# **COMMUNICATIONS**

## Tetrasupersilyldiindium(In-In) and Tetrasupersilyldithallium(Tl-Tl): $(tBu_3Si)_2M-M(SitBu_3)_2$ (M = In, Tl)\*\*

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#### Dedicated to Professor Heinz Peter Fritz

Donor-free, uncharged molecular compounds (RM), and (R<sub>2</sub>M), with clusters formed from the boron homologues M = Al, Ga, In, Tl have-unlike such compounds with boron clusters<sup>[1]</sup> --only been known for about ten years. In fact, the compounds of the boron homologues have a tendency to disproportionate (6 RM  $\rightarrow$  3 R<sub>2</sub>M + 3 M  $\rightarrow$  2 R<sub>3</sub>M + 4 M); however, this process can be stopped at the (RM), stage (very bulky groups) or at the  $(R_2M)_2$  stage (medium-sized bulky groups) by employing bulky substituents R such as C<sub>5</sub>Me<sub>5</sub> (Cp\*), C<sub>5</sub>(CH<sub>2</sub>Ph)<sub>5</sub> (Cp\*\*), CH(SiMe<sub>3</sub>)<sub>2</sub> (Disyl), C(SiMe<sub>3</sub>)<sub>3</sub> (Trisyl),  $2,4,6-i\Pr_{3}C_{6}H_{2}$  (Trip),  $2,4,6-(CF_{3})_{3}C_{6}H_{2}$  (R<sup>F</sup>), Si(SiMe<sub>3</sub>)<sub>3</sub> (Hypersilyl), and SitBu<sub>3</sub> (Supersilyl). Known examples of R<sub>4</sub>M<sub>2</sub> and  $(RM)_n$  compounds with normal covalent M-M bonds are  $[(Me_3Si)_2CH]_4M_2$  (M = Al, Ga, In),<sup>[1]</sup> (2,4,6-*i*Pr\_3C\_6H\_2)\_4M\_2 (M = AI, Ga),<sup>[2]</sup> [2,4,6-(CF<sub>3</sub>)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>]<sub>4</sub>M<sub>2</sub> (M = Ga, In),<sup>[1]</sup> or  $[(Me_3Si)_3Si]_4Tl_2$ ,<sup>[3]</sup> and  $(RAl)_4$  (R = SitBu<sub>3</sub>, Cp\*),<sup>[4]</sup> (RGa)<sub>4</sub>  $(R = C(SiMe_3)_3, {}^{[1]}Si(SiMe_3)_3 {}^{[5]}) \text{ or } [(Me_3Si)_3CIn]_4, {}^{[6]}respec$ tively. Only very weak M-M interactions are present in the compounds  $(Cp^*In)_6^{[7]}$  and  $(Cp^{**}M)_2$   $(M = In, Tl).^{[8]}$ 

It should be possible to stabilize compounds of the type  $(RM)_n$  by using, as we have done previously, the readily accessible and chemically comparably inert supersilyl group.<sup>[4a]</sup> The ability of this group to potentially stabilize such compounds arises from its very high steric demand<sup>[9]</sup> and its prominent tendency to donate electrons to its bonding partners<sup>[1, 4e]</sup> with this donation having a cluster stabilizing effect. Indeed, the reaction of aluminum monochloride in toluene/diethyl ether<sup>[10]</sup> with supersilylsodium  $tBu_3SiNa$  in dibutyl ether at  $-78 \,^{\circ}C$  gave, among others, the deep violet tetraalatetrahedrane  $(tBu_3SiA)_4$  1 [Eq. (a)], which as expected was metastable (sublimation at 180  $^{\circ}C$  under high vacuum; Al–Al: calcd. 2.64 Å, Al–Al disso-



[\*] Prof. Dr. N. Wiberg, Dipl.-Chem. K. Amelunxen, Prof. Dr. H. Nöth, Dr. M. Schmidt, Dipl.-Chem. H. Schwenk Institut für Anorganische Chemie der Universität Meiserstrasse 1, D-80333 München (Germany) Fax: Int. code + (89)5902-451 ciation energy per edge of the tetrahedron: calcd. ca. 100 kJ mol<sup>-1</sup>; for comparison (Cp\*Al)<sub>4</sub>: thermolysis at 70 °C; Al-Al: found 2.77 Å; Al-Al dissociation energy per edge of the tetrahedron: calcd. 25 kJ mol<sup>-1</sup>).<sup>[4, 11]</sup>

To our surprise the reactions of indium bromide and thallium bromide with supersilyl sodium  $tBu_3SiNa$  in tetrahydrofuran at -78 °C did not lead to the tetrahedranes  $(tBu_3SiM)_4$  (M = In, TI)<sup>161</sup> but gave the diindium compound **2** and indium and the dithallium compound **3** and thallium, respectively, [Eq. (b)]. In addition,  $tBu_3SiH$ ,  $tBu_3SiBr$ , and  $(tBu_3Si)_2$  were formed in these reactions.



That 2 and 3, respectively, are formed in these reactions is probably a result of how the reaction was carried out, since the tetraindatetrahedrane  $[(Me_3Si)_3CIn]_4$  is accessible from corresponding starting materials.<sup>[6]</sup> Possibly, 2 and 3 are formed on the surface of the MBr crystals, which are insoluble in THF. The formation of  $(tBu_3Si)_2$  in high yields indicates the existence of intermediary  $tBu_3Si'$  radicals.

Compound 2 is obtained as deep violet and compound 3 as black-green crystals, which decompose at about 125 and about 52 °C, respectively. The thermolysis of 2 in [D<sub>8</sub>]toluene at 40 °C occurs slowly ( $t_{1/2} \approx 8$  d), that of compound 3 very quickly; *t*Bu<sub>3</sub>SiD and (*t*Bu<sub>3</sub>Si)<sub>2</sub> are formed in these reactions, together with other *t*Bu<sub>3</sub>Si-containing compounds and elemental thallium, respectively.<sup>[12]</sup> Compound 2 is attacked only very slowly by methanol at room temperature.<sup>[12]</sup>

The structures of compounds 2 and 3, which crystallize isomorphically, were determined by X-ray diffraction (Fig. 1).<sup>[13]</sup> However, due to the decomposition of compound 3 in the X-ray beam, only its Tl and Si positions could be determined with sufficient precision; thus, in this case the crystal structure analysis should only be considered as evidence for the constitution of the compound. The central structural element of both compounds is the M-M grouping. The M atoms are each coordinated in a trigonal planar fashion by two Si atoms and one M atom; the MMSi<sub>2</sub> planes are orthogonal (Si-In-In-Si angle between 89.5 and 90.5°, Fig. 1). The high steric demand of the supersilyl groups leads to the very long M-M distances of 2.921 Å (2; for comparison [(Me<sub>3</sub>Si)<sub>2</sub>CH]<sub>4</sub>In<sub>2</sub>: 2.828 Å<sup>[1]</sup>) and 2.966 Å (3; for comparison [(Me<sub>3</sub>Si)<sub>3</sub>Si]<sub>4</sub>Tl<sub>2</sub>: 2.914 Å<sup>[3]</sup>). The angles between the MMR<sub>2</sub> planes are significantly smaller in  $R_4M_2$  compounds with less bulky substituents R, (e.g.  $[(Me_3Si)_2CH]_4M_2$ :<sup>[1]</sup> 8°  $(M = Al), 5.0^{\circ} (M = Ga), 6.7^{\circ} (M = In); (2,4,6-iPr_3C_6H_2)_4Ga_2:$ 43.8°;<sup>[2]</sup> with regard to the conformation of  $R_4M_2$  see ref.[1]). The Si-M-Si and M-M-Si angles in both compounds are about 130 and 115°, respectively. The C-Si-C angle (av 109.7°) of the supersilyl group  $tBu_3Si$  in 2 is at the lower end of the normal range of 110-112° (extreme C-Si-C angles are exhibited by the very sterically bulky  $(tBu_3Si)_2$  (107.3 °[9a]) and by the less bulky tBu<sub>3</sub>SiH (113.7°<sup>[14]</sup>)).

 <sup>[\*\*]</sup> Sterically Overloaded Silicon Compounds, Part 8, Silicon Compounds Part 99. This work was supported by the Deutsche Forschungsgemeinschaft. Part 7: N. Wiberg in Progress in Organosilicon Chemistry (Eds.: B. Marciniee, J. Chojnewski), Gordon and Breach Science Publishers, Amsterdam, 1995, pp. 19-39. Part 6: Ref.[9b]. Part 98: N. Wiberg, M. Link, Chem. Ber. 1995, 128, 1241.

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Fig. 1. Crystal structure of **2**. The H atoms were omitted for clarity. Important bond lengths [Å] and angles [°]: In1–In2 2.9217(11), In1–Si1 2.778(4), In1–Si2 2.779(4), In2–Si3 2.778(4), In2–Si4 2.778(4), Si1–C1 1.95(2), Si1–C5 1.94(2), Si1–C9 1.95(2) [mean value of Si–C distances 1.95], C1–C2 1.50(3), C1–C3 1.48(3), C1–C4 1.59(3); Si1-In1-Si2 129.43(11), Si3-In2-Si4 129.25(12), In2-In1-Si1 115.27(9), In2-In1-Si2 115.30(9), In1-In2-Si3 115.15(9), In1-In2-Si4 115.60(9), In1-Si1-C5 109.0(7), C5-Si1-C9 109.2(9) [mean value of the C-Si-C angles 109.7°]. Crystal structure of **3** (T1 instead of In in Fig. 1). The compound is isomorphic to **2**. Only the T1 and the Si positions can be given with sufficient precision: bond lengths [Å] and angles [°]: T11–T12 2.966(2), T11–Si1 2.801(11), T11–Si2 2.765(12), T12–Si3 2.800(12), T12–Si4 2.790(11) [the T1–Si bond lengths are of the same length within the limits of error]; Si1-T11-Si2 130.3(4), Si3-T12-Si4 130.1(3), T12-T11-Si1 114.4(2),

#### **Experimental** Procedure

2: tBu<sub>3</sub>SiNa (2.91 mmol) in THF (10mL) was added dropwise to a suspension of InBr (0.566 g, 2.91 mmol) in THF (15 mL) at -78 °C. The deep brown reaction solution was stirred for 12 h at -78 °C and then allowed to slowly warm to room temperature. According to the <sup>1</sup>H NMR spectrum of the crude mixture, compound 2 (33%), tBu<sub>3</sub>SiH (5%), tBu<sub>3</sub>SiBr (4%), and (tBu<sub>3</sub>Si)<sub>2</sub> (58%, yields based on the amount of /Bu<sub>3</sub>SiNa employed) were formed. All the volatile compounds were removed in the oil pump vacuum, the residue was taken up in pentane (20 mL) and the dark precipitate (In) was filtered off from the dark violet solution. Compound 2 (0.483 g, 0.47 mmol, 16.2%) precipiated from the latter solution at -23 °C within one week in the form of deep violet crystals. These dissolved very well in nonpolar solvents such as benzene and alkanes, but not very well in polar solvents such as THF and acetone. Heating the crystalline compound 2 obtained from pentane led to the evolution of a gas (pentane?) at 105 °C and subsequent decomposition at 125 °C which was accompanied by an irreversible change in color first to orange and then to black under concomitant formation of (tBu<sub>3</sub>Si)<sub>2</sub>. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, TMS, internal):  $\delta = 1.35$  (s; 12 *t*Bu); <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, TMS, internal):  $\delta = 26.82$  (12  $CMe_3$ ), 34.00 (12  $CMe_3$ ); <sup>29</sup>Si NMR ( $C_6D_6$ , INEPT, TMS, external):  $\delta = 76.83$  (4 SitBu<sub>3</sub>); MS: m/z: 513 [(M/2)<sup>+</sup>]; C,H analysis (C<sub>48</sub>H<sub>108</sub>In<sub>2</sub>Si<sub>4</sub>, 1027.4): calcd. C 56.12, H 10.60; found 55.75, H 10.53.

3: tBu<sub>3</sub>SiNa (2.88 mmol) in THF (10 mL) was added dropwise to a suspension of TIBr (0.826 g, 2.88 mmol) in THF (15 mL) at -78 °C. The resulting solution changed color first to red, then green, and finally brown. The reaction mixture was stirred for 12 h at -78 °C and then slowly allowed to warm to room temperature. According to the <sup>1</sup>H NMR spectrum of the crude mixture, compound 3 (27%), tBu<sub>3</sub>SiH (12%), tBu<sub>3</sub>SiBr (4%), and (tBu<sub>3</sub>Si)<sub>2</sub> (57%, yields based on the amount of tBu<sub>3</sub>SiNa employed) were formed [15]. All the volatile compounds were removed in the oil pump vacuum, the residue was taken up in Et<sub>2</sub>O (20 mL), and the dark precipitate (Tl) was filtered off from the deep green solution. Compound 3 (0.314 g, 0.26 mmol, 9.0%) precipiated from the latter solution at -23 °C within one week in the form of black-green crystals. Compound 3 exhibited a similar solubility to 2. It decomposed above 52 °C with a change in color to black and concomitant formation of silyl compounds such as  $(tBu_5Si)_2$ . <sup>1</sup>H NMR ( $C_6D_6$ , TMS, internal):  $\delta = 1.32$  (d; <sup>4</sup>J(H,Tl) = 6.7 Hz; 12 tBu); <sup>13</sup>C{<sup>1</sup>H} NMR ( $C_6D_6$ , TMS, internal):  $\delta = 28.57$  (d, <sup>2</sup>*J*(C,Tl) = 155.8 Hz; 12 CMe<sub>3</sub>), 33.12 (d, <sup>3</sup>*J*(C,Tl) = 49.9 Hz; 12 CMe<sub>3</sub>); <sup>29</sup>Si NMR (C<sub>6</sub>D<sub>6</sub>, INEPT, TMS, external):  $\delta = 100.2$  (d, <sup>1</sup>*J*(<sup>2</sup>9Si,<sup>205</sup>Tl) = 1451,  ${}^{1}J({}^{29}\text{Si}, {}^{203}\text{Tl}) = 1436 \text{ Hz}; 4 \text{ Si}t\text{Bu}_{3}); \text{MS}: m/z: 601/603 [(M/2)^+; with {}^{203}\text{Tl})$ and <sup>205</sup>Tl, respectively]; C,H analysis (C48H108Tl2Si4, 1206.4): calcd. C 47.79, H 9.02; found 53.54, H 10.08.

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- [1] W. Uhl, Angew. Chem. 1993, 105, 1449; Angew. Chem. Int. Ed. Engl. 1993, 32, 1386, and references therein.
- [2] X. He, R. A. Bartlett, M. M. Olmstead, K. Ruhlandt-Senge, B. E. Sturgeon, P. P. Power, Angew. Chem. 1993, 105, 761; Angew. Chem. Int. Ed. Engl. 1993, 32, 717.
- [3] S. Henkel, K. W. Klinkhammer, W. Schwarz, Angew. Chem. 1994, 106, 721; Angew. Chem. Int. Ed. Engl. 1994, 33, 681.
- [4] a) N. Wiberg in Frontiers of Organosilicon Chemistry (Eds.: A. R. Bassindale, P. P. Gaspar), The Royal Society of Chemistry, Cambridge, 1991, pp. 263– 270; b) C. Dohmeier, C. Robl, M. Tacke, H. Schnöckel, Angew. Chem. 1991, 103, 594; Angew. Chem. Int. Ed. Engl. 1991, 30, 564; c) with regard to the ab initio calculations see N. Schneider, R. Ahlrichs, H. Horn, A. Schäfer, *ibid*. 1992, 104, 327 or 1992, 31, 353.
- [5] G. Linti, Inorg. Chem., in press.
- [6] R. D. Schluter, A. H. Cowley, D. A. Atwood, R. A. Jones, J. L. Atwood, J. Coord. Chem. 1993, 30, 25; W. Uhl, R. Graupner, M. Layh, U. Schütz, J. Organomet. Chem. 1995, 493, C1.
- [7] O. T. Beachley, Jr., R. Blom, M. R. Churchill, K. Faegrie, J. C. Fettinger, J. C. Pazik, L. Victoriano, Organometallics 1989, 8, 346.
- [8] a) H. Schumann, C. Janiak, J. Pickardt, U. Börner, Angew. Chem. 1987, 99, 788; Angew. Chem. Int. Ed. Engl. 1987, 26, 789; H. Schumann, C. Janiak, F. Görlitz, J. Loebel, A. Dietrich, J. Organomet. Chem. 1989, 363, 243; b) with regard to the ab initio calculations see C. Janiak, R. Hoffmann, J. Am. Chem. Soc. 1990, 112, 5924.
- [9] a) N. Wiberg, H. Schuster, A. Simon, K. Peters, Angew. Chem. 1986, 98, 100; Angew. Chem. Int. Ed. Engl. 1986, 25, 79; b) N. Wiberg, C. M. M. Finger, K. Polborn, *ibid.* 1993, 105, 1140 and 1993, 32, 1054.
- [10] M. Tacke, H. Schnöckel, Inorg. Chem. 1989, 28, 2895.
- [11] Additional information to ref.[4a] (established together with H. Schnöckel, T. Passler, C. Dohmeier): On warming a solution of AlCl (4.70 mmol) in toluene/ Et<sub>2</sub>O [10] (20 mL) and tBu<sub>3</sub>SiNa (4.75 mmol) in Bu<sub>2</sub>O (25 mL) from  $-78^{\circ}$ C, the solution became dark red at about 0 °C. According to the <sup>1</sup>H NMR spectrum of the crude mixture, tBu<sub>3</sub>SiH (60%), (tBu<sub>3</sub>Si)<sub>2</sub> (27%), and I (13%) are formed together with intermediary traces of a radical (as revealed by the ESR spectrum which shows a line-rich signal indicating a species containing three Al atoms). Compound I could so far not be isolated by crystallization from the reaction solution; however, by sublimation of the reaction mixture at 180 °C under high vacuum, I was obtained as a deep violet, X-ray amorphous, pentane-soluble, oxygen- and moisture-sensitive solid. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, TMS, internal):  $\delta = 1.35$  (br., 12 tBu); <sup>29</sup>Si NMR (C<sub>6</sub>D<sub>6</sub>, TMS, external):  $\delta = 15.34$  (br., 4 Sit/Bu<sub>3</sub>); <sup>27</sup>Al NMR (C<sub>6</sub>D<sub>6</sub>, Al(NO<sub>3</sub>), external in D<sub>2</sub>O):  $\delta = 64.48$  (line width = 148 Hz); MS: m/z: 904 [ $M^+$ ].
- [12] N. Wiberg, K. Amelunxen, unpublished results. Additional properties of **2** and **3**: Compound **2** reacted with AgF<sub>2</sub> in heptane at room temperature to give among others  $(tBu_3Si)_2InF$  ( $C_{24}H_{34}FInSi_2$  (532.7); <sup>1</sup>HNMR ( $C_6D_6$ , TMS, internal):  $\delta = 1.27$  (s, 6 tBu); <sup>29</sup>Si NMR ( $C_6D_6$ , INEPT, TMS, internal):  $\delta = 50.27$  (d, <sup>2</sup>J(Si,F) = 6.5 Hz; 2 SitBu<sub>3</sub>); MS: m/z: 532 [ $M^+$ ]). Its thermoly: sis in  $C_6D_6$  at 40 °C yields  $tBu_3SiF$ , ( $tBu_3Si)_2$ , and In. The reaction of **3** with AgF<sub>2</sub> in Et<sub>2</sub>O at room temperature led, possibly via ( $tBu_3Si)_2$ TIF, to  $tBu_3SiF$ , ( $tBu_3SiD_2$ , and TI. The reaction of **2** with Na in  $C_6D_6$  at 40 °C led after 3 d to  $tBu_3SiNa$ , ( $tBu_3Si)_2$ ,  $tBu_3SiD$ ,  $tBu_3SiC_6D_5$ , and In, whereas the reaction of **3** with Na in  $C_6D_6$  at 40 °C led after 1 d to  $tBu_3SiNa$ ,  $tBu_3SiD$  as well as to two additional  $tBu_3Si$ -containing compounds and TI. Compound **3** shows a linerich ESR signal in  $C_6D_6$  at room temperature (dissociation in intermediary ( $tBu_3Si$ )<sub>2</sub>TI radicals?). Compounds **2** and **3** are intensely colored (deep violet and black green; in comparison [(Me\_3Si)\_2CH]\_4In\_2 and [2,4,6-(CF\_3)\_3C\_6H\_2]\_4In\_2: orange [1]; [(Me\_3Si)\_3Si]\_4TI\_2: dark red [3]), which might be attributed to the presence of radicals such as ( $tBu_3Si_2$ TI.
- [13] Crystallographic data of 2:  $(C_{48}H_{108}In_2Si_4 \cdot C_5H_{12}, M_r = 1027.34)$ : a = 20.471(3), b = 15.553(3), c = 41.746(6) Å,  $\beta = 99.84(1)^\circ$ , V = 13095(4) Å<sup>3</sup>, monoclinic, space group C/c, Z = 8,  $\rho_{calcd} = 1.042$  gcm<sup>-3</sup>,  $\mu = 8.01$  cm<sup>-1</sup>, F(000) = 4400. Crystal dimensions =  $0.6 \times 0.6 \times 0.5$  mm<sup>3</sup>. The single crystal was mounted in perfluoroether oil and all measurements were performed at 183 K. Data collection:  $\omega$  scans,  $2\theta = 3-50^{\circ}$  in -24 < h < 3; 0 < k < 18; -47 < l < 48. 11816 measured reflections, 10938 symmetry independent, 6720 with  $F > 4\sigma(F)$ , max/min transmission: 0.645/0.569. Structure solution and refinement: heavy atom method, full matrix refinement against  $F^2$ , 604 parameters refined, 105 restraints,  $R_1 = 0.086$ , wR2 = 0.229, GOF = 1.129; largest residual electron density =  $1.889 \text{ e} \text{ Å}^{-3}$ . The non-hydrogen atoms were refined with anisotropic temperature parameters, the H atoms were included into the refinement in calculated positions with a riding model. The temperature factors indicated that the *tert*-butyl groups were rotationally disordered. For eight of these 36 methyl groups this disorder was taken into consideration by refinement of the sites into two positions. The relatively large residual electron density, which was not located near the In or Si atoms, indicated the presence of a possible additional disordered solvent molecule in the unit cell. Crystallographic data of 3 ( $C_{48}H_{108}Tl_2Si_4$ ,  $M_r = 1206.4$ ): a = 20.309(6),

b = 15.387(4), c = 41.57(2) Å,  $\beta = 99.44(3)^{\circ}$ , V = 12814.5 Å<sup>3</sup>, monoclinic, space group C2/c, Z = 8,  $\rho_{calcd} = 1.251$  gcm<sup>-3</sup>,  $\mu = 51.2$  cm<sup>-1</sup>, F(000) = 4912. Crystal mounted in perflouroether oil; measurements at 213 K. Data collection:  $\omega$  scans,  $2\theta = 3-46^{\circ}$  in  $h, k, \pm 1$ . 7738 measured reflections, 7354 of which were independent and 4339 with  $F > 4\sigma(F)$ . Structure solution and refinement: heavy atom method, TI and Si atoms anisotropically refined, C atoms isotropically. The structure solution converged without inclusion of H atoms and possible solvent molecules at  $R_1 = 0.135$ , wR2 = 0.417, GOF = 1.097. The crystal decomposed considerably during the measurement; the measurement was stopped when the intensity of two standard reflections became smaller than 50%, which is why the C atoms were not refined anisotropically. Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany) on quoting the depository number CSD-404429.

- [14] S. H. Down, L. S. Wartell, J. Molec. Struct. 1980, 67, 249.
- [15] The solution contains an additional *i*Bu<sub>3</sub>Si-containing thallium compound in traces [<sup>29</sup>Si NMR (C<sub>6</sub>D<sub>6</sub>, INEPT, TMS, external):  $\delta = 99.79$  (d, <sup>1</sup>*J*(<sup>29</sup>Si,<sup>205</sup>Tl) = 1652, <sup>1</sup>*J*(<sup>29</sup>Si,<sup>203</sup>Tl) = 1636 Hz)]. This compound was formed from the reaction of CpTl with *i*Bu<sub>3</sub>SiNa in THF (red reaction solution) in higher yields.

## Synthesis and Structure of Seven-Coordinate Bismuth(v) Complexes with Benzenoid and Non-Benzenoid Arene Ligands: Tri(aryl)tropolonatobismuth(v) Complexes\*\*

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To obtain stable bismuth(v) compounds, starting materials are required that behave as strongly electronegative bonding partners or, at least, show rather large group electronegativities, as is true for substituted phenyl groups and similar aromatic systems.<sup>[1]</sup> By far the best known example of an arylbismuth(v)compound is pentaphenylbismuth which was prepared by G. Wittig and K. Clauss, and later crystallographically characterized in 1987.<sup>[2, 3]</sup> Many of the bismuth(v) compounds prepared to date are five-coordinate; the synthesis of the hexaphenylbismutate complex ion provided a six-coordinate bismuth(v) ion.<sup>[4, 5]</sup> Tri(organo)bismuth sulfonates and tri(aryl)bismuth dicarboxylates are compounds for which a five- and seven-coordinate bismuth(v) ion, respectively, are discussed.<sup>[6-9]</sup> Little information is available regarding the biological activity of bismuth(v) compounds, since most of these complexes are too unstable for biological and medicinal studies. We now report the synthesis of tri(aryl)tropolonatobismuth(v) complexes that are suitable for such investigations.

Tropolone and its derivatives are well-studied non-benzenoid aromatic systems.<sup>[10]</sup> Following removal of the proton of the hydroxy group, metals can bind to the two oxygen atoms, resulting in the formation of chelates (Scheme 1). Tropolonatobis-



Scheme 1. Mesomeric structures of the tropolone ligands in the tropolonato complexes.

muth(III) complexes are stable compounds that have been shown to exhibit biological activity, for example, against *Helicobacter pylori* bacteria, which are responsible for gastritis and other gastrointestinal diseases.<sup>[11]</sup> The heretofore unknown tropolonatobismuth(v) complexes might have similar properties and for this reason we decided to pursue their synthesis and characterization.

Treatment of diacetetotri(aryl)bismuth(v) compounds with tropolone derivatives results in the cleavage of the two acetate groups and their exchange for two tropolone rings. Diacetatotri(phenyl)bismuth(v) **4** can be prepared readily in ether from triphenylbismuth and acetic acid in the presence of *tert*-butylhydroperoxide.<sup>[12]</sup> We employed this method to synthesize diacetatotri(*p*-tolyl)bismuth(v) **1** in good yield. The reaction of **1** with tropolone **2** in methanol (heating under reflux for 30 min, yield 69%) led to water- and air-stable yellow crystals of di(*O*,*O*-tropolonato)tri(*p*-tolyl)bismuth(v) **3**, suitable for a crystal structure analysis (Fig. 1).<sup>[13]</sup> Complex **3** has a distorted pentagonal-



Fig. 1. Molecular structure of **3** in the crystal. Selected distances [Å] and angles [<sup>2</sup>]: Bi(1)-O(1) 2.317(16), Bi(1)-O(2) 2.498(15), Bi(1)-O(3) 2.310(16), Bi(1)-O(4) 2.456(14), Bi(1)-C(20) 2.215(23), Bi(1)-C(26) 2.156(24), Bi(1)-C(32) 2.119(28), O(1)-C(1) 1.266(31), O(2)-C(7) 1.316(33), O(3)-C(8) 1.286(26), O(4)-C(14) 1.263(31); O(1)-Bi(1)-O(2) 67.6(6), O(1)-Bi(1)-O(3) 156.7(5). O(2)-Bi(1)-O(3) 134.7(5), O(1)-Bi(1)-O(2) 67.6(6), O(1)-Bi(1)-O(4) 70.0(5), O(3)-Bi(1)-O(3) 134.7(5), C(20)-Bi(1)-C(26) 101.7(9), C(1)-Bi(1)-C(32) 93.5(8), O(2)-Bi(1)-C(32) 82.4(7), O(3)-Bi(1)-C(32) 99.4(9), Bi(1)-O(1) 121.5(14), Bi(1)-C(27) 112.6(13), Bi(1)-O(3)-C(8) 120.7(14), Bi(1)-O(4)-C(14) 119.5(13).

bipyramidal structure; the base of the pyramid comprises a tolyl group (C17) and two tropolone rings (twist angle  $11.7^{\circ}$ ). The remaining two tolyl groups occupy axial positions; the angle between them (C32-Bi1-C20) is 158.8°. The interaction between

the oxygen atoms of the tropolone rings and the bismuth atom leads to Bi–O bonds of different lengths; two are shorter (Bi–O1 2.316, Bi–O3 2.310 Å) and two are longer (Bi–O2 2.497, Bi–O4 2.455 Å). Opposite bonds are of approximately similar length. The measured Bi-O-C angles lie in the range 119.5–121.5°, a finding consistent with sp<sup>2</sup>-hybridization of the oxygen atoms. For the short Bi–O bond lengths we ex-

pected elongation of the corresponding C–O bonds, since the electron pull exerted by the bismuth atom and transmitted through the oxygen atom should weaken the C–O bond. This prediction was indeed confirmed for the O3–C8 bond (1.286 Å) and the O4–C14 bond (1.263 Å); however, the short Bi-O1

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