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SYNTHESIS AND SPECTROSCOPIC PROPERTIES OF ADDUCTS OF ORGANOTIN(IV) NITRATES WITH DIPHOSPHINES

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Summary

Triphenyltin(IV) nitrate and diphenyltin(IV) dinitrate react with the diphosphines 1,2-bis(diphenylphosphino)ethane (DPPE) and *cis*-1,2-bis(diphenylphosphino)ethylene (DPPET) in methanol/benzene or acetonitrile/benzene to yield adducts of the general formula $\{Ph_{4-n}Sn(NO_3)_n\}_2 \cdot L$ ($n = 1,2$; L = DPPE, DPPET). Infrared and tin-119 Mössbauer data indicate a *mer*-six-coordinated geometry when $n = 1$ and a pentagonal bipyramidal stereochemistry with mutually *trans* axial phenyl groups when $n = 2$, with bidentate nitrate groups. The diphosphine ligand bridges two tin centres in each case. When the reactions are performed in other solvents, oxidation of the diphosphine ligand occurs.

Introduction

In spite of the wide interest in the coordination chemistry of the organo-derivatives of both tin and phosphorus, only a few compounds containing coordinate P → Sn interaction have been described [1—3].

We have previously examined the chemical and structural properties of some adducts obtained from the interaction of organotin(IV) nitrates with phosphine oxides [4,5]. In all these adducts the Sn—O—P linkage is present, and the adducts adopt different stereochemistries depending on the number and nature of the organic and inorganic groups bonded to the tin atom. We have now attempted to synthesise coordinate P → Sn-bonded complexes by employing diphosphines of the type $Ph_2P{-}R{-}PPh_2$ (R = $CH_2CH_2CH_2$, CH_2CH_2, CH=CH, C≡C), and in this paper we report the synthesis and spectroscopic characterisation (infrared and ^{119}Sn Mössbauer) of adducts obtained from the phenyltin-

(IV) nitrates, $Ph_{4-n}Sn(NO_3)_n$ (n = 1,2) and 1,2-bis(diphenylphosphino)ethane (DPPE) and *cis*-1,2-bis(diphenylphosphino)ethylene (DPPET).

Results and discussion

Whilst both DPPE and DPPET are soluble in various solvents (acetone, benzene, carbon tetrachloride and chloroform), the choice of solvent for the reactions is limited to acetone and acetonitrile for Ph_3SnNO_3 and to acetone and methanol for $Ph_2Sn(NO_3)_2$. When acetone was employed as the reaction medium, a phosphine oxide-tin adduct was always isolated (confirmed by the observation of a strong band at 1180 cm^{-1} due to $\nu(P{=}O)$ in the infrared) from oxidation of the phosphine. The influence which acetone exerts on the nature of the reaction products is similar to the observed previously for other organotin compounds [6], and the oxidation of the diphosphine in the present case may be ascribed to nitric acid formed by partial hydrolysis of the organotin(IV) nitrate by water derived by the autocondensation of acetone. A similar effect was also observed when chloroform was used as the solvent, although in this case the mechanism of the oxidation process was not well clarified. However, when methanol or acetonitrile were used as the solvent medium, oxidation of the phosphine ligand was not observed. In order to confirm that the formation of diphosphine oxides depends only on the nature of the solvent, several of the reaction conditions were changed, e.g.: (i) the reaction was performed in benzene at room temperature whilst bubbling a stream of oxygen for 60 minutes, (ii) the reaction was repeated increasing the temperature in the range 20—80°C (above 80°C decomposition was observed), and (iii) the reaction solution was exposed for 8 hours to ultraviolet irradiation. In all cases, no oxidation of the diphosphine was observed.

In the light of these observations, methanol/benzene and acetonitrile/benzene were used as the media for the reaction of DPPE and DPPET with $Ph_2Sn(NO_3)_2$ and Ph_3SnNO_3, respectively. From the analytical data it can be deduced that the adducts are of the general formula $\{Ph_{4-n}Sn(NO_3)_n\}_2 \cdot L$ (n = 1,2; L = DPPE, DPPET). They are white, microcrystalline solids, which are almost insoluble in the common organic solvents except dimethylsulphoxide and acetonitrile, in which they are sparingly soluble at room temperature.

Infrared spectra

The principal infrared bands of the complexes are listed in Table 1. Oxidation of the phosphine may also be distinguished by the strong $\nu(P{=}O)$ absorption which occurs in the 1200—1000 cm^{-1} region. Such bands are absent in the spectra of all four complexes, which are mainly characterised by the vibrational bands of the nitrate group, the diphosphine ligand, and the phenyltin moiety. Bands in the 1600—1800 cm^{-1} region are indicative of a bidentate nitrate group in all cases, the separation of the symmetric and antisymmetric modes, $\Delta\nu = \nu_{as}(NO_3) - \nu_s(NO_3)$, falling in the range 215—230 cm^{-1} [8—10]. However, due to the presence of a strong band at ca. 1380 cm^{-1} in the spectra of both diphenyltin dinitrate complexes, it is not possible to establish unequivocally whether both nitrate groups are bidentate, or both bidentate and ionic nitrate are present. The presence of ionic nitrate may be due to adventitious

TABLE 1

MAIN VIBRATIONAL BANDS (cm^{-1}) AND RELATIVE ASSIGNMENTS

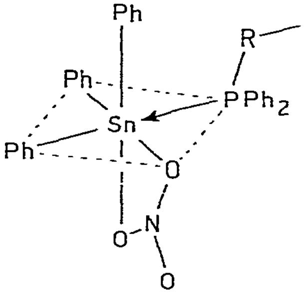
DPPE[a]	$(Ph_3SnNO_3)_2 \cdot DPPE$	$\{Ph_2Sn(NO_3)_2\}_2 \cdot DPPE$	DPPET[a]	$(Ph_3SnNO_3)_2 \cdot DPPET$	$\{Ph_2Sn(NO_3)_2\}_2 \cdot DPPET$	Assignment
3070w	3070w	3070w	3070w	3070w	3070w	ν(CH) aryl
2940w	2920w	2940w	2940w		2940w	ν(CH) alkyl
—	1495s	1520sh		1510s	1510s	$\nu_{as}(NO_3)$
1480s	1480m	1480s	1480s	1480sh	1480sh	ring
				1470s		
1430s	1430s	1430s	1430s	1430s	1430s	
		1380s			1385s	$\nu(NO_3)$
	1280s	1290s		1290s	1290s	$\nu_s(NO_3)$
1180w	1190w	1190w	1180w		1180w	
1160m	1150m	1170m	1170m		1170w	
1100m	1120m	1140m				
1070m		1080w		1070m	1080m	
1000m	1000m	1020m	1000m	1000m	1000m	ring
		800w			800w	$\delta(NO_3)$
500s	470sh	460sh	470s			
470s	450m	450m	440m	450s	450m	ν(PC)
440m		410w			410w	
	300sh	320s		300sh	310s	ν(SnP)
	270m	270sh		280ms	270sh	ν(SnC)

[a] DPPE = 1,2-bis(diphenylphosphino)ethane; DPPET = *cis*-1,2-bis(diphenylphosphino)ethylene.

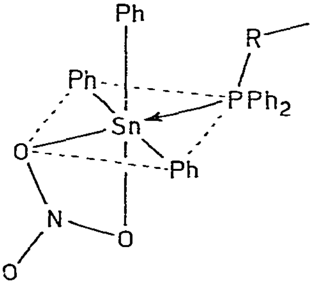
hydrolysis during the recording of the spectra as we have previously observed in other cases. Assignment of the ν(Sn—P) vibration was made by comparison with literature data [11—13].

^{119}Sn Mössbauer spectra

The spectra of two of the adducts, $(Ph_3SnNO_3)_2 \cdot$ DPPET and $\{Ph_2Sn(NO_3)_2\}_2 \cdot$ DPPE were recorded at 77 K, and comprised in both cases a quadrupole-split doublet resonance, indicating the chemical equivalence of both tin atoms in each adduct (Table 2). The diphosphine must therefore function as a bridging ligand in both cases. Assuming bidentate nitrate, the coordination number at tin will be six and seven, respectively. Of the two possible six-coordinate geometries for $(Ph_3SnNO_3)_2 \cdot$ DPPET, the *fac* isomer (I) may be excluded since this would be expected to exhibit a quadrupole splitting of ca. zero. On the other hand, the corresponding *mer* isomer(II) would be expected to show a large splitting as observed in the present case.

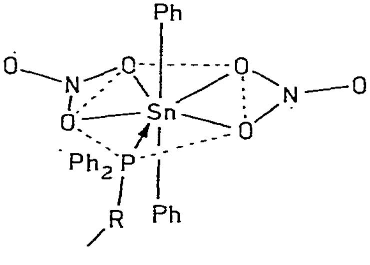


I



II

If both nitrate groups are bidentate in $\{Ph_2Sn(NO_3)_2\}_2 \cdot$ DPPE, the tin atom will be seven-coordinated, and the large quadrupole splitting exhibited by this complex suggests a pentagonal bipyramidal geometry with the two phenyl groups mutually *trans* occupying the axial positions (III).



III

This unusual stereochemistry has been already found by us in other adducts of $Ph_2Sn(NO_3)_2$ [14,15].

NMR spectra

Unfortunately, the low solubility of the complexes in most solvents pre-

TABLE 2

TIN-119 MÖSSBAUER DATA

Compound	I.S. ^{a,b}	Q.S. ^{a}	Γ_- ^{a}	Γ_+ ^{a}	I_-/I_+
$(Ph_3SnNO_3)_2 \cdot$ DPPET	1.51	3.61	0.882	0.993	1.135
$\{Ph_2Sn(NO_3)_2\}_2 \cdot$ DPPE	1.36	4.03	0.933	0.781	1.067

^{a} mm s^{-1}. ^{b} Relative to CaSnO$_3$ = 0.

vented recording of their NMR spectra. Suspensions of the compounds in $CDCl_3$ or in C_6D_6 showed resonances in the phenyl region only, whilst dissolution in $(CD_3)_2SO$ or CD_3CN afford spectra of the reagents only due to a decomposition reaction, which resulted in the precipitation of $Ph_2Sn(NO_3)_2$ or Ph_3SnNO_3 after some minutes.

Experimental

All manipulations were carried out under dry nitrogen. Solvents were dried, distilled and stored under nitrogen. Elemental C, H, N analyses were made on a Perkin-Elmer Mod. 240 automatic analyser. The quantitative determination for tin was obtained by AAS on a Perkin-Elmer Mod. 303 spectrophotometer.

Diphosphines were commercially available from Strem Chemicals and used without purification. $Ph_2Sn(NO_3)_2$ and Ph_3SnNO_3 were prepared according Fenster [16]. The adducts of organotin(IV) nitrates were prepared as follows in a similar way: Ph_3SnNO_3 in methanol (or $Ph_2Sn(NO_3)_2$ in acetonitrile) was added, under a nitrogen atmosphere, to a benzene solution of diphosphine (2 : 1 molar ratio) and allowed to stir for 60 minutes at room temperature. After 24 hours by slow evaporation of the solvent a white solid was isolated and washed with small portions of a cold methanol/benzene (or acetonitrile/benzene) mixture.

The infrared spectra were measured with a Perkin-Elmer Mod. 457 instrument in the range 4000—250 cm^{-1}, in KBr discs. The Mössbauer spectrometer has been described previously [17]. A sample of the material was finely ground and made up into a disc of density ca. 10 mg ^{119}Sn cm^{-2} between aluminium foil windows. Spectra were recorded at 77 K versus a Ca^{119}SnNO$_3$ source (Radiochemical Centre, Amersham).

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