

Synthesis and crystal structure of dimeric 2,4,6-triphenylphenylbismuthdichloride

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Abstract

Reaction of BiCl_3 with one equivalent of 2,4,6-triphenylphenyllithium in toluene results in the formation of crystalline 2,4,6-triphenylphenylbismuthdichloride toluene disolvate (**1**). The crystal structure of **1** has been determined by X-ray diffraction. In spite of the extremely bulky substituents at the bismuth atom, complex **1** is dimeric in the solid state with intramolecular Bi–Cl bond lengths of 2.530(1) Å and bridging Bi–Cl of 3.074(1) Å.

Keywords: Bismuth; Arylbismuth compounds; X-ray diffraction

1. Introduction

Previously we described the synthesis, structure and chemical behaviour of arylbismuth compounds with the 2,4,6-triphenylphenyl substituent as a bulky ligand [1]. We expected that the use of bulky ligands at the bismuth atom would lead to a kinetic stabilization of low-valent bismuth compounds, the latter having been very little investigated so far.

Our first attempts at the reduction of bis(2,4,6-triphenylphenyl)bismuthchloride with sodium in liquid ammonia, or with magnesium in THF, led to 1,3,5-triphenylbenzene as the only identifiable product. In contrast, the reaction between 2,4,6-triphenylphenylbismuthdichloride (**1**) and cobaltocene results in the formation of a deep red coloured, unstable species, formulated to be a monovalent organobismuth compound. The latter quickly decomposes to tris(2,4,6-triphenylphenyl)bismuth and metallic bismuth, even at temperatures below -70°C . Regarding these results we postulated an oligomeric composition for the monovalent bismuth compound, e.g. $\{(\text{C}_6\text{H}_5)_3\text{C}_6\text{H}_2\text{Bi}\}_x$ (**2**). It is now of interest to know whether the starting material in the

reduction reaction, i.e. $(\text{C}_6\text{H}_5)_3\text{C}_6\text{H}_2\text{BiCl}_2$ (**1**), also possesses an oligomeric structure, which would allow for a prediction of the formation of the unstable oligomeric **2**. Following this idea we report here the crystal and molecular structure of **1** determined by an X-ray diffraction study.

2. Results and discussion

2.1. Synthesis of $(\text{C}_6\text{H}_5)_3\text{C}_6\text{H}_2\text{BiCl}_2$ (**1**)

As reported earlier, **1** can be prepared by a comproportionation reaction of BiCl_3 with tris(2,4,6-triphenylphenyl)bismuth in THF [1]. The yield of this reaction varies from 30 to 60%, but the product is difficult to purify owing to its low solubility in common organic solvents. Furthermore, all attempts to recrystallize **1** from dilute THF or toluene solutions result in a yellowish-grey powder. Contrary to this observation, we have found that the reaction between 2,4,6-triphenylphenyllithium and BiCl_3 in a 1:1 ratio in toluene leads to the formation of small amounts of **1** (ca. 20%) together with bis(2,4,6-triphenylphenyl)bismuthchloride (**3**). These products can be separated by diffusional crystallization: **1** crystallizes as a toluene disolvate giving well-shaped crystals separating at 5°C , while the main product (**3**) remains in solution at this temperature.

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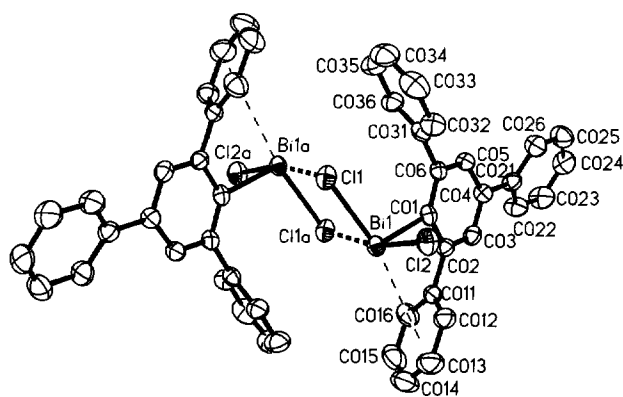


Fig. 1. A view of **1** with atomic numbering scheme. The thermal ellipsoids are scaled to 50% probability level.

Table 1
Crystal data and structure refinement for **1**

Identification code	avtbi
Empirical formula	$C_{24}H_{17}BiCl_2 \cdot 2C_7H_8$
Formula weight	769.52
Temperature (K)	223(2)
Wavelength (Å)	0.71073
Crystal system	monoclinic
Space group	$P2_1/n$, $Z = 4$
Unit cell dimensions ^a	$a = 16.245(2)$ Å $b = 9.7147(8)$ Å, $\beta = 101.51(1)^\circ$ $c = 21.404(2)$ Å $V = 3310.0(5)$ Å ³
Density (calc.) (g cm ⁻³)	1.544
Absorption coefficient (Mo K α) (mm ⁻¹)	5.512
$F(000)$	1512
Crystal size (mm ³)	$0.35 \times 0.30 \times 0.30$
θ range for data collection	2.46 to 24.91°
Index ranges	$-18 \leq h \leq 0$, $0 \leq k \leq 10$, $-24 \leq l \leq 23$
Diffractometer type	Enraf–Nonius CAD4
Scan mode	ω -scans
Scan width	$(0.81 + 0.14 \tan \theta)^\circ$
Reflections collected	5060
Independent reflections	4869 [$R(I) = 0.0268$]
Intensity control	3 reflections every 197, no decay
Absorption correction	from Ψ scans
Min./max. transmission	0.315/0.439
Refinement method	Full-matrix least-squares on F^2
Data/parameters	4868/423
Goodness-of-fit on F^2	1.026
Final R indices [$I > 2\sigma(I)$] ^b	$R_1 = 0.0248$, $wR_2 = 0.0597$
R indices (all data)	$R_1 = 0.0411$, $wR_2 = 0.0655$
Extinction coefficient ^c	0.00037(10)
Largest difference peak and hole (e Å ⁻³)	0.652 (at Bi) and -0.861

^a From 25 reflections with $17.5 < \theta < 22.3^\circ$.

^b $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$; $w = [\sigma^2(F_o^2) + 0.0372 P]^2 + 3.6138 P]^{-1}$, $P = (\max(F_o^2, 0) + 2F_c^2)/3$.

^c Extinction correction formula $F_c^* = F_c k[(1 + 0.001 XF_c^2 \lambda^3) / \sin 2\theta]^{-1/4}$, k = overall scale factor.

Table 2

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **1**

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
Bi(1)	6308(1)	5575(1)	248(1)	31(1)
Cl(1)	4923(1)	6767(1)	247(1)	39(1)
Cl(2)	7146(1)	7780(1)	454(1)	45(1)
C(01)	6394(3)	5531(5)	-795(2)	31(1)
C(02)	6951(3)	4501(5)	-894(2)	31(1)
C(03)	7035(3)	4189(5)	-1513(2)	35(1)
C(04)	6570(3)	4881(5)	-2033(2)	32(1)
C(05)	6005(3)	5871(5)	-1918(2)	34(1)
C(06)	5905(3)	6222(5)	-1306(2)	29(1)
C(011)	7443(3)	3747(5)	-338(2)	34(1)
C(012)	8032(3)	4452(7)	116(2)	45(1)
C(013)	8451(4)	3774(9)	659(3)	63(2)
C(014)	8300(5)	2427(9)	749(3)	71(2)
C(015)	7728(5)	1720(9)	312(4)	70(2)
C(016)	7302(4)	2370(6)	-233(3)	50(2)
C(021)	6684(3)	4587(5)	-2694(2)	37(1)
C(022)	6978(4)	3333(7)	-2859(3)	49(1)
C(023)	7100(4)	3069(8)	-3470(3)	61(2)
C(024)	6925(4)	4085(8)	-3925(3)	58(2)
C(025)	6627(4)	5324(7)	-3777(3)	57(2)
C(026)	6509(4)	5584(7)	-3166(3)	48(1)
C(031)	5288(3)	7317(5)	-1233(2)	33(1)
C(032)	5554(4)	8575(6)	-950(3)	45(1)
C(033)	4963(5)	9563(7)	-890(3)	59(2)
C(034)	4130(5)	9353(7)	-1106(3)	65(2)
C(035)	3864(4)	8127(7)	-1394(3)	56(2)
C(036)	4441(3)	7115(6)	-1457(3)	42(1)
C(2)	5102(6)	1907(10)	-5915(4)	95(3)
C(1)	5209(9)	2320(16)	-5234(7)	111(4)
C(3)	4391(8)	918(13)	-6118(6)	63(3)
C(4)	4264(10)	428(17)	-6694(8)	85(4)
C(5)	4731(9)	796(13)	-7135(6)	68(3)
C(6)	5409(7)	1699(13)	-6908(6)	59(3)
C(7)	5571(7)	2221(11)	-6286(5)	60(3)
C(1A)	5531(17)	3267(29)	-5592(13)	111(4)
C(3A)	4658(14)	1290(22)	-5826(11)	63(3)
C(4A)	4297(17)	303(31)	-6267(14)	85(4)
C(5A)	4393(16)	300(26)	-6907(13)	68(3)
C(6A)	5060(16)	1069(25)	-7047(11)	59(3)
C(7A)	5418(13)	1996(23)	-6591(12)	60(3)
C(8)	4735(5)	2683(8)	-2275(4)	92(3)
C(9)	3991(4)	3532(7)	-2318(3)	64(2)
C(10)	3434(4)	3336(6)	-1928(3)	50(1)
C(11)	2723(4)	4141(7)	-1969(3)	62(2)
C(12)	2537(5)	5163(8)	-2409(3)	70(2)
C(13)	3103(5)	5384(8)	-2819(3)	71(2)
C(14)	3808(5)	4598(7)	-2778(3)	70(2)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

2.2. Crystal structure of **1**

The crystal structure of **1** was determined by a single crystal X-ray diffraction study. The molecular structure of **1** with the atomic numbering scheme is shown in Fig. 1; experimental data of the crystal structure determination are given in Table 1; partial atomic coordinates with equivalent isotropic displacement parameters in Table 2. Selected bond lengths and angles are summa-

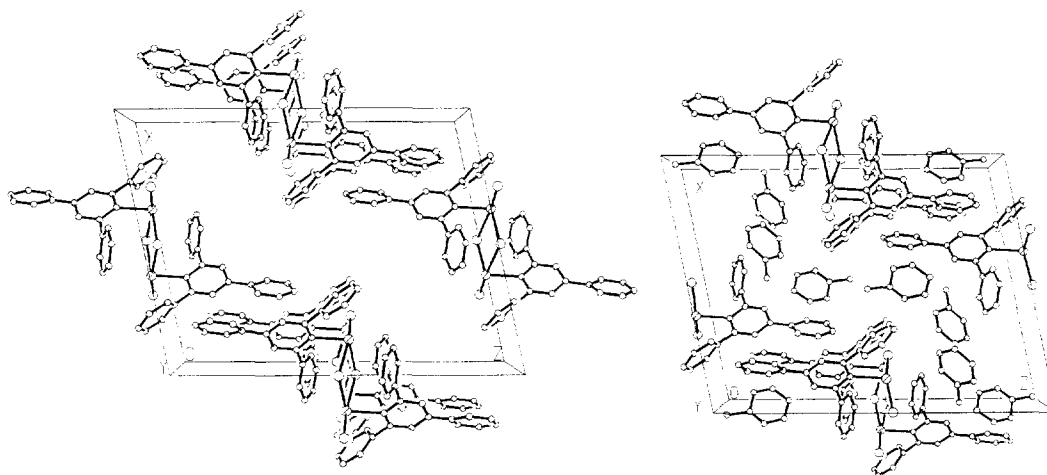


Fig. 2. Cell plots of **1** showing the filling of the 'free space' by toluene molecules.

rized in Table 3. The structure of **1** is dimeric with two terminal and two bridging chlorine substituents: Bi–Cl distances in the monomeric fragment are almost identical with an average value of 2.530(1) Å. These bond lengths are somewhat longer than those in BiCl₃ (2.48 Å), which have been determined by electron diffraction methods in the gas phase [2], but they are shorter than in pentavalent bismuth compounds, e.g. in Ph₃BiCl₂ (2.58 Å) or Tol₃BiCl₂ (2.59 Å) [3,4]. In polymeric PhBiCl₂ · THF the distance between non-bridging chlorine atoms and the bismuth atom is similar to that in **1**, whereas the distance Bi–Cl (bridging) of 2.65 Å is significantly longer [5]. The intermolecular bond Bi(1)–Cl(1a) of 3.074(1) Å is by 0.14 Å longer than that in PhBiCl₂ · THF. This could be explained by a repulsive force between the bismuth atoms. The intermolecular distance Bi–Bi of 4.316(1) Å is smaller than the sum of the van der Waals radii of both bismuth atoms, which is 4.68 Å [6]. The bond length Bi(1)–C(01) of 2.266(4) Å is exactly the same as in PhBiCl₂ (2.266 Å) and somewhat smaller than that in [2,4,6-(C₆H₅)₃C₆H₂]₃Bi (2.36 Å) [1]. The geometry around the bismuth atom can best be described as a square-based pyramid: the sum of the angles Cl(1)–Bi(1)–Cl(2), Cl(1a)–Bi(1)–Cl(2) and Cl(1)–Bi(1)–Cl(1a) adds up to 351°, indicating that all four atoms are nearly positioned in one plane. Accepting this view the chlorine substituents can be referred to

as the caps of a pyramid cage, one absent corner of this is found in the centroid of the phenyl ring and defined by the C(011)–C(016) carbon atoms. The carbon atom C(01) would then accomplish a pyramidal coordination sphere at bismuth.

The intramolecular interaction between the bismuth atom and the phenyl group is remarkable: the distances between Bi(1) and the C(011)–C(016) carbon atoms are in the range 3.01–3.83 Å, resulting in a distance Bi(1)–centroid of 3.53 Å. The sum of the van der Waals radii of the bismuth atom and the carbon atoms is 4.04 Å, and thus by 0.5 Å larger than the values found here. The triphenylphenyl ligand can therefore be considered as acting in a bifunctional way: such interactions with aromatic compounds and complexes containing trivalent bismuth or antimony halides are well known and are termed Men'shutkin interactions [7].

The packing of the highly crowded molecules bearing the bulky triphenylphenyl ligand opens much space which can be filled by solvent molecules. In addition to the dimeric **1** there are two molecules of toluene in the asymmetric cell unit. To emphasize this effect, cell diagrams without and with incorporated solvent molecules are shown in Fig. 2.

In summary, we have investigated the crystal and molecular structure of **1** and found that even with very bulky organic substituents the arylbismuthdichloride complexes do remain associated, in our case to dimers, at least in the solid state. A typical 'aryl-to-metal' interaction, so far shown in many antimony and bismuth complexes, has also been observed in **1**.

Table 3
Selected bond lengths (Å) and angles (deg.) for **1**

Bi(1)–C(01)	2.266(4)	Bi(1)–Perp.	2.804
Bi(1)–Cl(2)	2.529(13)	Cl(2)–Bi(1)–Cl(1)	93.45(4)
Bi(1)–Cl(1)	2.5305(12)	C(01)–Bi(1)–Cl(1a)	79.05(12)
Bi(1)–Cl(1a)	3.0738(12)	Cl(2)–Bi(1)–Cl(1a)	167.77(4)
Bi(1)–C(011)	3.009(5)	Cl(1)–Bi(1)–Cl(1a)	79.72(4)
Bi(1)–C(012)	3.071(5)	Bi(1)–Cl(1)–Bi(1a)	100.28(4)
Bi(1)–C(013)	3.838(7)	C(06)–C(01)–Bi(1)	128.9(3)
Bi(1)–C(016)	3.745(6)	C(02)–C(01)–Bi(1)	109.4(3)
Bi(1)–Cent.	3.527	Cent–Bi(1)–Perp.	37.4

3. Experimental section

3.1. Preparation of crystalline **1** · 2 tol

A procedure described for the synthesis of bis(2,4,6-triphenylphenyl)bismuth chloride [1] was used for the

preparation of **1** with the only exception that reagents were used in a 1:1 ratio. After filtering off LiCl the reaction mixture was cooled to 5 °C and allowed to stay overnight at this temperature. Small amounts of well-shaped, deep-yellow crystals (yield 20%) were obtained after decantation of the yellow solution which contained bis(2,4,6-triphenylphenyl)bismuthchloride. NMR spectra of both compounds were in accord with those reported in Ref. [1].

3.2. X-ray crystallographic study of **1**

A small yellow crystal was mounted onto a glass capillary and investigated on an Enraf–Nonius CAD4 four-circle diffractometer. Data were corrected for Lorentz and polarization effects, the structure was solved by direct methods using the SHELXTL-5.0 program [8]. The positions and anisotropic thermal displacement parameters of non-hydrogen atoms were refined by full-matrix least-square procedures against F^2 using SHELXL-93 [9]. The positions of hydrogen atoms were either located from a difference Fourier map and freely refined, or included on calculated positions with $d(\text{C}–\text{H}) = 0.96 \text{ \AA}$ and $U_{\text{eq}} = 0.08 \text{ \AA}^2$. One of two toluene molecules was found to be disordered with 60% and 40% occupation sites. Additionally, an empirical absorption correction, based on Ψ scans, was applied. The final refinement cycle led to convergence with the following discrepancy factors: $R_1 = 2.48$, $wR_2 = 5.97\%$.

4. Supplementary material available

Additional material on the crystal structure investigation is obtainable from Fachinformationszentrum Karls-

ruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen 2, Germany, on specifying the depository number CSD-405694, the names of the authors and the journal citation.

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