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CRYSTAL AND MOLECULAR STRUCTURE OF {3-[t-BUTYL(PHENYL)PHOSPHINO]PROPYL}DIMETHYLTIN CHLORIDE

H. WEICHMANN,

Department of Chemistry, Martin-Luther-University, Halle-Wittenberg, DDR-4020 Halle (S.), Weinbergweg 16 (G.D.R.)

J. MEUNIER-PIRET and M. VAN MEERSSCHE

Laboratoire de Chimie Physique et de Cristallographie, Université de Louvain, Place Louis Pasteur, 1, B-1348 Louvain-la-Neuve (Belgium)

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Summary

{3-[t-Butyl(phenyl)phosphino]propyl}dimethyltin chloride crystallizes in the space group $P2_1/a$. The unit cell, with a 22.798(9), b 9.578(4), c 8.385(7) Å, β 102.16(3)°, V 1789.9(26) Å^3, contains 4 discrete molecules. The structure was refined to a final R value of 0.040. The tin atom has a distorted trigonal bipyramidal environment with the phosphorus and chlorine atom in axial positions. The tin–phosphorus intramolecular interaction distance is 3.078(2) Å.

Introduction

The organotin halides R_nSnX_{4-n}, are hard Lewis acids which have a marked tendency to increase their coordination number by adduct formation with Lewis bases, preferably N and O donors [1]. Stable complexes with organophosphines which are soft bases are known only with the strong acceptors monoorganotin trihalides [2,3], and in a few cases with diorganotin dihalides [4]. In the case of triorganotin halides the acceptor strength of the tin atom is so weak that, to our knowledge, no stable adducts with phosphines were previously known. Efforts to estimate thermodynamic data for adduct formation between triorganotin chlorides and tertiary phosphines failed because the enthalpy changes and the equilibrium constants are too small [5,6].

Recently we obtained indications from NMR spectra of an intramolecular Sn–P interaction in solutions of P-functional triorganotin chlorides of the type $Me_2Sn(Cl)[(CH_2)_3PR_2]$ [7]. The main evidence for the existence of an intramolecular Sn–P coordination in these compounds is provided by (i) the distinct high-field shift of their ^{119}Sn NMR signal compared with that for the corresponding tetracoor-

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dinated β-substituted compounds $Me_2Sn(Cl)[(CH_2)_2PR_2]$, and (ii) the high values of the $J(^{119}Sn-^{31}P)$ coupling constant. In non-coordinating solvents there is obviously an equilibrium between the intramolecular coordinated cyclic and the non-coordinated open structure of $Me_2Sn(Cl)[(CH_2)_3PR_2]$ as revealed by the temperature dependence of both the ^{119}Sn chemical shift and the $J(^{119}Sn-^{31}P)$ coupling constant.

In order to confirm the presence of an intramolecular Sn–P coordination in $Me_2Sn(Cl)[(CH_2)_3PR_2]$ we have carried out an X-ray study, and we describe here the crystal structure of {[3-t-butyl(phenyl)phosphino]propyl}dimethyltin chloride.

Experimental

The synthesis of $Me_2Sn(Cl)[(CH_2)_3P(Ph)Bu\text{-}t]$ has been described elsewhere [7]. Crystals suitable for X-ray study were obtained from a concentrated solution in benzene.

The space group and preliminary cell dimensions were deduced from oscillation and Weissenberg photographs. Accurate unit-cell parameters were obtained by least-squares refinement of angular position of 15 reflections.

Crystal data. $C_{15}H_{26}PClSn$, $M = 391.49$; monoclinic $P2_1/a$, a 22.798(9), b 9.578(4), c 8.385(7) Å, β 102.16(3)°, V 1789.9(26) Å^3, $Z = 4$, D_{calc} 1.45, $F(000)$ 792. The intensities of 2650 reflections were measured on a Syntex $P2_1$ four-circle diffractometer, with graphite monochromatized Mo-K_α radiation (2θ max = 47°), and 2284 non-equivalent reflections with $I > 2.5\sigma(I)$ were used in the refinement. No corrections were made for absorption effects (ν 15.2 cm^{-1}). The structure was solved by Patterson synthesis and by the DIRDIF-program. The refinement was carried out with the SHELX-program (all atoms anisotropic, atom scattering factors included in the program, weighting scheme $|\sigma^2(F) + 0.0010F^2|^{-1}$) to a final

TABLE 1

FRACTIONAL ATOMIC COORDINATES (×10^4) AND B_{eq} values (Å^2)

Atom	x	y	z	B_{eq}
Sn(1)	7272(3)	6968(4)	29291(6)	3.11
P(1)	1203(1)	3668(2)	3805(2)	3.11
Cl(1)	170(1)	−1545(2)	2306(3)	5.96
C(1)	−63(3)	1998(7)	2362(9)	4.68
C(2)	53(3)	3514(7)	1876(8)	4.29
C(3)	425(3)	4349(6)	3280(8)	3.88
C(4)	1523(3)	4434(6)	5883(7)	3.67
C(41)	2198(3)	4042(10)	6313(9)	6.23
C(42)	1209(4)	3741(8)	7131(8)	5.40
C(43)	1432(4)	6040(8)	5887(9)	5.84
C(5)	1243(3)	609(8)	1056(9)	5.29
C(6)	1166(4)	46(8)	5330(8)	5.68
C(10)	1592(3)	4624(6)	2447(6)	3.25
C(11)	2146(3)	4046(7)	2249(8)	4.12
C(12)	2500(3)	4770(8)	1332(8)	4.58
C(13)	2304(4)	6026(8)	601(8)	5.01
C(14)	1752(4)	6554(7)	756(8)	5.26
C(15)	1399(3)	5872(6)	1683(7)	4.03

conventional R value of 0.040. There are no significant peaks in final ΔF synthesis. The final atomic coordinates are listed in Table 1. Table of observed and calculated structure factors may be obtained from one of the authors (J.M.P.).

Results and discussion

The structure of the title compound with the atom numbering is shown in Fig. 1. The bond lengths, bond angles and torsion angles are summarized in Tables 2 and 3. The molecular packing in the unit-cell is illustrated in Fig. 2: the crystal structure consists of discrete monomeric molecular units which are separated by normal Van der Waals distances. The most striking feature of the molecular structure is the Sn–P distance of 3.078 Å and the P–Sn–Cl bond angle of 169.8°. Both indicate the presence of an intramolecular donor–acceptor interaction between tin and phosphorus. For a comparison of the strength of this interaction with those of other tin(IV) donor element coordinations the use of a formal correlation between intramolecular tin element distances and the nature of the bonding between these elements is very informative [8]. In this approach the limiting distance for a bonding interaction between tin and another main group element in the same molecule is the average value of the experimentally determined tin–element single bond lengths (bond order 1) on the one side and on the other side that distance increased by 1 Å, as the limiting distance for an intramolecular nonbonding interaction (bond order 0). Between these two values a linear relationship between the bond order from 1 to 0 and distance length is assumed. On the basis of an average value of 2.52 Å for the few known Sn^{IV}–P single bond lengths [9,10] (sum of the single bond radii: 2.50 Å [11]) the Sn–P distance of 3.078 Å in the title compound corresponds to a formal bond order of 0.44. Analogous considerations for triorganotin halide complexes involving an intra- or intermolecular Sn–N or Sn–O coordination [12–24] indicate bond orders of about 0.6 to 0.7. In accord with the relatively weak Sn–P donor–acceptor interaction the intramolecular coordination in the title compound is easily broken both by external strong donors (pyridine, HMPT, DMF) and by

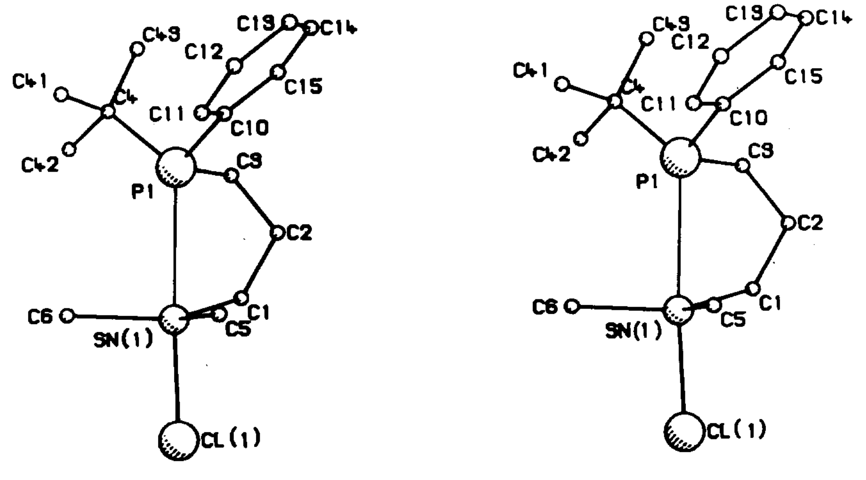

Fig. 1. Stereoscopic view of the molecular structure with atom numbering.

TABLE 2

BOND DISTANCES (Å) AND BOND ANGLES (°), WITH STANDARD DEVIATIONS

Sn(1)–C(1)	2.160(6)	C(4)–C(41)	1.551(10)
Sn(1)–C(5)	2.153(7)	C(4)–C(42)	1.536(9)
Sn(1)–C(6)	2.143(7)	C(4)–C(43)	1.552(9)
Sn(1)–P(1)	3.078(2)	C(10)–C(11)	1.421(9)
Sn(1)–Cl(1)	2.494(2)	C(11)–C(12)	1.409(9)
P(1)–C(3)	1.852(6)	C(12)–C(13)	1.380(10)
P(1)–C(4)	1.890(6)	C(13)–C(14)	1.388(11)
P(1)–C(10)	1.830(6)	C(14)–C(15)	1.393(9)
C(1)–C(2)	1.546(9)	C(15)–C(10)	1.383(8)
C(2)–C(3)	1.525(9)		
C(1)–Sn(1)–C(5)	114.8(3)	C(3)–P(1)–C(4)	104.3(3)
C(1)–Sn(1)–C(6)	125.3(3)	C(3)–P(1)–C(10)	103.9(3)
C(5)–Sn(1)–C(6)	117.1(3)	C(4)–P(1)–C(10)	103.6(3)
Cl(1)–Sn(1)–C(1)	94.9(2)	C(3)–P(1)–Sn(1)	89.8(2)
Cl(1)–Sn(1)–C(5)	98.4(2)	C(4)–P(1)–Sn(1)	128.8(2)
Cl(1)–Sn(1)–C(6)	93.6(2)	C(10)–P(1)–Sn(1)	120.4(2)
P(1)–Sn(1)–C(1)	75.8(2)	Sn(1)–C(1)–C(2)	114.8(4)
P(1)–Sn(1)–C(5)	89.5(2)	C(1)–C(2)–C(3)	112.8(5)
P(1)–Sn(1)–C(6)	88.5(2)	C(2)–C(3)–P(1)	110.3(4)
Cl(1)–Sn(1)–P(1)	169.8(1)		

TABLE 3

TORSION ANGLES IN THE FIVE-MEMBERED CHELATE RING (°)

Sn(1)–C(1)–C(2)–C(3)	−66.6
C(1)–C(2)–C(3)–P(1)	68.3
C(2)–C(3)–P(1)–Sn(1)	−33.8
C(3)–P(1)–Sn(1)–C(1)	3.0
P(1)–Sn(1)–C(1)–C(2)	28.5

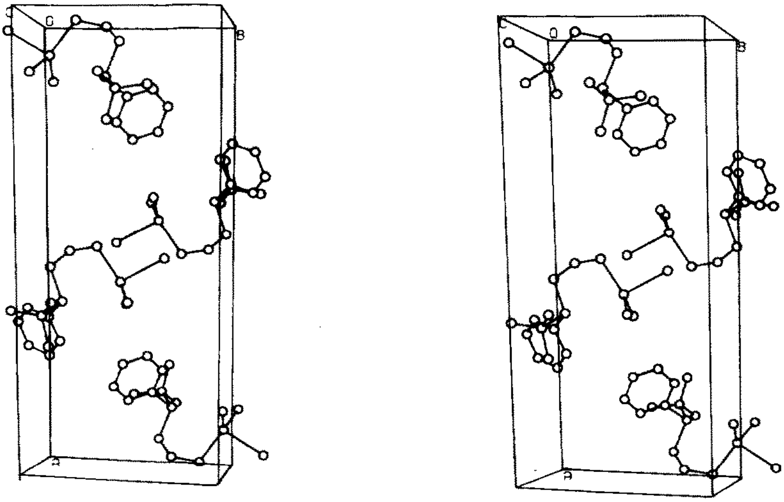

Fig. 2. Crystal packing of $Me_2Sn(Cl)[(CH_2)_3P(Ph)Bu\text{-}t]$ (Sn–P interaction is not represented).

raising the temperature [7]. In contrast the intramolecular Sn–O coordination in $Me_2Sn(Cl)(CH_2)_2P(O)PhBu$-t, for example, is stable under these conditions [18].

As a consequence of the intramolecular Sn–P interaction the geometry at the tin atom in the title compound is that of a slightly distorted trigonal bipyramid. The equatorial positions are occupied by carbon atoms, and the axial sites by phosphorus and chlorine. The C–Sn–C and the P–Sn–C bond angles are smaller than the ideal values of 120 and 90°, respectively, so that the tin atom lies 0.21 Å below the plane defined by the three carbon atoms C(1), C(5) and C(6). Furthermore, as a result of the Sn–P interaction the Sn–Cl bond distance shows a slight lengthening, which falls in the range observed for other pentacoordinated adducts of triorganotin chlorides [15–17,19–24]. In fact the lengthening of the Sn–Cl bond varies with the strength of the coordinative interaction. The Sn–C equatorial lengths are in good agreement with values in the literature.

The torsion angles quoted in Table 3 and the molecular geometry shown in Fig. 1 indicate a half chair conformation for the five-membered chelate ring. The P(1), Sn(1), C(1) and C(3) atoms are nearly coplanar, and the ring is puckered at the C(2) edge in the direction of the phenyl and C(5) methyl groups. A Newman projection along the Sn–P bond shows that the Sn–C and P–C bonds are almost in eclipsed positions.

Acknowledgments

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