Synthesis and structure of [2-(4,4-dimethyl-2-oxazoline)-5-methylphenyl]methylphenyltin bromide. A novel triorganotin halide having a configurationally stable chiral tin center

Johann T.B.H. Jastrzebski, Erik Wehman, Jaap Boersma, Gerard van Koten *

University of Utrecht, Debye Research Institute, Department of Metal-Mediated Synthesis, Padualaan 8, 3584 CH Utrecht (Netherlands)

Kees Goubitz and Dick Heijdenrijk

Laboratory for Crystallography, University of Amsterdam, J.H. van 't Hoff Instituut, Nieuwe Achtergracht 166, 1018 WV Amsterdam (Netherlands)

Abstract

Reaction of [2-(4,4-dimethyl-2-oxazoline)-5-methylphenyl]copper with dimethyltin dibromide or methylphenyltin dibromide affords [2-(4,4-dimethyl-2-oxazoline)-5-methylphenyl]dimethyltin bromide (1) and [2-(4,4-dimethyl-2-oxazoline)-5-methylphenyl]methylphenyltin bromide (2), respectively. The crystal structure of 2 has been determined by X-ray diffraction methods. $C_{19}H_{22}BrNOSn$ is monoclinic, space group $P2_1/a$ with $a = 18.1258(9)$, $b = 11.5704(11)$, $c = 9.5315(6)$ Å, $\beta = 95.143(6)°$ and $Z = 4$, final $R = 0.038$ for 2760 observed reflections. As a result of intramolecular coordination of the nitrogen atom of the oxazoline ring to the tin atom, the geometry about tin in 1 is trigonal bipyramidal. The carbon ligands are at the equatorial sites, while the more electronegative nitrogen and bromine atoms are at the axial positions. An ^1H NMR spectroscopic study showed that in solution the chiral tin center is configurationally stable up to 120°C (the highest temperature studied).

Introduction

Previously we reported on the synthesis and structural characterization in the solid state (X-ray structures) and in solution (by NMR techniques) of a series of triorganotin bromides containing C,N-chelating ligands for which the structures are schematically shown in Fig. 1.

All these compounds have in common that the dimethylamino group, present in the ligand systems, is intramolecularly coordinated to the tin center. This results in a trigonal bipyramidal coordination geometry at the tin center, with the carbon ligands at the equatorial sites and the more electronegative nitrogen and bromine atoms at the axial positions. As a result of the intramolecular coordination in compounds of type **A** and **B** a six-membered chelate ring is formed [1], while in **C** [2], **D** [3–6] and **E** [7,8] a five-membered chelate ring is present.
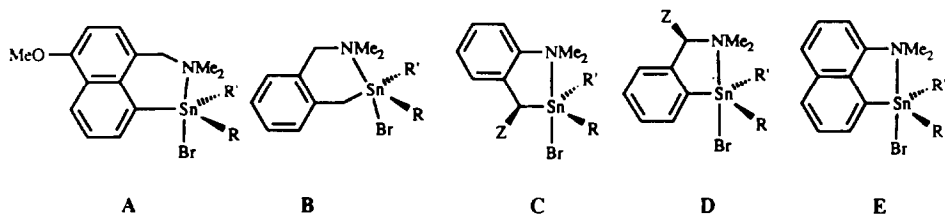
Fig. 1.

For the triorganotin bromides, in which either the tin center ($R \neq R'$), or the benzylic carbon atom ($Z \neq H$) or both are chiral, the configurational stability of the tin center in solution could be studied by NMR techniques. Conclusions drawn from these studies are: *i*, in compounds in which a six-membered chelate ring is present (**A** and **B**) the tin center is only configurationally stable at low temperature (below $0°C$) [1], *ii*, the tin center in triorganotin bromides in which a flexible five-membered chelate ring is present (**C** and **D**) is much more stable on the NMR time scale (up to $130°C$, the highest temperature studied), while a process is involved that consists of Sn–N dissociation, rotation around the C–N bond, pyramidal inversion at nitrogen and finally Sn–N association. This process is fast on the NMR time scale above $0°C$ [2–6], and *iii*, in triorganotin bromides containing a rigid five-membered chelate ring (**E**) the tin center is configurationally stable while Sn–N coordination is inert, on the NMR time scale, at temperatures up to at least $130°C$ [7,8].

Finally, it was shown by studying an enantiomerically pure diastereoisomer of type **D**, R = Me, R' = Ph and Z = Me [5], that inversion of configuration at the tin center does occur on the laboratory time scale, even at as low a temperature as $-15°C$, i.e. under conditions in which the tin center is pentacoordinate.

In this paper we report on the synthesis and structural characterization of novel triorganotin bromides containing the rigid 2-(4,4-dimethyl-2-oxazoline)-5-methyl-phenyl group. This ligand has two different heteroatoms, one imine-N and an ether-O, which in principle are both in a proper position to coordinate to a metal in the ortho position by forming a five-membered chelate ring. In contrast to the reaction of aryllithium compounds with organotin halides, which often give mixtures of organotin products, we have previously shown that arylcopper compounds react in a very selective way with diorganotin dihalides and monoorganotin trihalides giving pure triorganotin halides [5,9] and diorganotin dihalides [10], respectively. Therefore, the here described triorganotin compounds were prepared from recently reported 2-(4,4-dimethyl-2-oxazoline)-5-methylphenylcopper for which it was established by X-ray crystallography that the nitrogen atom coordinates preferentially to copper [11].

Results and discussion

Synthesis and structure in solution of [2-(4,4-dimethyl-2-oxazoline)-5-methylphenyl]dimethyltin bromide (1) and [2-(4,4-dimethyl-2-oxazoline)-5-methylphenyl]methylphenyltin bromide (2)

Addition of a diethyl ether solution of dimethyltin dibromide or methylphenyltin dibromide to a diethyl ether solution of [2-(4,4-dimethyl-2-oxazoline)-5-methyl-

phenyl]copper, which was prepared starting from pure 2-(4,4-dimethyl-2-oxazoline)-5-methylphenyllithium, according to the procedures given in ref. 11, in a 1:1 molar ratio give rise to the formation of the corresponding triorganotin bromides **1** and **2** in 75 and 85% yield, respectively (eq. 1).
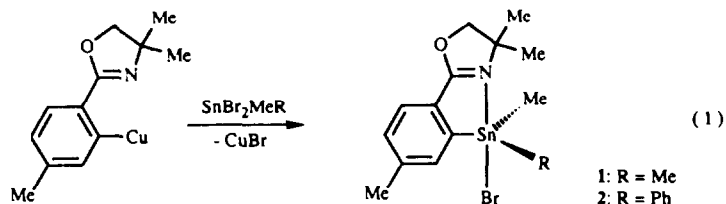
These triorganotin bromides, **1** and **2**, are white crystalline solids which were identified by elemental analysis and ^{1}H NMR spectroscopy (see Experimental part). According to their molecular weight data (cryoscopy in benzene) **1** and **2** exist as monomers in solution.

The structures of **1** and **2** in solution were studied by ^{1}H NMR spectroscopy (see Experimental part). The $^2J(^{117,119}Sn-^1H)$ values of 73 and 75 Hz (in **1**) and 73 and 76 Hz (in **2**) indicate that the tin center in these compounds is pentacoordinate [1–8,12,13]. Furthermore, the observation of two resonances for the CMe_2 group and an AB pattern for the OCH_2 group of the oxazoline ring in **2** indicates that the tin atom in this compound is a chiral center which is configurationally stable on the NMR time scale, most likely as a result of intramolecular coordination.

Since the oxazoline ring bears two heteroatoms (N and O), in principle the tin atom in **1** and **2** can reach pentacoordination via intramolecular Sn–N or Sn–O coordination. In both cases a five-membered chelate ring is formed. Because the ^{1}H NMR spectra do not allow conclusions to be drawn on the question of which of the two heteroatoms is involved in intramolecular coordination *, an X-ray crystal structure determination of **2** was carried out.

Molecular geometry and crystal structure of [2-(4,4-dimethyl-2-oxazoline)-5-methylphenyl]methylphenyltin bromide (2)

The crystal structure of **2** involves the packing of four discrete mononuclear molecules in the unit cell. Figure 2 shows a PLUTO view of **2** together with the adopted numbering scheme. Selected geometrical data for **2** are given in Table 1.

In **2** the tin atom has a trigonal bipyramidal coordination geometry as a result of C,N-chelate bonding of the 2-(4,4-dimethyl-2-oxazoline)-5-methylphenyl group. The carbon ligands are at the equatorial sites and the more electronegative nitrogen and bromine atoms are at the axial positions. This coordination geometry is normally found in pentacoordinate triorganotin halides [1–8]. The Sn–N distance of 2.414(4) Å found in **2** is about 0.1 Å shorter than the Sn–N distances in triorganotin halides containing a C,N-chelating ligand in which the nitrogen atom is sp^3-hybridized.

---

* The absolute difference in $\delta\nu$ values (0.20 ppm for the diastereotopic CMe_2 group and 0.02 ppm for the diastereotopic CH_2 group) of the oxazoline ring, observed in the ^{1}H NMR spectrum of **2**, suggests that the CMe_2 group is closer to the chiral tin center than the CH_2 group, i.e. Sn–N coordination occurs. However, Sn–O coordination would be more favorable for steric reasons.
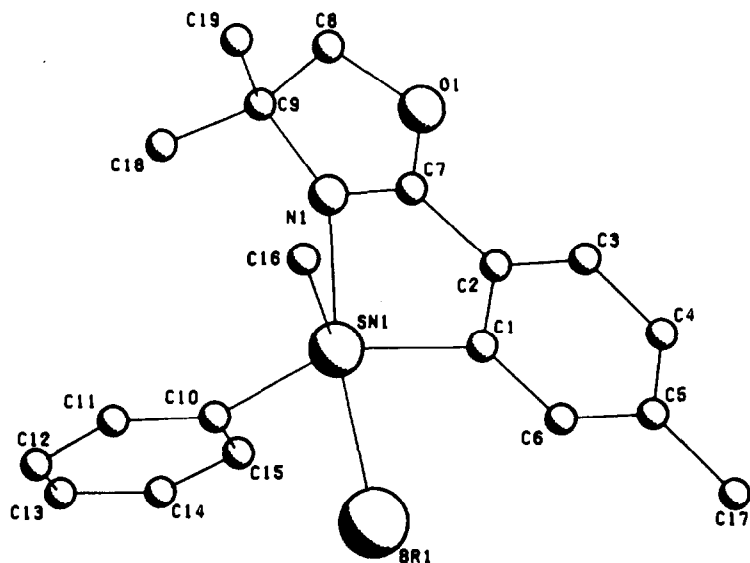
Fig. 2. PLUTO drawing of 2 with the adopted numbering scheme.

Since in 2 the coordinating nitrogen atom is sp^2-hybridized, a shorter Sn–N distance is indeed expected. This distance is in the same range as found in the 2,2'-bipyridyl complex of diethyltin dichloride, 2.368(4) and 2.382(4) Å [14]. Recently, the X-ray crystal structure determination of N-methyl-2-trichlorostannyldiphenylmethylenea-mine has been reported [15]. This compound contains a sp^2-hybridized nitrogen atom which is coordinated to tin, with a Sn–N distance of 2.284(4) Å. This extremely short Sn–N distance may be a result of the increased Lewis acidity of the tin center due to the presence of three chlorine atoms.

These studies have shown that the nitrogen atom of the oxazoline ring prefer-entially coordinates to tin, although Sn–O coordination would lead to a sterically less crowded molecule. Furthermore it was shown that the chiral tin center in 2 is configurationally stable on the NMR time-scale.

Table 1

Relevant data on the geometry of 2

Bond lengths (Å)			
Sn1–Br1	2.6788(8)	Sn1–N1	2.414(5)
Sn1–C1	2.148(6)	Sn1–C10	2.125(6)
Sn1–C16	2.129(7)	N1–C7	1.282(9)
O1–C7	1.326(9)		
Bond angles (deg.)			
Br1–Sn1–N1	171.3(1)	Br1–Sn1–C1	95.8(2)
Br1–Sn1–C10	95.8(2)	Br1–Sn1–C16	93.2(2)
N1–Sn1–C1	75.6(2)	N1–Sn1–C10	88.6(2)
N1–Sn1–C16	90.8(3)	C1–Sn1–C10	112.4(2)
C1–Sn1–C16	123.8(3)	C10–Sn1–C16	121.7(3)

Experimental

Syntheses were carried out using standard Schlenk techniques in an atmosphere of purified nitrogen. The solvents were dried and distilled from sodium prior to use. [2-(4,4-dimethyl-2-oxazoline)-5-methylphenyl]copper was prepared according to published methods [11]. ^{1}H NMR spectra were recorded on a Bruker AC200 spectrometer.

Synthesis of the triorganotin bromides 1 and 2

To a solution of [2-(4,4-dimethyl-2-oxazoline)-5-methylphenyl]copper (2.8 mmol) in diethyl ether (50 mL) was added a solution of dimethyltin dibromide or methylphenyltin dibromide (2.8 mmol) in diethyl ether (20 mL). The resulting pale yellow suspension was stirred for 15 min and subsequently evaporated to dryness *in vacuo*. The remaining residue was extracted with two 50 mL portions of hot (70°C) benzene. The combined benzene extracts were evaporated at reduced pressure and the remaining solid material was washed with pentane, giving the triorganotin bromides 1 and 2 as white solids in 75 and 85% yield, respectively. For analytical purposes the compounds were recrystallized from a toluene–pentane mixture (50 : 50). 1: Anal. Found: C, 40.21; H, 4.73; Br, 19.22; N, 3.31; MW 401 (cryoscopy in C_6H_6). $C_{14}H_{20}BrNOSn$ calcd.: C, 40.33; H, 4.84; Br, 19.17; N, 3.36%; MW 417. ^{1}H NMR (CDCl$_3$, 25°C): δ 0.73 ((CH_3)$_2$Sn, s, 6H, $^2J(^{117,119}Sn-^1H)$ 73, 75 Hz); 1.22 ((CH_3)$_2$C, s, 6H); 2.25 (CH_3-ar, s, 3H); 4.20 (CH_2O, s, 2H); 8.03 (H(3), s, 1H).

2: Anal. Found: C, 47.35; H, 4.51; Br, 16.58; N, 2.90; MW 461 (cryoscopy in C_6H_6). $C_{19}H_{22}BrNOSn$ calcd.: C, 47.64; H, 4.63; Br, 16.68; N, 2.92%; MW 479. ^{1}H NMR (CDCl$_3$, 25°C): δ 0.80 (CH_3Sn, s, 3H, $^2J(^{117,119}Sn-^1H)$ 73, 76 Hz); 1.11 and 1.31 ((CH_3)$_2$C, s and s, 3H and 3H); 2.45 (CH_3-ar, s, 3H); 4.24 and 4.26 (CH_2O, d and d, 1H and 1H, $^2J(HH)$ 12 Hz); 8.28 (H(3), s, 1H).

Crystal structure determination of 2 *

Transparent colorless crystals of 2 were obtained by diffusion of pentane vapor into a benzene solution of 2.

Crystal data. $C_{19}H_{22}BrNOSn$, M = 478.99, monoclinic, space group $P2_1/a$, $a = 18.1258(9)$, $b = 11.5704(11)$, $c = 9.5315(6)$ Å, $\beta = 95.143(6)°$; $U = 1991$ Å^3, $Z = 4$, $D_c = 1.60$ g cm^{-3}, $F(000) = 944$. 3574 independent intensities ($2.5 < \theta < 65°$) were measured on a Enraf Nonius CAD4 diffractometer at 25°C using graphite monochromated Cu-K_α radiation ($\lambda(Cu$-$K_\alpha) = 1.5418$ Å); 814 of these were below the $2.5\sigma(I)$ level and were treated as unobserved.

The Sn and Br positions were located by means of the symbolic addition program set SIMPEL [16]. The positions of the C, N and O atoms were obtained by standard difference Fourier techniques. After isotropic block-diagonal least-squares refinement an empirical absorption correction (DIFABS [17]) was applied (crystal dimensions $0.2 \times 0.15 \times 0.2$ mm; $\mu(Cu$-$K_\alpha) = 128.6$ cm^{-1}). Hydrogen atoms were introduced at their calculated positions, Continued refinement, anisotropic for Sn, Br, N, C and O (the temperature factors of the hydrogen atoms were kept fixed at 0.04 Å^2) converged to $R = 0.038$ ($R_w = 0.065$). A weighting scheme $w = 1/(7.3 + F_o + 0.015F_o^2)$ was applied and the anomalous dispersions of Sn and Br were taken into account. Final coordinates are given in Table 2.

---

* Complete tables of atomic coordinates, bond distances and angles and lists of thermal parameters and structure factors can be obtained from the authors.

Table 2

Atomic fractional coordinates and equivalent isotropic thermal parameters ($\mathring{A}^2$) for **2**

	x	y	z	U_{eq} [a]
Sn(1)	0.33249(2)	0.38444(4)	0.63546(4)	0.0413(2)
Br(1)	0.20079(4)	0.49101(7)	0.60784(9)	0.0616(4)
C(1)	0.3934(4)	0.5292(6)	0.7272(7)	0.045(3)
C(2)	0.4687(4)	0.5106(6)	0.7635(7)	0.047(3)
C(3)	0.5132(4)	0.5946(7)	0.8339(8)	0.061(4)
C(4)	0.4818(4)	0.6997(7)	0.8631(8)	0.061(4)
C(5)	0.4080(5)	0.7233(7)	0.8248(8)	0.060(4)
C(6)	0.3642(4)	0.6359(6)	0.7573(8)	0.049(4)
C(7)	0.4988(4)	0.3972(6)	0.7302(8)	0.051(4)
C(8)	0.5833(5)	0.2586(9)	0.713(1)	0.097(7)
C(9)	0.5075(4)	0.2145(7)	0.6539(9)	0.059(4)
C(10)	0.3040(3)	0.2634(5)	0.7894(6)	0.038(3)
C(11)	0.2687(4)	0.1603(6)	0.7531(7)	0.051(4)
C(12)	0.2522(5)	0.0806(7)	0.8589(9)	0.065(5)
C(13)	0.2770(5)	0.1022(8)	0.9956(9)	0.070(5)
C(14)	0.3101(5)	0.2048(9)	1.0327(7)	0.076(6)
C(15)	0.3245(5)	0.2853(7)	0.9299(8)	0.062(4)
C(16)	0.3278(5)	0.3408(8)	0.4178(7)	0.065(5)
C(17)	0.3728(6)	0.8372(8)	0.852(1)	0.086(7)
C(18)	0.4826(7)	0.1136(8)	0.739(1)	0.090(7)
C(19)	0.5048(6)	0.182(1)	0.501(1)	0.093(7)
N(1)	0.4587(3)	0.3167(5)	0.6709(6)	0.047(3)
O(1)	0.5704(3)	0.3759(5)	0.7601(8)	0.081(4)

$$U_{eq} = 1/3 \sum_i \sum_j U_{ij} a_i^* a_j^* (\mathbf{a}_i \cdot \mathbf{a}_j).$$

References

1 G. van Koten, J.T.B.H. Jastrzebski, J.G. Noltes, G.J. Verhoeckx, A.L. Spek and J. Kroon, J. Chem. Soc., Dalton Trans., (1980) 1352.
2 J.T.B.H. Jastrzebski, G. van Koten, C.T. Knaap, A.M.M. Schreurs, J. Kroon and A.L. Spek, Organometallics, 5 (1986) 1551.
3 G. van Koten, J.G. Noltes and A.L. Spek, J. Organomet. Chem., 118 (1976) 183.
4 G. van Koten and J.G. Noltes, J. Am. Chem. Soc., 98 (1976) 5393.
5 G. van Koten, J.T.B.H. Jastrzebski, J.G. Noltes, W.M.G.F. Pontenagel, J. Kroon and A.L. Spek, J. Am. Chem. Soc., 100 (1978) 5021.
6 J.T.B.H. Jastrzebski, J. Boersma and G. van Koten, J. Organomet. Chem., (1991) in press (JOM 21391, dedicated to Professor P.L. Pauson, to appear in August 1991).
7 J.T.B.H. Jastrzebski, C.T. Knaap and G. van Koten, J. Organomet. Chem., 255 (1983) 287.
8 J.T.B.H. Jastrzebski, J. Boersma, P. Esch and G. van Koten, Organometallics, (1991) in press.
9 G. van Koten, C.A. Schaap and J.G. Noltes, J. Organomet. Chem., 99 (1975) 157.
10 G. van Koten, J.T.B.H. Jastrzebski and J.G. Noltes, J. Organomet. Chem., 177 (1979) 283.
11 E. Wehman, G. van Koten, J.T.B.H. Jastrzebski, M.A. Rotteveel and C.H. Stam, Organometallics, 7 (1988) 1477.
12 T.N. Michel, J. Organomet. Chem., 59 (1973) 189.
13 M. Gielen, Pure Appl. Chem., 52 (1980) 657.
14 S.L. Chadha, P.G. Harrison and K.C. Molloy, J. Organomet. Chem., 202 (1980) 247.
15 W. Clegg, C.M.J. Grievson and K. Wade, J. Chem. Soc., Chem. Commun., (1987) 969.
16 A.B. Overbeek and H. Schenk, in H. Schenk, R. Olthof, H. van Koningsveld and C.G. Bassi (Eds.), Computing in Crystallography, Delft University Press, Delft, 1978.
17 N. Walker and D. Stewart, Acta Crystallogr., Sect. A, 39 (1983) 158.