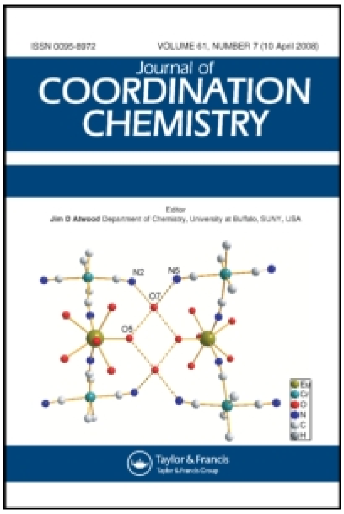

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Ligation to tin(IV) organometallics: crystal structure of tribenzyl(chloro)(4-*N*,*N*-dimethylaminopyridine)tin(IV)

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Ligation to tin(IV) organometallics: crystal structure of tribenzyl(chloro)(4-*N*,*N*′-dimethylaminopyridine)tin(IV)

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The preparation and characterization of the air-stable, five-coordinate complex of 4-(dimethylamino)pyridine with tribenzyltin chloride is reported. The complex crystallizes in space group $P2_1/n$ with $a = 10.3743(17)$, $b = 24.356(17)$, $c = 10.628(2)$ Å, $\beta = 102.504(15)°$. Single crystal X-ray analysis confirms the structure to be monomeric in which the geometry around tin is a trigonal bipyramid with equatorial benzyl groups. The ^{119}Sn NMR signal of the complex in $CDCl_3$ occurs upfield with respect to the corresponding signal in $(C_6H_5CH_2)_3SnCl$, indicating lack of dissociation of the ligand in solution. Computations using the PM3 hamiltonian for the complex yielded a trigonal bipyramidal structure with satisfactory agreement in metrical parameters with those obtained from X-ray analysis.

Keywords: X-ray structure; Trigonal bipyramid; ^{119}Sn NMR; PM3 calculations; Tin(IV); Organometallics; Ligation

1. Introduction

Ligand association and dissociation are important steps in homogeneous catalysis. Organotin(IV) compounds, except for the tetraorganotins, react with various ligands to form complexes. Reactions beyond complexation also occur that include oxidation [1], oligomerization [2] and ligand scrambling [3]. Dialkyl and trialkyltin halides show differences in reactivity. Unlike dibenzyltin chloride, tribenzyltin chloride resists direct complexation with 1,10-phenanthroline but forms dibenzyl(dichloro)(1,10-phenanthroline)tin(IV) [4], which involves ligand scrambling. Dibenzyltin chloride also reacts with 4-(dimethylamino)pyridine to form a hydrolyzed product, bis[chloro(methoxy)(tetrabenzyl)stannoxane]. Five-coordinate tin complexes can assume square pyramidal [5] as well as trigonal bipyramidal geometries with *cis*, *mer* and *trans* configurations, the majority being *trans* isomers [6]. The present investigation was undertaken to assess the reactivity of pyridine bases towards tribenzyltin chloride.

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4-(Dimethylamino)pyridine (DMAP) was chosen because of its catalytic [7], basic and ligation properties [8].

2. Experimental

2.1. *Materials and physical measurements*

4-(Dimethylamino)pyridine was purchased from Aldrich and used as received. Dibenzyltin chloride and tribenzyltin chloride were prepared by the action of benzyl chloride on tin powder in toluene and water as reported previously [9,10]. NMR spectra were recorded on an AMX 400 MHz spectrophotometer and IR spectra were recorded on a JASCO 460 PLUS FT-IR spectrophotometer in the range 4000–400 cm^{-1}. C, H and N contents were analyzed using Carlo Erba 1160 and model 240 Perkin-Elmer CHN instruments.

2.2. *Synthesis of tribenzyl(chloro)(4- N,N′-dimethylaminopyridine)tin(IV)*

A solution of 4-(dimethylamino)pyridine (0.34 g, 2.8 mmol) in methanol was added dropwise to tribenzyltin chloride (0.56 g, 1.4 mmol) also in methanol. After completion of addition, the reaction mixture was stirred overnight. The solvent was then removed *in vacuo* and an oil was obtained. Addition of petroleum ether to the oil yielded colorless crystals, which were dried in high vacuum. Yield = 0.7 g, 97.2%; mp 91–93°C. Anal. Calcd. for $(C_6H_5CH_2)_3SnCl\cdot(4\text{-DMAP})$(%): C, 61.12; H, 5.68; N, 5.09. Found: C, 61.10; H, 5.75; N, 5.15. IR (cm^{-1}) 3014, 2927, 1622, 1595, 1539, 1490, 1449, 1414, 1393, 1346, 1291, 1231, 1205, 1183, 1150, 1114, 1028, 1059, 1046, 1028, 1007, 952, 905, 803, 760, 728, 696, 616, 576, 529. ^{1}H NMR: δ 2.69 (t, 6H) ($^2J_{\mathrm{Sn-H}}$ 68.7 Hz), 3.02 (s, 6H), 6.44 (d, 2H), 6.83–6.90 (m, 5H), 7.02–7.07 (m, 5H), 7.12–7.18 (m, 5H), 7.98 (d, 2H). ^{119}Sn NMR: δ–34.5.

2.3. *Crystal structure determination*

X-ray intensity data were collected on an Enraf-Nonius CAD-4 diffractometer using graphite-monochromatized Mo Kα radiation to a $2\theta_{\max}$ of 24.99°. Among the 4883 data collected, 4616 reflections were unique ($R_{\mathrm{int}} = 0.0619$). Usual Lp and empirical absorptions were applied. The structure was solved by direct methods using the program SIR92 [11] followed by Fourier synthesis. Nonhydrogen atoms were refined anisotropically using 3114 observed reflections [$I > 2\sigma(I)$] with the SHELXL-97 package [12]. Hydrogen atoms were included in the calculated positions with thermal parameters fixed as 1.2 U_{eq} of their corresponding carrier atoms.

2.3.1. *Crystal data.*

$C_{28}H_{31}ClN_2Sn$, $M = 549.71$, Monoclinic, $P2_1/n$, $a = 10.3743(17)$, $b = 24.356(17)$, $c = 10.628(2)$ Å, $\beta = 102.504(15)°$, $V = 2622(2)$ Å^3, $Z = 4$, $F(000) = 1120$, $D\mathrm{x} = 1.393$ mg m^{-3}, μ(Mo Kα) = 1.094 mm^{-1}, $R_1 = 0.0520$, $wR_2 = 0.1205$, GOF = 1.047, no. of variables = 255, $(\Delta\rho)\max = 1.322$ e Å^{-3}.

3. Results and discussion

In the IR spectrum of the complex, one of the $\nu_{C=C/C=N}$ frequencies observed at 1600 cm^{-1} in DMAP was shifted to 1622 cm^{-1} in the product. Such an increase in frequency has been observed in similar complexes [13]. In the ^1H NMR spectrum of the complex, a satellite triplet was observed at 2.69 ppm, due to the protons of the three methylene groups attached to tin. $^2J_{Sn–H}$ at 68.7 Hz is higher than the value of 65.0 Hz observed for tribenzyltin chloride. This may indicate higher *s* character on tin for the Sn–C bonds in the product. The ^{119}Sn NMR signal observed at 49.4 ppm for tribenzyltin chloride was shifted to −34.5 ppm in the product. The upfield signal is attributed to high electron density on tin because of complexation. ^{119}Sn NMR shifts in the range of −42 to −53 ppm have been reported for triorganotin tetrazolylpyridine complexes [14].

Final fractional atomic coordinates and equivalent isotropic thermal parameters for non-H atoms are listed in table 1. Selected bond lengths and angles are given in table 2. The ORTEP diagram (figure 1) indicates the discrete molecular structure for the complex with trigonal bipyramidal geometry for tin. The three benzyl groups occupy equatorial positions while the DMAP and chlorine ligands occupy axial positions.

Table 1. Atomic coordinates and equivalent isotropic displacement parameters of the nonhydrogen atoms for tribenzyl(chloro)-(4-*N*,*N*′-dimethylaminopyridine)tin(IV).

Atom	*x*/*a*	*y*/*b*	*z*/*c*	*U*(eq) (Å^2)
Sn1	0.69438(5)	0.15731(2)	0.40005(4)	0.0430(2)
Cl1	0.9043(2)	0.18920(12)	0.5619(2)	0.0778(9)
N1	0.5012(6)	0.1337(3)	0.2455(5)	0.0470(19)
N2	0.1688(8)	0.0990(4)	−0.0440(7)	0.075(3)
C1	0.6027(8)	0.2369(3)	0.4083(8)	0.056(3)
C2	0.4913(5)	0.2309(3)	0.4773(6)	0.056(3)
C3	0.5175(7)	0.2295(3)	0.6112(5)	0.084(4)
C4	0.4152(11)	0.2216(3)	0.6748(6)	0.116(6)
C5	0.2865(9)	0.2151(3)	0.6045(11)	0.140(9)
C6	0.2603(5)	0.2164(3)	0.4706(11)	0.121(7)
C7	0.3626(6)	0.2243(3)	0.4070(6)	0.079(4)
C8	0.8261(8)	0.1289(4)	0.2807(8)	0.061(3)
C9	0.7708(6)	0.1058(3)	0.1480(4)	0.058(3)
C10	0.7149(7)	0.0537(2)	0.1328(6)	0.074(4)
C11	0.6616(7)	0.0337(3)	0.0100(7)	0.095(5)
C12	0.6642(8)	0.0658(3)	−0.0975(5)	0.106(6)
C13	0.7202(8)	0.1179(3)	−0.0823(4)	0.095(5)
C14	0.7734(7)	0.1379(2)	0.0405(6)	0.072(4)
C15	0.6519(8)	0.0983(3)	0.5387(7)	0.050(3)
C16	0.7165(5)	0.04342(19)	0.5340(5)	0.047(3)
C17	0.8415(5)	0.0350(2)	0.6109(5)	0.070(3)
C18	0.9043(5)	−0.0153(3)	0.6087(6)	0.086(4)
C19	0.8421(7)	−0.0572(2)	0.5295(7)	0.086(4)
C20	0.7171(7)	−0.0488(2)	0.4526(6)	0.068(4)
C21	0.6543(4)	0.0015(2)	0.4548(5)	0.058(3)
C22	0.4041(8)	0.1012(4)	0.2648(7)	0.055(3)
C23	0.2939(8)	0.0896(4)	0.1744(8)	0.062(3)
C24	0.2745(8)	0.1115(4)	0.0498(8)	0.054(3)
C25	0.3753(9)	0.1474(4)	0.0301(8)	0.061(3)
C26	0.4820(7)	0.1581(4)	0.1277(7)	0.052(3)
C27	0.0659(10)	0.0634(6)	−0.0163(12)	0.110(6)
C28	0.1587(12)	0.1154(5)	−0.1765(9)	0.096(5)

Table 2. Selected bond lengths (Å) and angles (°) for tribenzyl(chloro)-(4-*N*,*N*′-dimethylaminopyridine)tin(IV).

	X-ray [PM3] values
Sn1–Cl1	2.585(3) [2.44]
Sn1–N1	2.371(6) [2.63]
Sn1–C1	2.169(8) [2.16]
Sn1–C8	2.169(9) [2.16]
Sn1–C15	2.171(8) [2.16]
Cl1–Sn1–N1	176.34(18) [179.61]
N1–Sn1–C1	86.1(3) [86.92]
Cl1–Sn1–C1	91.0(2) [93.22]
N1–Sn1–C8	93.6(3) [85.69]
Cl1–Sn1–C8	86.5(2) [93.92]
N1–Sn1–C15	92.5(3) [85.02]
Cl1–Sn1–C15	90.7(2) [95.22]
C1–Sn1–C8	130.2(3) [120.19]
C1–Sn1–C15	114.1(3) [119.07]
C8–Sn1–C15	115.6(3) [119.21]

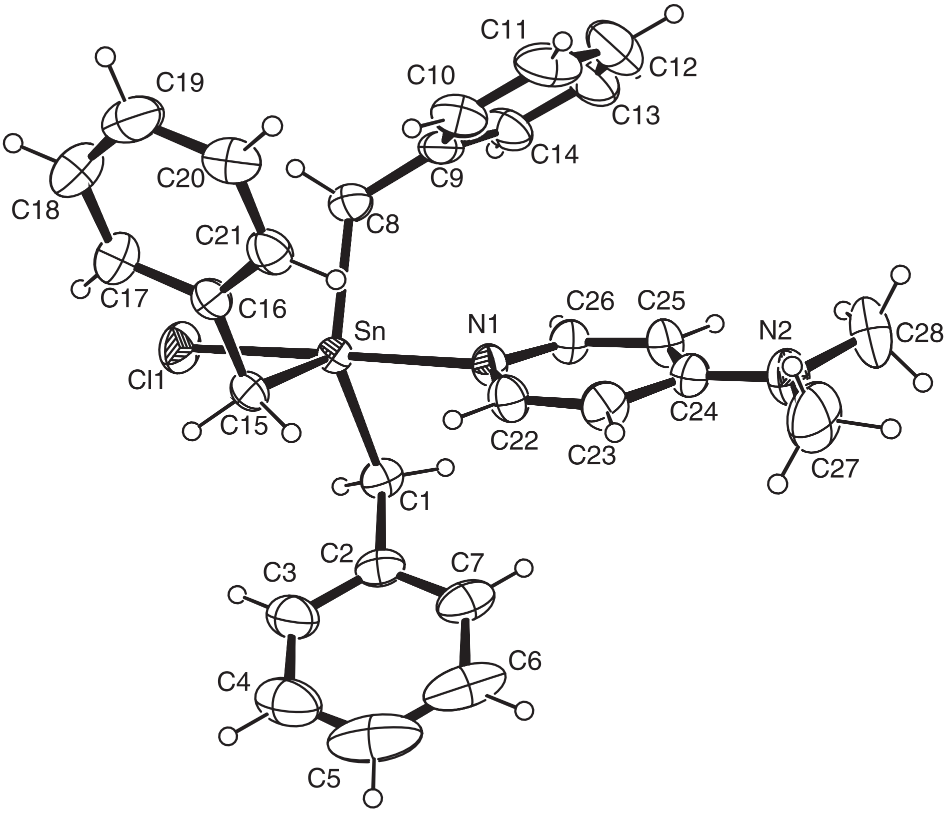

Figure 1. Molecular structure of the title complex showing 30% probability displacement ellipsoids and the atom numbering scheme.

Table 3. Mean planes (*x*, *y*, *z* in crystal coordinates) and deviations (Å) from them for the complex.

The mean plane **1** formed by N(1), C(22), C(23), C(24), C(25) and C(26) atoms
$-5.7306x + 18.8800y + 4.4524z = 0.7689$
N(1) −0.0234, C(22) 0.0043, C(23) 0.0148, C(24) −0.0151, C(25) −0.0036, C(26) 0.0229
The mean plane **2** formed by C(1), C(8), C(15) and Sn(1) atoms
$6.8655x + 7.6568y + 5.5391z = 8.2068$
C(1) 0.0066, C(8) 0.0067, C(15) 0.0056, Sn(1) −0.0190
Dihedral angle between planes **1** and **2** = 85.0(2)°

Plane calculations show that the dihedral angle between the aromatic ring and the C1, C8, C15 and Sn1 plane is 85.02(1)° (table 3). The three Sn–C bond lengths [2.169(8), 2.171(7) and 2.169(8) Å] are comparable to the mean value observed in tribenzyltin chloride [2.136(3) Å]. The Sn–Cl bond length [2.585(2) Å] is higher than that reported for tribenzyltin chloride [2.387(2) Å] [15]. The Sn–N bond [2.371(6) Å] is longer than Sn–C bond lengths, which indicates that the Sn–N bond is a coordinate bond.

The metrical parameters of the complex obtained for the PM3 optimized geometry are very close to those obtained by X-ray analysis except for Sn–Cl and Sn–N bond lengths, which are underestimated and overestimated, respectively. Optimized geometry of the trimethyl analog by *ab initio* methods [3-21G(*)] results in considerable improvement for these parameters (2.50 and 2.47 Å, respectively). A molecular orbital energy level diagram obtained through PM3 calculations shows that there are five low energy levels characterized by the orbital energies −16.33, −15.08, −15.08, −15.04 and −14.48 eV. This is characteristic for the *trans* isomer $R_3SnCl \cdot X$ and differs from the energy level order for *cis* and *mer* isomers [16]. All bonds around the metal center are formed by the lower contribution of tin orbitals when compared with those of tribenzyltin chloride. This accounts for the longer bond lengths around tin in the complex. In particular, the contribution of tin orbitals to the Sn–N bond is only 5%. PM3 optimization using the initial geometry with Cl–Sn–N angles of 90° and 180° resulted in structures with heats of formation of 75.2 and 71.8 kcal mol^{-1}, respectively (1 cal = 4.184 J). Corresponding angles in the optimized geometry were 73.3° and 179.6°. This indicates the higher thermodynamic stability of the *trans* isomer. The crystal structure reveals no strong intermolecular interactions and the molecules are held together by van der Waals forces only.

Supplementary data

Crystallographic data for the structure reported in this article have been deposited with the Cambridge Crystallographic Data Centre (CCDC No. 234958). Copies of this information can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 IEZ, UK; fax: +44 1223 336033.

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