CRYSTAL STRUCTURE OF BROMOTRI(*p*-TOLYL)TIN HEXAMETHYLPHOSPHORAMIDE

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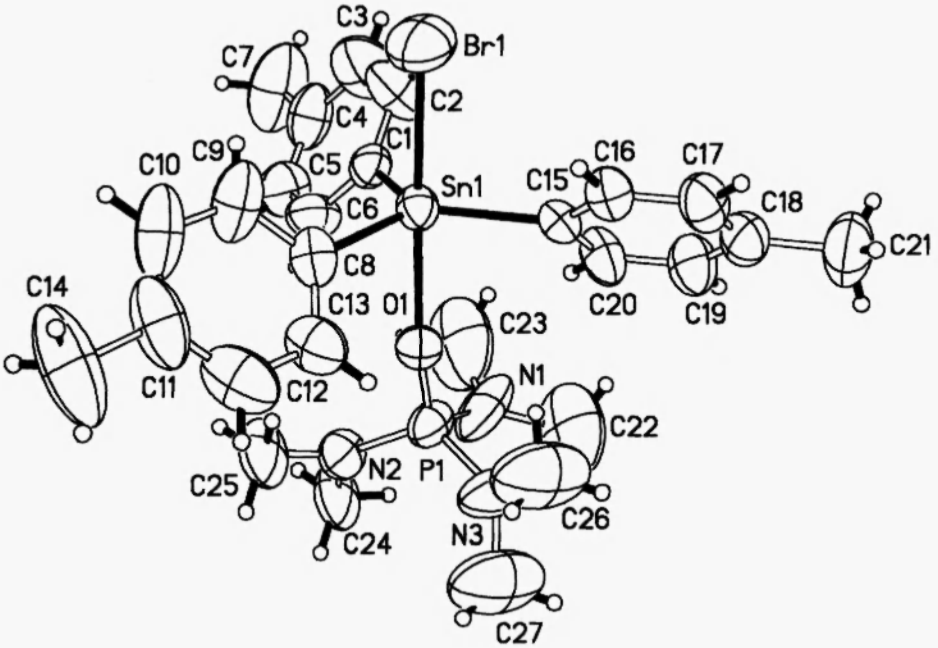

Figure 1. *ORTEP* plot of the title complex at the 50% probability level; only the major component of the disordered dimethylamino groups is illustrated. Selected bond distances and angles: Sn1-C1 = 2.149(3), Sn1-C8 = 2.154(4), Sn1-C15 = 2.150(3), Sn1-O1 = 2.315(4), Sn1-Br1 = 2.634(1) Å; C1-Sn1-C8 = 114.6(2), C1-Sn1-C15 = 117.6(2), C1-Sn1-O1 = 88.4(2), C1-Sn1-Br1 = 94.8(1), C8-Sn1-C15 = 126.7(2), C8-Sn1-O1 = 85.5(2), C8-Sn1-Br1 = 93.6(1), C15-Sn1-O1= 86.0(2), C15-Sn1-Br1 = 92.0(1), O1-Sn1-Br1 = 176.7(1)°.

Comment

An unusually large Sn←O=P angle is a typical feature found in organotin complexes of phosphine oxides [1] of which there are over 140 in the structural literature. For example, the hexamethylphosphoramide adduct of triphenyltin bis(*N,N*-dimethylthiocarbamoylthiolylacetate) has an almost linear (167.8(2)°) skeleton [2], as does the adduct of bis(triphenyltin) succinate (166.6(3)°) [3]. The triphenylphosphine oxide adduct of triphenyltin bromide features a similar angle (166.5(3)°) [4]. The 169.3(3)° angle in the title complex belongs to the higher end of the range of angles in these five-coordinate triorganotin compounds.

Experimental

The disproportionation of tetra(*p*-tolyl)tin (synthesized by using the Grignard route) and stannic chloride yielded tri(*p*-tolyl)tin chloride; the chloride was hydrolyzed by sodium hydroxide in an etherwater mixture to form tri(*p*-tolyl)tin hydroxide. Tri(*p*-tolyl)tin bromide was prepared by treating the hydroxide with aqueous hydrobromic acid in ether [5]. The Lewis acid and an excess of hexamethylphosphoramide were heated in a small volume of chloroform; slow evaporation of the solvent yielded fine colorless crystals of the adduct. The structure is disordered in the dimethylamino groups of the donor ligand; the occupancy was fixed as 2:1 as the disorder refined to an approximate 2:1 ratio. The aromatic rings were refined as rigid hexagons; distance and other restraints were applied in order to treat the disorder.

Table 1. Crystal data for bromotri(*p*-tolyl)tin·hexamethylphosphoramide

Empirical formula	$C_{27}H_{39}BrN_3OPSn$	Formula weight	651.18
Temperature	298 K	Wavelength	0.71073 Å
Crystal system	Monoclinic	Space group	$P2_1/n$
Unit cell dimensions	a = 11.0142(2), b = 22.0168(4) Å	Volume	3069.8(1) Å^3
	c = 12.6730(3) Å, β = 92.702(1)°	Z	4
Density, Mg m^{-3}	1.409	μ, mm^{-1}	2.208
$F(000)$	1320	θ range of data	1.9 - 25.0°
Index ranges	$-12 \le h \le 13$, $-16 \le k \le 26$, $-14 \le l \le 15$	Reflections collected	16998
Independent reflections	5398 (R_{int} = 0.071)	Completeness of data	99.7 %
Reflections with $I > 2\sigma(I)$	4067	Restraints /parameters	204/301
R (all data), wR	0.079, 0.199	Final R [$I > 2\sigma(I)$], wR	0.062, 0.189
Goodness-of-fit on F^2	1.28	Diff. hole and peak, eÅ^{-3}	-1.73 - 0.83
Weighting scheme	$w = [\sigma^2(F_o^2) + (0.1P)^2]^{-1}$ where $P = (F_o^2 + 2F_c^2)/3$		
Programs	*SHELXS*-97, *SHELXL*-97, *SADABS*, *ORTEP* [6-9]	CCDC deposition no.	162191

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