Cl ($SnPh_3Cl$ acts as a Lewis base).

In conclusion, the title polynuclear $SnPh_3X$ adducts have discrete structures which consist of a central halide coordinated to two $SnPh_3X$ (X=Br,Cl) molecules (in the formation of some $SnPh_3X$ adducts, halide exchange takes place), or a central $SnPh_3X$ produced *in situ* linked to one, two or three molecules of $SnPh_3Cl$.

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