

Synthesis and characterization of aryl bismuth compounds using 2,4,6-triphenylphenyl as a bulky ligand [☆]

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Abstract

Reaction of BiCl_3 with 2,4,6-triphenylphenyllithium in THF solution in a 1:3 ratio, or in toluene solution in a 1:2 ratio affords tris(2,4,6-triphenylphenyl)bismuth (1) and bis(2,4,6-triphenylphenyl)bismuth chloride (2) respectively. 1 can be recrystallized from THF; the crystal structure has been determined with a yellow crystal of composition (1) • 4.8THF (3). The comproportionation reaction of 1 with BiCl_3 in a 1:2 ratio, or of 2 with BiCl_3 in a 1:1 ratio gives 2,4,6-triphenylphenylbismuth dichloride (4). Reduction of 2 with sodium in ammonia, with magnesium in THF, or with cobaltocene in toluene leads only to the isolation of 1,3,5-triphenylbenzene. Similarly, the reduction of 4 with sodium in ammonia, or with magnesium in THF leads only to 1,3,5-triphenylbenzene as a decomposition product, however, reducing 4 with cobaltocene in toluene affords 1, the latter presumably resulting from a disproportionation reaction of a (not isolated) monovalent bismuth compound, e.g. “2,4,6-triphenylphenylbismuth (I)” (6).

Keywords: Aryl; Bismuth; X-ray diffraction; Aryl bismuth compounds; 2,4,6-triphenylphenyl; Bulky ligands

1. Introduction

Since the 1980s, the chemistry of homonuclear Main Group V compounds with element–element bonds has attracted much attention: some of these compounds may behave thermochromically [1], and provide evidence for the existence of a non-classical form of bonding, coined “secondary bonding” [2]. In order to synthesize stable compounds of this type, we tried to prepare new arylbismuth compounds by reduction reactions of specific arylbismuth chlorides.

Arylbismuth compounds are widely reported in the literature: they are very useful as catalysts for organic reactions [3] and in the synthesis of drugs [4]; a general procedure for their synthesis is via Grignard-, organolithium- or organomercury reagents. Challenger et al. [5] reported the preparation of triphenylbismuth by the

reaction of bismuth chloride with diphenylmercury; related diorganobismuth chlorides were synthesized by reacting bismuth chloride with suitable Grignard reagents. Blicke et al. [6a] and Zhitkova et al. [7a] synthesized triphenylbismuth and trimesitylbismuth from bismuth bromide or chloride and the appropriate Grignard reagents, while recently Whitmire et al. [8] reported the synthesis of tris[2,4,6-tris(trifluoromethyl)phenyl]bismuth and bis[2,4,6-tris(trifluoromethyl)phenyl]bismuth chloride by arylation reactions of bismuth chloride with organolithium reagents. Moreover, Manato et al. [9] prepared some sterically crowded triaryl-bismuth compounds and diarylbismuth chlorides, e.g. tris(2,4,6-triethylphenyl)bismuth, bis(2,4,6-tris-*i*-propylphenyl)bismuth chloride and other compounds in order to establish how many “bulky” aryl groups can be bonded directly onto a trivalent bismuth atom by conventional procedures.

In this work, we report our investigations on the synthesis and characterization of arylbismuth compounds using 2,4,6-triphenylphenyl as a bulky, sterically demanding ligand, and our attempts to obtain lower-valent organobismuth derivatives.

[☆] Dedicated to Professor F. Huber, Dortmund, on the occasion of his 65th birthday.

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2. Results and discussion

2.1. $\text{Bi}[\text{C}_6\text{H}_2(\text{C}_6\text{H}_5)_3]_3$ (**1**)

Reaction of BiCl_3 with 2,4,6-triphenylphenyllithium in THF solution in a ratio of 1:3 at 70°C for 3 h gives a yellow solution and a white precipitate. After evaporation of the solvents in vacuo at 50°C, the yellow residue was extracted with toluene and filtered, the yellow

filtrate was concentrated and cooled to -30°C . The yellow crystals formed from this solution were separated and dried in vacuo. Finally, **1** was obtained as a yellow powder with a yield of 57% according to Eq. (1):

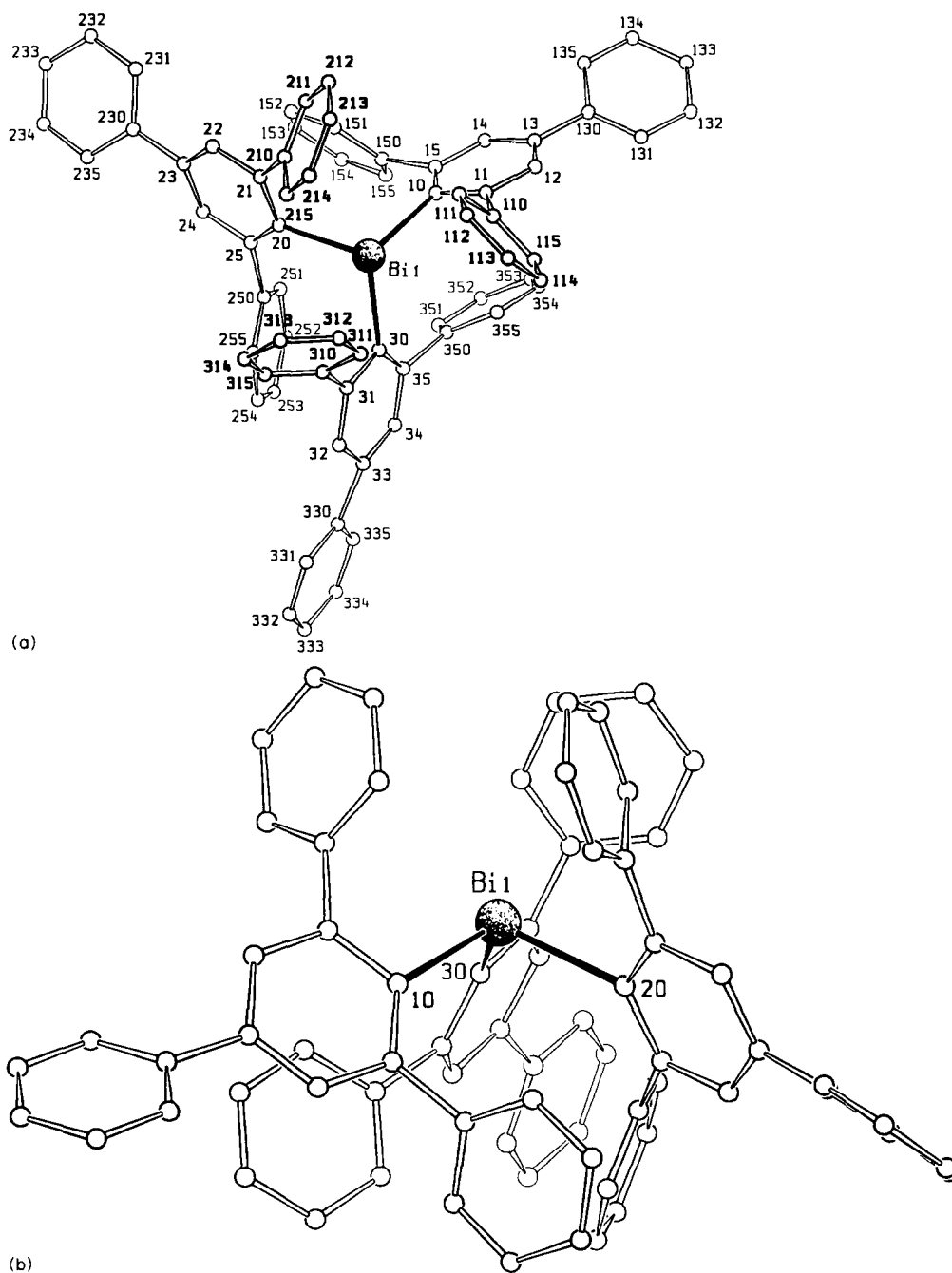
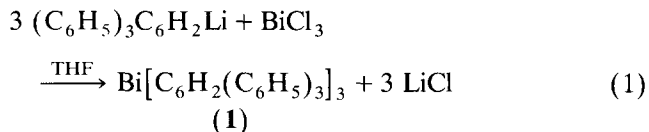


Fig. 1. (a) Molecular structure of **1** projected from the pseudo C_3 axis, showing the propeller-like conformation of the ligands [22]. (b) Side view of the pyramidal coordination sphere at the bismuth atom.

Table 1
Crystallographic data of **3**

Formula	C _{91.2} H _{89.4} BiO _{4.8}
Molecular weight (g mol ⁻¹)	1471.17
Crystal size (mm × mm × mm)	~ 0.2 × 0.2 × 0.15
Crystal system	monoclinic
Space group	Cc
<i>a</i> (Å)	14.197(3)
<i>b</i> (Å)	25.071(5)
<i>c</i> (Å)	21.005(4)
β (°)	93.56(3)
<i>Z</i>	4
<i>D</i> (calculated) (Mg m ⁻³)	1.310
μ (Mo K α) (mm ⁻¹)	2.45, empirical corr., Ψ -scans
Measuring temperature (K)	293(2)
2 θ range (°)	3–50°
Radiation	Mo K α , graphite monochromator
Scan type	ω -scan
Independent reflections	5703
Reflections with $I > 2\sigma$	4303
Structure refinement	full matrix least squares refinement on F^2
<i>R</i> (refl. with $I > 2\sigma$)	0.066
wR_2 (all reflections)	0.171
$\Delta\rho$ (max./min)	1.9/–2.3 e Å ⁻³ (near Bi)

Additional material about the crystal structure investigation is obtainable from Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen 2, Germany, on specifying deposit number CSD-58618, names of the authors and the journal reference.

Compound **1** was characterized by elemental analysis, IR, NMR and mass spectrometry. **1** is an air-stable compound which melts at 235°C in air, without decomposition. **1** is only slightly soluble in diethyl ether and *n*-hexane, but readily soluble in THF, toluene and chloroform. In the EI-mass spectrum the molecular ion peak appears at $m/e = 1123$, other logically derived fragments support the molecular formula. Recrystallization of **1** from THF gives large, bright yellow crystals, which were identified as a THF solvate of **1**, viz. “**1** • 4.8 THF” (**3**); the ¹H-NMR spectrum indicates that there are 4.8 THF molecules per molecule of **1**. **3** has a m.p. of 225°C and was also characterized by

Table 2

Selected bond lengths (Å) and bond angles (°) in **3** (with standard deviations in parentheses)

Bi(1)–C(30)	2.337(8)	Bi(1)–C(20)	2.355(8)
Bi(1)–C(10)	2.379(8)		
C(30)–Bi(1)–C(20)	104.2(4)	C(30)–Bi(1)–C(10)	109.4(4)
C(20)–Bi(1)–C(10)	103.7(4)		

elemental analysis, NMR, FD-mass and IR spectroscopy; the FD-mass spectrum exhibits the molecular ion peak for **1** at $m/e = 1124(\pm 1)$, indicating that the THF solvate is not stable during evaporation of the substance.

2.2. Crystal structure of **3**

The crystal structure of **3** was determined by a single crystal X-ray diffraction study. A small yellow crystal of **3** was investigated at 293 K on a 4-circle diffractometer; the experimental and crystallographic data are listed in Table 1. The structure was solved using Patterson and difference Fourier methods [10], and refined against F^2 data using the SHELXL-93 program package [11]. Due to the problem caused by the presence of the very heavy bismuth atom and the observed disorder phenomena of the THF solvent molecules (4.8 molecules per complex molecule), all phenyl groups were treated as rigid groups with idealized geometry; only for bismuth was an anisotropic temperature factor refined, for the hydrogen atoms, which were included on calculated positions, 1.2 *U* of the respective carbon atom was used. The refinement of 157 parameters with all 5703 independent reflections led to $wR_2 = 0.171$, corresponding to a conventional $R = 0.066$ for the 4303 F_o data with $I > 2\sigma(I)$. The correct orientation of the non centrosymmetric structure with respect to the cell axes was confirmed by refinement of the Flack parameter $x = -0.02(1)$.

In **3** the bismuth atom displays a distorted pyramidal coordination with a pseudo C_3 symmetry and phenyl

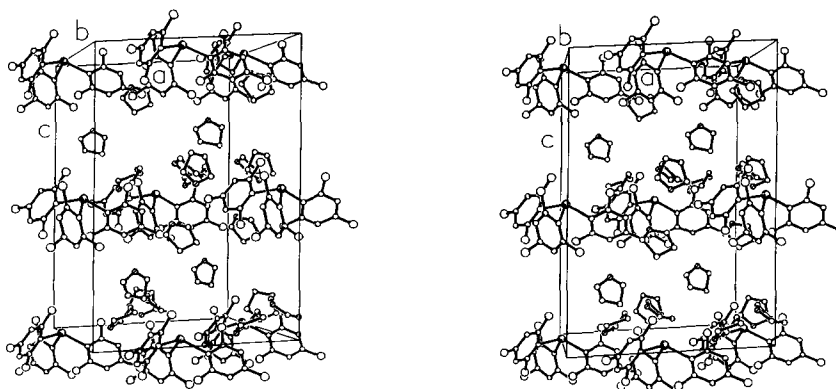


Fig. 2. Stereo plot of a unit cell of **3**, displaying the uniform orientation.

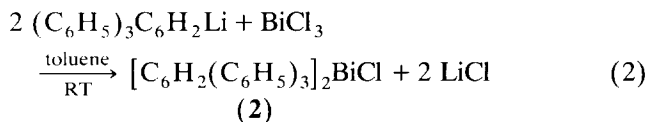
ligands orientated propeller-like (Fig. 1a). There is no direct contact between the oxygen atoms of the THF molecules and the central bismuth atom, which is linked to the three carbon atoms of the organic ligands with an average bond distance of 2.36 Å. This value agrees very well with those found for some other bismuth compounds, e.g., $\text{Bi}[\text{C}_6\text{H}_2(\text{CF}_3)_3]_3$ (2.36–2.38 Å) and $[\text{C}_6\text{H}_2(\text{CF}_3)_3]_2\text{BiCl}$ (2.34–2.36 Å) [8], but it is somewhat larger than values for bismuth derivatives with less bulky groups, e.g. $\text{Bi}(\text{C}_6\text{H}_5)_3$ (2.24 Å) [6b], $\text{Bi}[\text{C}_6\text{H}_2(\text{CH}_3)_3]_3$ (2.24–2.32 Å) [7b] and $\text{Bi}_2(\text{C}_6\text{H}_5)_4$ (2.28 Å) [12] or $[\text{C}_6\text{H}_2(\text{CH}_3)_3]_2\text{Bi}_2\text{O}$ (2.27–2.28 Å) [13]. Observed bond angles (C–Bi–C) at bismuth are 104.2°, 103.8° and 109.4°. This unusual difference between the first two similar angles and the last one may result from a molecular packing effect, connected with the THF solvate molecules (Fig. 2). These THF molecules are localized at 20 places in the unit cell, 5 molecules per complex, between layers of uniformly oriented complex molecules stacked along the *c*-axis. One of the five positions proved to be occupied to the extent of 80% only, two other show orientational disorder.

Overall the molecule may be best described as a rather flat pyramid (Fig. 1b): the sum of the bond angles at the bismuth atom is 317.4°, one of the largest values among those reported for arylbismuth compounds, e.g., $\text{Bi}(\text{C}_6\text{H}_5)_3$ (282°) [6b], $[\text{C}_6\text{H}_2(\text{CF}_3)_3]_2\text{BiCl}$ (294°) [8], $\text{Bi}[\text{C}_6\text{H}_2(\text{CH}_3)_3]_3$ (308°) [7b] and $\text{Bi}[\text{C}_6\text{H}_2(\text{CF}_3)_3]_3$ (318°) [8]. Not unexpectedly, bulky ligands such as 2,4,6-triphenylphenyl and 2,4,6-tris(trifluoromethyl)phenyl are much more space-demanding at the bismuth centres, therefore bismuth–carbon bond distances in these compounds have to be longer than those in other compounds with less bulky ligands. Table 3 provides a comparison of structural parameters for some selected arylbismuth compounds.

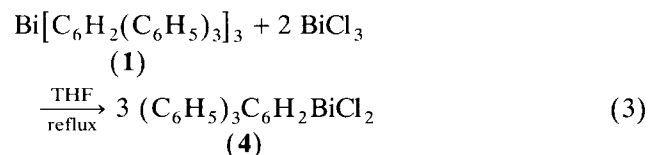
2.3. $[\text{C}_6\text{H}_2(\text{C}_6\text{H}_5)_3]_2\text{BiCl}$ (2) and $(\text{C}_6\text{H}_5)_3\text{C}_6\text{H}_2\text{BiCl}_2$ (4)

Reaction of BiCl_3 with 2,4,6-triphenylphenyllithium in toluene solution in a ratio of 1:2 at room temperature for 70 h gives a yellow solution and a white precipitate. After filtration, the yellow liquid was con-

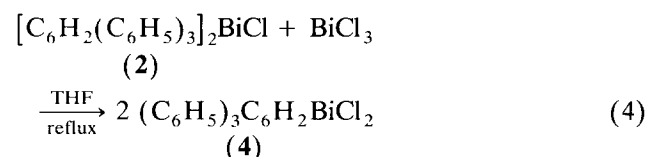
centrated and cooled to -30°C . The large yellow crystals formed from this solution were separated and dried in vacuo. After drying, **2** was obtained in the form of a yellow powder with a yield of 59% according to Eq. (2):



Compound (**2**) is sparingly soluble in diethyl ether and *n*-hexane, but very soluble in THF, toluene, chloroform and benzene. The stable compound melts at 158–163°C in air without decomposition; **2** was characterized by elemental analysis, NMR, mass and IR spectroscopy. Both the comproportionation reaction of BiCl_3 with **1** in a 1:2 ratio, and the comproportionation reaction of BiCl_3 with **2** in a 1:1 ratio afford **4** according to Eqs. (3) and (4). Compound **4** was obtained as a hygroscopic, light-yellow powder, soluble in THF and ethyl glycol; it was characterized by elemental analysis, mass and IR spectroscopy.

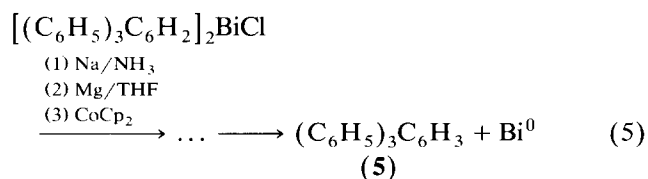


or



2.4. Reduction reactions

Reduction of **2** with sodium in liquid ammonia at low temperature, with magnesium in THF solution, and with cobaltocene in toluene only led to the isolation of 1,3,5-triphenylbenzene **5**, the final product of decomposition, according to Eq. (5):



As a rule, tetraorganodibismuth compounds are thermodynamically unstable and air sensitive due to the very weak Bi–Bi bond. However, because of the protection obtained from bulky organic ligands, these thermodynamically unstable organoelement compounds can be stabilized and therefore characterized [14–16]: e.g. tetraphenyldibismuth has been obtained and fully characterized [12]. 2,4,6-Triphenylphenyl is an

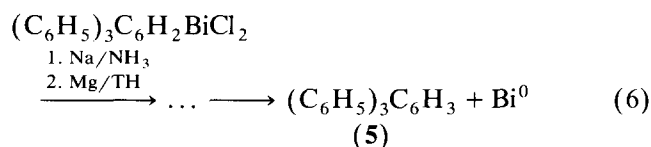
Table 3

Comparison of structural parameters for some selected arylbismuth compounds

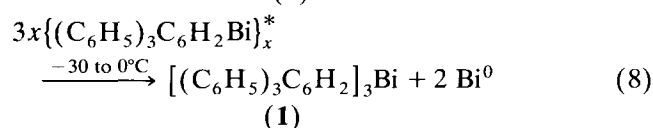
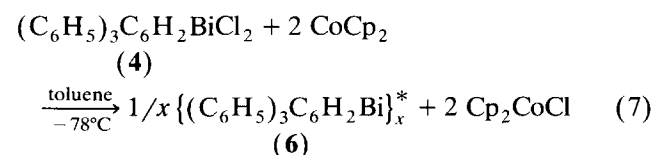
Compound	sum of angles at bismuth (°)	bismuth–carbon distance (Å)	Ref.
$\text{Bi}(\text{C}_6\text{H}_5)_3$	282	2.24	[7]
$\text{Bi}_2(\text{C}_6\text{H}_5)_4$		2.28	[12]
$[\text{C}_6\text{H}_2(\text{CF}_3)_3]_2\text{BiCl}$	294	2.34–2.36	[8]
$[\text{C}_6\text{H}_2(\text{CH}_3)_3]_2\text{Bi}_2\text{O}$	295	2.27–2.28	[13]
$\text{Bi}[\text{C}_6\text{H}_2(\text{CH}_3)_3]_3$	308	2.24–2.32	[7]
$\text{Bi}[\text{C}_6\text{H}_2(\text{CH}_3)_3]_3$	318	2.36–2.38	[8]
$\text{Bi}[\text{C}_6\text{H}_2(\text{C}_6\text{H}_5)_3]_3$	317	2.34–2.38	this work

even more bulky ligand than phenyl groups. Probably due to the strong repulsion of these bulky ligands, in particular the repulsion of phenyl rings which are substituted in the two *ortho*-positions of a phenyl ligand, the formally divalent bismuth compound tetrakis(2,4,6-triphenylphenyl)dibismuth is unstable and it has not so far been isolated.

We also tried to reduce compound **4** with sodium in liquid ammonia at low temperature, and with magnesium in THF solution, but again 1,3,5-triphenylbenzene was the only isolated product:



However, when compound **4** was reduced with the mild reducing reagent cobaltocene in toluene solution at -70°C , only **1** could be isolated: from this result, and from the remarkable colour change from deep red to straw-yellow of the reaction mixture during the reduction, we conclude that a monovalent bismuth compound, e.g. “2,4,6-triphenylphenylbismuth (I) **6**” was formed during the reduction of **4**. However, this intermediate again seems to be too unstable, and decomposes instantaneously with disproportionation to form compound **1** and metallic bismuth according to Eqs. (7) and (8):



{ }*-compound not isolated

In catalytic processes of arylbismuth compounds used in organic reactions, and in thermal decomposition or reduction processes of some organobismuth compounds, reductive elimination reactions or ligand couplings have often been reported [3,13,17]. In contrast to these findings, during the reduction of **2** and **4**, which contain the bulky ligand 2,4,6-triphenylphenyl, we have not observed an analogous ligand coupling phenomenon typical for arylbismuth compounds: dimerization of the 2,4,6-triphenylphenyl radical seems to be practically impossible, or at least very difficult, for steric reasons.

3. Conclusion

Our attempts to synthesize new, sterically hindered arylbismuth compounds, stable at room temperature

or at moderate low temperatures, failed and resulted in the formation and identification of $\text{Bi}[(\text{C}_6\text{H}_5)_3\text{C}_6\text{H}_2]_3$, which has been structurally characterized, and the two halides $[(\text{C}_6\text{H}_5)_3\text{C}_6\text{H}_2]_2\text{BiCl}$ and $(\text{C}_6\text{H}_5)_3\text{C}_6\text{H}_2\text{BiCl}_2$. During the reduction reactions, interesting colour change phenomena from red to orange-yellow took place, indicating a transient dibismuth (or oligomeric) species, probably our elusive $1/x \{(\text{C}_6\text{H}_5)_3\text{C}_6\text{H}_2\text{Bi}\}_x^*$ with bismuth–bismuth bonds, but too unstable to be isolated yet. Even by applying the concept of steric shielding it is still very difficult to synthesize lower valent organobismuth compounds with formal oxidation states two or one at bismuth.

4. Experimental section

All manipulations were carried out under an argon atmosphere; solvents were dried by standard methods and freshly distilled prior to use. NMR spectra were recorded on a Bruker AMX-500 (500 MHz) spectrometer, EI mass spectra on a Varian MAT-CH-7A spectrometer and IR spectra on a Perkin-Elmer spectrometer. Brom-1,3,5-triphenylbenzene [18], 1,3,5-triphenylphenyllithium [19] and biscyclopentadienylcobalt (cobaltocene) [20,21] were prepared according to the literature procedures. Bismuth chloride was sublimed at 190°C in vacuo at 0.01 mbar immediately prior to use.

4.1. Synthesis of **1**

A solution of BiCl_3 (3.15 g; 10 mmol) in THF (50 ml) was added to a stirred solution of 2,4,6-triphenylphenyllithium-bis(diethyl ether) adduct (13.80 g, 31 mmol) in THF (80 ml) at -70°C for 1 h; a white precipitate was formed. The mixture was stirred at room temperature for another 12 h, then refluxed for an additional 5 h. The solvents were evaporated in vacuo at 50°C , the residue extracted with toluene (80 ml) and filtered. The yellow filtrate was concentrated and cooled to -30°C ; from this concentrated solution large yellow crystals were formed, these were separated and dried in vacuo: **1** was obtained as a yellow powder, yield: 6.40 g; 6 mmol of **1**, 57%. m.p. 235°C . **1** was recrystallized from THF and tris(2,4,6-triphenylphenyl)bismuth 4.8 THF **3** was obtained in the form of bright yellow crystals, m.p. 225°C .

Found for **1**: C, 76.40; H, 4.70. $\text{C}_{72}\text{H}_{51}\text{Bi}$ calc.: C, 76.86; H, 4.57%. EI-MS (70 eV): m/e , ion, intensity (%): 1123, $\text{M}^+ - 2\text{H}$, 0.14; 819, $[(\text{C}_6\text{H}_5)_3\text{C}_6\text{H}_2]_2\text{Bi}$, 0.52; 610, $(\text{C}_6\text{H}_5)_3\text{C}_6\text{H}_2 - \text{C}_6\text{H}_2(\text{C}_6\text{H}_5)_3$, 9.65. Found for **3**: C, 72.33; H, 6.05; Bi, 15.14. $\text{C}_{91.2}\text{H}_{89.4}\text{BiO}_{4.8}$ calc.: C, 73.25; H, 5.15; Bi, 15.19%. $^1\text{H-NMR}$ (CDCl_3): δ (ppm): THF hydrogen: 1.86, (t, 19H); 3.73, (t, 19H). aromatic hydrogen: 6.68–6.70, (d, 6H); 6.83–6.93, (m,

8H); 7.13–7.14, (d, 3H); 7.25–7.36, (m, 22H); 7.37–7.42 (t, 6H); 7.55–7.57; (d, 6H). ^{13}C -NMR: δ (ppm): THF carbons: 25.47; 67.82. aromatic carbons: 125.74; 126.81; 126.93; 127.19; 128.16; 128.69; 129.32; 131.00; 138.81; 140.68; 143.55; 144.60; 150.64; 152.32. FD-MS: m/e , ion, intensity (%): 1124, $\text{M}^+ - \text{H}$, 13.13; 818, $[(\text{C}_6\text{H}_5)_3\text{C}_6\text{H}_2]_2\text{Bi}-\text{H}$, 100.00; 514, $(\text{C}_6\text{H}_5)_3\text{C}_6\text{H}_2\text{Bi}$, 6.39. IR (Nujol, ν cm^{-1}): 123w br; 140m; 347m; 397vst; 413st; 498vst; 530m; 592m; 630m; 665m; 697vst; 734st; 754vst; 770m; 842m; 881vst; 913vst; 963m br; 996st; 1011m; 1030vst; 1072vst; 1134m; 1156st; 1178m; 1310st br; 1337vst; 1378vst br; 1463vst br; 1543st; 1575st; 1598st; 1677st br; 1763st br; 1805st br; 1865st br; 1884st br; 1953st br; 2723vst br.

4.2. Synthesis of 2

BiCl_3 (3.69 g, 12 mmol) was added to a solution of 2,4,6-triphenylphenyllithium-bis(diethyl ether) adduct (10.40 g, 23 mmol) in toluene (80 ml) at -70°C in the dark. After 1 h stirring at this temperature, the mixture was stirred at room temperature for 70 h; a white precipitate was formed. The mixture was filtered and the yellow filtrate was concentrated to about 40 ml and cooled to -30°C : large yellow crystals were formed, separated and dried in vacuo, **2** was obtained as a powder, yield 5.86 g; 7 mmol of **2**, 59%. m.p. $158\text{--}163^\circ\text{C}$.

Found: C, 69.85; H, 3.63. $\text{C}_{48}\text{H}_{34}\text{BiCl}$ calc.: C, 67.41; H, 4.01%. ^1H -NMR (CDCl_3): δ (ppm): aromatic hydrogen: 7.21–7.38, (m, 22H); 7.48–7.53, (t, 4H); 7.62 (s, 4H); 7.64–7.65, (m, 2H); 7.73–7.77, (m, 2H). ^{13}C -NMR: δ (ppm): aromatic carbons: 125.34; 127.18; 127.45; 127.62; 128.49; 128.91; 129.07; 130.94; 140.51; 141.00; 143.85; 151.65. EI-MS (70 eV): m/e , ion, intensity (%): 818, $[(\text{C}_6\text{H}_5)_3\text{C}_6\text{H}_2]_2\text{Bi}$, 100.0; 609, $(\text{C}_6\text{H}_5)_3\text{C}_6\text{H}_2\text{C}_6\text{H}_2(\text{C}_6\text{H}_5)_3$, 38.6; 548, $(\text{C}_6\text{H}_5)_3\text{C}_6\text{H}_2\text{BiCl}$, 10.6; 514, $\text{BiC}_6\text{H}_2(\text{C}_6\text{H}_5)_3$, 14.6; 244, BiCl , 2.0; 209, Bi , 19.3. IR (Nujol, ν cm^{-1}): 140m; 257m; 281vst; 336m; 358m; 405m; 416m; 466st; 612vw; 665vw; 697m; 736w; 755m; 765w; 774w; 831vw; 966w; 1314vw br; 1462m; 1489w; 1542vw; 1574vw; 1598vw; 2725w br; 3022m br; 3463m br.

4.3. Synthesis of 4

1 (20.0 g, 18 mmol) was added to a solution of BiCl_3 (11.30 g, 36 mmol) in THF (200 ml) at 0°C . The mixture was stirred at this temperature for 5 h, then at room temperature for an additional 10 h and finally refluxed for 20 h. The solvent was evaporated in vacuo and the residue washed under an argon atmosphere with a mixture of diethyl ether and n-hexane until the filtrate was colourless. The slightly yellow coloured solid was dried in vacuo to give **4** as a yellow powder, yield: 19.5 g; 33 mmol of **4**, 63% (in a second experiment **4** was also obtained by the reaction of **2** and

BiCl_3 in a 1:1 ratio in THF solution under similar reaction conditions).

Found: C, 45.07; H, 3.96. $\text{C}_{24}\text{H}_{17}\text{BiCl}_2$ calc.: C, 49.25; H, 2.93%. EI-MS (70 eV): m/e ion, intensity (%): 548, $\text{C}_{24}\text{H}_{17}\text{BiCl}$, 60.25; 514, $\text{C}_{24}\text{H}_{17}\text{Bi}$, 15.52; 305, $\text{C}_{24}\text{H}_{17}$, 62.23; 209, Bi , 3.2. IR (Nujol, ν cm^{-1}): 125m; 275vst br; 504vw; 698m; 752m; 872m; 1030m; 1075m; 1156w; 1178w; 1310w br; 1340m; 1411m; 1459vst; 1489m; 1543m br; 1575m; 1594m; 1949m br; 2725m br.

4.4. Reductions

4.4.1. Reduction of (2) with sodium

A solution of **2** (2.70 g; 3 mmol) in THF (30 ml) was added over 1 h to a solution of sodium (0.08 g, 3 mmol) in liquid ammonia (40 ml) at -78°C . The blue colour disappeared after 1 h stirring at -50°C and a red colour developed: the solvents were evaporated in vacuo between 0° and -10°C , the residue extracted at -50°C with n-hexane and filtered at -50°C . The yellow filtrate was concentrated and filtered again, the solution cooled to -30°C until colourless crystals were formed which were separated, dried in vacuo at -10°C and identified as compound **5**, yield: 0.80 g; 3 mmol of **5**, 81%. m.p. 171°C .

Found: C, 94.35; H, 6.26. $\text{C}_{24}\text{H}_{18}$ calc.: C, 94.08; H, 5.9%. EI-MS (70 eV): m/e , ion, intensity (%): 305, $\text{M}^+ - \text{H}$, 100.0; 229, $\text{C}_{18}\text{H}_{14}$, 14.5; 154, $\text{C}_{12}\text{H}_{10}$, 80.3.

4.4.2. Reduction of 2 with magnesium

Magnesium (0.04 g, 1.7 mmol) was added to a solution of **2** (2.87 g, 3.4 mmol) in THF (50 ml) at 0°C . After 8 h of stirring, no visible change in either the solution or the magnesium metal was observed. The mixture was stirred at room temperature for 2 h, after which the yellow colour of the solution changed to black. After 5 h stirring, the solvent was evaporated in vacuo and the residue extracted with n-hexane and filtered. The filtrate was concentrated and cooled to -30°C ; after 40 h, colourless crystals were formed, separated and dried in vacuo and identified as **5**. Yield: 1.50 g, 5 mmol of **5**, 73%, m.p. 170°C .

Found: C, 92.31; H, 6.03. $\text{C}_{24}\text{H}_{18}$ calc.: C, 94.08; H, 5.92%.

4.4.3. Reduction of 2 with cobaltocene

A solution of cobaltocene (1.54 g, 8 mmol) in toluene (40 ml) was added to a stirred suspension of **4** (6.73 g, 8 mmol) in toluene (40 ml) at -78°C ; the mixture developed a yellow colour. After 10 h stirring, the mixture was filtered at -50°C and the filtrate concentrated to about 30 ml at 0°C , then cooled to -30°C . After 40 h colourless crystals had formed, these were separated and dried at 0°C in vacuo and identified as **5**. Yield: 1.50 g, 5 mmol of **5** 76%, m.p. 171°C .

Found: C, 93.32; H, 6.57. $C_{24}H_{18}$ calc.: C, 94.08; H, 5.92%.

4.4.4. Reduction of **4** with sodium

Ammonia (100 ml) was condensed into a suspension of **4** (5.00 g, 8.6 mmol) in toluene (40 ml) at -78°C . Sodium metal (0.39 g, 17 mmol) was added to the stirred mixture; after 5 h of stirring at -78°C the blue colour had disappeared and a yellow colour was observed. The solvents were evaporated in vacuo at 0°C , the residue extracted at -50°C with toluene (80 ml) and filtered, the filtrate concentrated and cooled to -30°C . Colourless crystals were formed, separated, dried in vacuo and identified as **5**. Yield: 1.60 g; 5 mmol of **5** 61%, m.p. 169–171 $^{\circ}\text{C}$.

Found: C, 91.71; H, 6.26. $C_{24}H_{18}$ calc.: C, 94.08; H, 5.92%.

4.4.5. Reduction of **4** with magnesium

Magnesium (0.21 g, 8 mmol) was added to a solution of **4** (4.30 g, 7.4 mmol) in THF (80 ml) at -78°C . After 8 h of stirring at this temperature, no change in either the solution or the magnesium metal was observed. The mixture was then stirred at 0°C for 2 h, after which the yellow colour of the solution changed to black. After 40 h of stirring, the solvent was evaporated in vacuo at 0°C and the residue extracted with toluene (80 ml) and filtered, the filtrate concentrated and cooled to -30°C . After 40 h, colourless crystals had formed and were separated, dried in vacuo and identified as **5**. Yield: 0.80 g, 3 mmol of **5**, 37%, m.p. 169–170 $^{\circ}\text{C}$.

Found: C, 94.35; H, 6.26. $C_{24}H_{18}$ calc.: C, 94.08; H, 5.92%.

4.4.6. Reduction of **4** with cobaltocene

A solution of cobaltocene (2.91 g, 15 mmol) in toluene (40 ml) was added to a stirred suspension of **4** (4.50 g, 7.6 mmol) in toluene (40 ml) at -78°C . The mixture developed a yellow colour. After 10 h stirring, the mixture was filtered at -50°C and the filtrate concentrated to about 30 ml at 0°C , then cooled to -30°C . After 40 h, large yellow crystals had formed, these were separated, dried at 0°C in vacuo and identified as **1**. Yield: 1.80 g, 1.7 mmol of **1**, 64%, m.p. 235 $^{\circ}\text{C}$.

Found: C, 77.39; H, 5.16. $C_{72}H_{51}Bi$ calc.: C, 76.86; H, 4.57%. FD-MS: m/e , ion, intensity (%): 1123, $M^{+} - 2H$, 15.30.

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