supermolecule formed between  $\alpha, \alpha'$ -bis(benzylammonium)-*p*-xylene bis(hexafluorophosphate) and BPP34C10 [5a, 5b].) The <sup>1</sup>H NMR spectrum (300 MHz) of a 3:2 molar ratio of BPP34C10 and 1-H<sub>3</sub>·3PF<sub>6</sub> in CD<sub>2</sub>Cl<sub>2</sub>/CD<sub>3</sub>CN (4:1) at 20 °C showed several broad, featureless peaks, indicating that aggregation occurs in solution; however, no signals associated with the cage supermolecule could be identified. Liquid secondary ion mass spectrometry (LSIMS; VG Zabspec mass spectrometer equipped with a cesium ion source, *meta*-nitrobenzyl alcohol matrix) was employed for the characterization of the aggregate in the "gas phase"—no peaks corresponding to the [3 + 2] supermolecule were observed. Nevertheless, peaks at *m*/2 2595, 2449, and 2303 were detected, corresponding to the species [BPP34C10·(1-H<sub>3</sub>)<sub>2</sub>][PF<sub>6</sub>]<sub>6</sub>, with the loss of one, two, and three PF<sub>6</sub> counterions, respectively.

- [9] Similar arguments have been used by Lehn and co-workers to explain self-recognition processes involving metal-ligand interactions in helicate self-assembly: R. Krämer, J.-M. Lehn, A. Marquis-Rigault, *Proc. Natl. Acad. Sci. USA* 1993, 90, 5394-5398. We note that in this seminal paper the authors remark that, "These considerations also apply to systems where binding involves interactions other than metal coordination such as hydrogen bonding or donor-acceptor forces."
- [10] J.-M. Lehn, Angew. Chem. 1990, 102, 1347-1362; Angew. Chem. Int. Ed. Engl. 1990, 29, 1304-1319.
- [11] A suitable crown ether could be 1,4,7,10,13,26,29,32,35,38-decaoxa[13.0.13.0]paracyclophane where the hydroquinone rings of BPP34C10 are replaced by 4,4'-dioxybiphenyl units. See P. R. Ashton, D. Joachimi, N. Spencer, J. F. Stoddart, C. Tschierske, A. J. P. White, D. J. Williams, K. Zab, Angew. Chem. 1994, 106, 1563-1566; Angew. Chem. Int. Ed. Engl. 1994, 33, 1503-1506.

## $In_4S[C(SiMe_3)_3]_4$ : An Organoindium Compound with an $In_4S$ Core Isovalence Electronic to Pentahydro-*closo*-pentaborate(2-)\*\*

Werner Uhl,\* Rene Graupner, Wolfgang Hiller, and Markus Neumayer

Novel and unprecedented organoelement cluster compounds of the heavier elements of the third main group aluminum, gallium, and indium were reported recently.<sup>[1-8]</sup> Some derivatives like  $[Al(C_{s}Me_{s})]_{4}$ , <sup>[1]</sup>  $K_{2}[Al_{12}iBu_{12}]$ , <sup>[2]</sup>  $[Ga-C(SiMe_{3})_{3}]_{4}$ , <sup>[3]</sup> and  $[In-C(SiMe_{3})_{3}]_{4}^{[4,5]}$  were verified by crystal structure determinations, others like [Al-Si(CMe<sub>3</sub>)<sub>3</sub>]<sub>4</sub>,<sup>[6]</sup> [Al-CH<sub>2</sub>CMe<sub>3</sub>]<sub>4</sub>,<sup>[7]</sup> and [Ga-CH2CMe3],<sup>[8]</sup> by specific reactions, theoretical investigations, or further characterization. A few sterically highly shielded cyclopentadienides of the monovalent elements indium and thallium show a pseudodimeric or a pseudohexameric arrangement of the metal atoms; however, long distances between the atoms of the clusters confirm only a weak element-element bonding interaction,<sup>[9]</sup> the significance of which has been controversial.<sup>[10]</sup> Aluminum(I) and gallium(I) compounds were recently described in a concise survey by Schnöckel et al.[11] The cluster compounds cited above have already been employed in the syntheses of numerous further products with hitherto un-known molecular structures.<sup>[8, 11-13]</sup> At present we are interested in the chemical behavior of the tetrahedral cluster compound  $In_4[C(SiMe_3)_3]_4$  1,<sup>[4, 12, 13]</sup> which is obtained in high yield by

 [\*] Prof. Dr. W. Uhl, R. Graupner Fachbereich Chemie der Universität Postfach 2503, D-26111 Oldenburg (Germany) Fax: Int. code + (441)7983329
 Prof. Dr. W. Hiller, M. Neumayer Anorranisch-chemisches Institut der Technischen Universität München

(Germany)

treatment of InBr with LiC(SiMe<sub>3</sub>)<sub>3</sub>·2 THF.<sup>[4, 5]</sup> The reactions of 1 with an excess of elemental sulfur, selenium, or tellurium give In<sub>4</sub>X<sub>4</sub>[C(SiMe<sub>3</sub>)<sub>3</sub>]<sub>4</sub> derivatives that exhibit a In<sub>4</sub>X<sub>4</sub> heterocubane framework.<sup>[4, 13]</sup> Because of the easy insertion of four sulfur atoms under mild conditions, we hoped to synthesize compounds with the composition In<sub>4</sub>S<sub>4-x</sub>[C(SiMe<sub>3</sub>)<sub>3</sub>]<sub>4</sub> (x = 1to 3) by the reaction of elemental sulfur with an excess of 1; unlike the heterocubane molecules such derivatives would still contain indium atoms in an unusual low formal oxidation state.

However, elemental sulfur proved to be unsuitable for the syntheses of these compounds, because regardless of the reaction conditions only mixtures of  $In_4S_4[C(SiMe_3)_3]_4$  and the starting compound 1 were formed. As a very mild reagent for the transfer of sulfur atoms we finally used propylene sulfide, which, however, required extensive optimization of the reaction. A colorless solid precipitated from the reaction solution that could not be further characterized because of the small amounts formed; in addition, the  $In_4S_4$  derivative is partially formed from the beginning of the reaction by the complete sulfurization of 1. Nevertheless we found an easy and reproducible method for the syntheses of a further compound (2): A solution of 1 in hexane was treated with a small excess of propylene sulfide and heated to 60 °C for 90 minutes. <sup>1</sup>H NMR spectra recorded to monitor the reaction reveal the formation of a mixture of 1  $(\delta = 0.447)$ ,  $In_4S_4R_4$  ( $\delta = 0.443$ ), and the new product 2  $(\delta = 0.455)$ . Subsequently, additional propylene sulfide was added in portions, and each time the mixture was heated to 60 °C for 90 minutes, until 1 was completely consumed; the color of the solution changed from violet to red. The addition of the propylene sulfide in small portions gave a better result than the addition of a large excess of the reagent at the beginning of the reaction. Compound 2 and  $In_4S_4[C(SiMe_3)_3]_4$  are present in a molar ratio of about 0.6 to 0.4 (NMR spectroscopy), and 2 crystallizes almost quantitatively from a solution in pentane as the less soluble component. The reaction is summarized in Equation (a).

$$In_{4}[C(SiMe_{3})_{3}]_{4} + H_{3}C-HC-CH_{2} \longrightarrow$$

$$In_{4}S[C(SiMe_{3})_{3}]_{4} + H_{3}C-CH=CH_{2}$$
(a)
$$In_{4}S[C(SiMe_{3})_{3}]_{4} + H_{3}C-CH=CH_{2}$$

The deep red compound 2 is isolated in 44% yield (based on 1). According to elemental analysis the In:S ratio is 4:1, and the molar mass determined cryoscopically in benzene shows that 2 exists in the undissociated form. Single crystals of 2 were obtained from solutions of the compound in diisopropyl ether; they exhibit the same cell dimensions and space group as the starting compound 1; however, one face of the In<sub>4</sub> tetrahedron is capped by a sulfur atom leading to the formation of a trigonal In<sub>4</sub>S bipyramid (Figure 1).

The addition of the four-electron donor atom sulfur to the molecular core of 1 makes compound 2 isovalence electronic to the hitherto unknown compounds pentahydro-*closo*-pentaborate(2–)  $[B_5H_5]^{2-}$  and thia-*closo*-pentaborane(4)  $B_4H_4S^{[15]}$  as well as to the isolated and completely characterized 1,5-dicarba*closo*-pentaborane(5)  $B_3C_2H_5$ .<sup>[15]</sup> Almost identical structural parameters were observed or calculated for all three boron derivatives; the B–B distances to the axial atoms were appropriate for single bonds, the B–B distances in the equatorial plane

<sup>[\*\*]</sup> We are grateful to the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for generous financial support.



Figure 1. Molecular structure of 2; methyl groups are omitted for clarity, the long In-In distances in the equatorial plane are indicated by broken lines. Important bond lengths [pm] and angles ["]: In1-S1 257.6(2), In2-S1 260.7(2), In3-S1 258.9(2), In1-In4 283.0(1), In2-S1 257.6(2), In2-S1 260.7(2), In3-S1 258.9(2), In1-In4 283.0(1), In2-In4 283.3(1), In3-In4 285.0(1), In1-In2 338.4(1), In1-In3 36.2(1), In2-In3 341.42(9), In1-C1 221.1(8), In2-C2 223.9(7), In3-C3 223.0(8), In4-C4 225.7(7); In1-S1-In2 81.51(6), In1-S1-In3 81.21(6), In2-S1-In3 82.15(6), In1-In4-In2 73.37(3), In1-In4-In3 72.57(3), In2-In4-In3 73.85(3), S1-In1-In4 87.90(6), S1-In2-In4 87.23(5), S1-In3-In4 87.22(5).

were considerably longer  $([B_5H_5]^2 : B_{eq} - B_{ax} \ 168.1, B_{eq} - B_{eq} \ 187.4 \text{ pm}; B_4H_4S: B_{eq} - B_{ax} \ 165.1, B_{eq} - B_{eq} \ 192.3 \text{ pm}; B_3C_2H_5: B-C \ 155.6, B-B \ 185.3 \text{ pm}).^{[15]}$  The corresponding parameters for 2 are quite similar: The average In-In distance to the axial In atom In4 is 283.8 pm, and thus lies in the range of In-In single bonds in organoelement derivatives;<sup>[6, 16]</sup> it is 16 pm shorter than the average In-In distance in tetraindane(4) 1.<sup>[4]</sup> In contrast, the equatorial In-In distances are significantly longer (338.7 pm); they lie between the value found in 1 (300.2 pm) and that found in In<sup>1</sup> derivatives with sterically demanding cyclopentadienyl groups  $(>360 \text{ pm})^{[9]}$  and only negligible In–In interactions. Thus, 2 can be described as the first organoindium analog of the closo-borate ions, even if a classical description of the bonding with localized bonds and a hyperconjugative electron transfer from the  $\alpha$ -C-Si bonds to the unsaturated In atoms should not be ruled out completely. An approach towards the classical, localized bonding model with a significant lengthening of the equatorial B-B distance to 197 pm<sup>[17]</sup> is observed in 1,5-dicarbapentaborane(5) on substitution of hydrogen atoms by amino groups. The latter reduce the participation of the B atoms in delocalized multicenter bonding through a  $\pi$  interaction with their lone pair of electrons.

The In-S bond lengths in 2 (259.1 pm) are slightly longer than those in the  $In_4S_4$  heterocubane (254.9 pm),<sup>[13]</sup> which might be caused by the lower oxidation states of the In atoms; they still lie in the range normally associated with three-coordinate sulfur atoms.<sup>[18]</sup> The equatorial In-C bonds are shorter (av 222.7 pm) than the axial In-C bond (225.7 pm). Inside the In<sub>4</sub>S bipyramid the angles are more acute at the axial In atom In4 (73.26°) than at the sulfur atom S1 (81.62°); in the In<sub>3</sub> plane angles of between 59.3 and 60.8° are observed.

Chemically nonequivalent equatorial and axial  $C(SiMe_3)_3$ groups are present in the molecular structure of 2 in the solid state; however, only one sharp singlet is observed for the SiMe<sub>3</sub> atoms in both the <sup>1</sup>H and <sup>13</sup>C NMR spectra at room temperature. The spectra remain unchanged on cooling a solution of 2 in [D<sub>8</sub>]toluene to -70 °C. Compound 2 decomposes slowly in polar solvents; thus, solvent-dependent NMR spectra could not easily be recorded. Only in [D<sub>10</sub>]diethyl ether were we able to

## COMMUNICATIONS

obtain additonal temperature-dependent <sup>1</sup>H NMR spectra without significant decomposition. These spectra show a splitting of the resonance of the SiMe<sub>3</sub> group below -10 °C into two very narrow signals at  $\delta = 0.34$  and 0.33 with an intensity ratio of 3:1. These observations possibly indicate a fast equilibration of the position of the sulfur atom over all four faces of the In<sub>4</sub> tetrahedron in solution at room temperature. The spectroscopic data of 1 and 2 are very similar, and the differentiation between 1 and 2 is most apparent from the UV/Vis spectra, in which an absorption at 490 nm (shoulder at 570 nm)<sup>14, 51</sup> is observed for 1, while the most bathochromically shifted absorption of 2 occurs at only 400 nm.

## Experimental Section

A solution of propylene sulfide (7 mL, 0.065 M solution in toluene) was added to a solution of 1 (0.489 g, 0.35 mmol) in hexane (50 mL). The mixture was heated to 60 °C for 90 min, and the reaction monitored by NMR spectroscopy. Additional amounts of the solution of propylene sulfide was added (7 + 3 mL) and the mixture was heated each time to 60 °C for 90 min, until 1 was completely consumed. The solvent was evaporated under vacuum, and the residue was dissolved in a small volume of pentane and filtered. Compound 2 crystallized on cooling to -30 °C. Yield: 0.22 g (44%); red, slightly air-sensitive crystals. Decomposition at 170 °C (under argon). Molar mass (determined cryoscopically in benzene) [gmol<sup>-1</sup>]: found 1335; calcd 1417.66. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta = 0.455$ ; <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta = 6.95$  (SiMe<sub>3</sub>), *x*-C atom not detected. IR (Nujol, CsBr):  $\tilde{v}$  [cm<sup>-1</sup>] = 1327 w, 1289 w, 1252 vs  $\delta$ CH<sub>3</sub>; 1190 vw, 1167 w, 1127 w, 1111 w, 1015 m (diisopropyl ether): 856 vs, 839 vs, 774 s, 723 m  $\rho$ CH<sub>3</sub>(Si); 673 vs, 648 vs v<sub>as</sub>SiC; 615 m v,SiC : 583 vs vIn<sub>4</sub>C<sub>4</sub>; 517 vw, 448 vw vInC: 361 w, 311 m  $\delta$ SiC, vInS. UV/Vis (pentane):  $\lambda_{max}$  [mm] (lgc) = 250 (4.5), 400 (3.8).

Received: June 10, 1996 [Z 92091E] German version: Angew. Chem. 1997, 109, 62-64

Keywords: electron deficiency · indium · main group elements

- [1] C. Dohmeier, C. Robl, M. Tacke, H. Schnöckel, Angew. Chem. 1991, 103, 594-595; Angew. Chem. Int. Ed. Engl. 1991, 30, 564-565.
- [2] W. Hiller, K.-W. Klinkhammer, W. Uhl, J. Wagner, Angew. Chem. 1991, 103, 182-183; Angew. Chem. Int. Ed. Engl. 1991, 30, 179-180.
- [3] W. Uhl, W. Hiller, M. Layh, W. Schwarz, Angew. Chem. 1992, 104, 1378–1380; Angew. Chem. Int. Ed. Engl. 1992, 31, 1364–1366.
- [4] W. Uhl, R. Graupner, M. Layh, U. Schütz, J. Organomet. Chem. 1995, 493, C1-C5.
- [5] R. D. Schluter, A. H. Cowley, D. A. Atwood, R. A. Jones, J. L. Atwood, J. Coord. Chem. 1993, 30, 25-28.
- [6] N. Wiberg, K. Amelunxen, H. Nöth, M. Schmidt, H. Schwenk, Angew. Chem. 1996, 108, 110-112; Angew. Chem. Int. Ed. Engl. 1996, 35, 65-67.
- [7] E. P. Schram, N. Sudha, Inorg. Chim. Acta 1991, 183, 213 216.
- [8] O. T. Beachley, J. C. Pazik, M. J. Noble, Organometallics 1994, 13, 2885-2889.
- [9] a) O. T. Beachley, M. R. Churchill, J. C. Fettinger, J. C. Pazik, L. Victoriano, J. Am. Chem. Soc. 1986, 108, 4666-4668; b) H. Schumann, C. Janiak, F. Görlitz, J. Loebel, A. Dietrich, J. Organomet. Chem. 1989, 363, 243-251, c) H. Schumann, C. Janiak, J. Pickardt, U. Börner, Angew. Chem. 1987, 99, 788-789; Angew. Chem. Int. Ed. Engl. 1987, 26, 789 - 790.
- [10] a) C. Janiak, R. Hoffmann, J. Am. Chem. Soc. 1990, 112. 5924-5946; b) P. Schwerdtfeger, Inorg. Chem. 1991, 30, 1660-1661.
- [11] C. Dohmeier, D. Loos, H. Schnöckel, Angew. Chem. 1996, 108, 141-161; Angew. Chem. Int. Ed. Engl. 1996, 35, 129-149.
- [12] a) W. Uhl, S. U. Keimling, W. Hiller, M. Neumayer, Chem. Ber. 1996, 129, 397-400. b) W. Uhl, S. U. Keimling, W. Hiller, M. Neumayer, *ibid.* 1995, 128, 1137-1139.
- [13] W. Uhl, R. Graupner, M. Pohlmann, S. Pohl, W. Saak, Chem. Ber. 1996, 129, 143-146.
- [14] Single crystals of 2 were obtained by recrystallization from diisopropyl ether; the crystals include one molecule of the solvent for each formula unit with only weak van der Waals interactions to hydrogen atoms of the trimehylsilyl groups; C<sub>46</sub>H<sub>122</sub>In<sub>4</sub>OSSi<sub>12</sub>, diffractometer CAD-4, Mo<sub>8x</sub> radiation. -70 °C, programs SHELXTL PLUS REL 4.1 and SHELXL-93; orthorhombic, P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>, a = 1364.5(1), b = 1787.1(1), c = 3049.7(3) pm. V = 7437 Å<sup>3</sup>, Z = 4, ρ<sub>cated</sub> = 1.357 gcm<sup>-3</sup>, crystal size: 0.55 × 0.4 × 0.35 mm, θ-2θ scan, range: 6 ≤ 20 ≤ 50<sup>°</sup>, 12443 independent reflections; 11222 reflections F > 4σ(F), 637 parameters, R = 0.041 and wR<sup>2</sup> = 0.134 (all data); max. residual electron density: 1.08 × 10<sup>30</sup> em<sup>-3</sup>. The molecule shows slight disorder, and a second In<sub>4</sub>S trig-

onal bipyramid could be refined with an occupancy factor of 0.08. The second position of the cluster can be explained by a rotation of the molecule and formally by the occupation of another face of the  $In_4$  tetrahedron; its In atoms exhibit normal distances to quarternary C atoms, so that the rest of the molecular structure seems to be little influenced by the disorder. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-179-128. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: Int. code + (1223) 336-033; e-mail: deposit@chemerys.cam.ac.uk).

- [15] a) E. A. McNeill, K. L. Gallaher, F. R. Scholer, S. H. Bauer, *Inorg. Chem.* 1973, *12*, 2108–2111; b) D. A. Dixon, D. A. Kleier, T. A. Halgren, J. A. Hall, W. N. Lipscomb, *J. Am. Chem. Soc.* 1977, *99*, 6226–6237; c) E. D. Jemmis, G. Subramanian, B. V. Prasad, *Inorg. Chem.* 1994, *33*, 2046–2048.
- [16] a) W. Uhl, M. Layh, W. Hiller, J. Organomet. Chem. 1989, 368, 139-154;
   b) R. D. Schluter, A. H. Cowley, D. A. Atwood, R. A. Jones, M. R. Bond, C. J. Carrano, J. Am. Chem. Soc. 1993, 115, 2070-2071.
- [17] a) D. Bromm, U. Seebold, M. Noltemeyer, A. Meller, *Chem. Ber.* 1991, *124*, 2645–2649; b) W. Maringgele, H. Knop, D. Bromm, A. Meller, S. Dielkus, R. Herbst-Irmer, G. M. Sheldrick, *ibid.* 1992, *125*, 1807–1813.
- [18] W. Uhl, R. Graupner, H. Reuter, J. Organomet. Chem. 1996, 523, 227-234.

## Tl<sup>1</sup>[C(SiMe<sub>3</sub>)<sub>3</sub>]—An Alkylthallium(1) Compound with a Distorted Tetrahedron of Tl Atoms in the Solid State\*\*

Werner Uhl,\* Sven Uwe Keimling,

Karl Wilhelm Klinkhammer, and Wolfgang Schwarz

Tetrahedral clusters with monovalent elements of the third main group are at the center of current research in the field of organoelement chemistry that has already produced remarkable novel compounds:  $B_4(CMe_3)_4$ ,<sup>[1]</sup>  $Al_4Cp_4^*$  ( $Cp^* = C_5Me_5$ ),<sup>[2]</sup>  $Al_4(CH_2CMe_3)_4$ ,<sup>[3]</sup>  $Al_4[Si(CMe_3)_3]_4$ ,<sup>[4]</sup>  $Ga_4[C(SiMe_3)_3]_4$ ,<sup>[5]</sup> and  $In_4[C(SiMe_3)_3]_4$ .<sup>[6, 7]</sup> In addition to the preparative aspects, the chemical bonding has been investigated by theoretical studies.<sup>[8]</sup> Corresponding thallium compounds are up to now unknown. Cyclopentadienides of monovalent thallium preferably form cyclopentadienyl-bridged oligomers and polymers;<sup>[9, 10]</sup> a pseudodimer was obtained with the sterically demanding pentabenzylcyclopentadienyl ligand, in which the Tl atoms, although they approach each other, show only a weak Tl–Tl interaction with a long Tl–Tl distance.<sup>[11, 12]</sup>

Initially we tried to synthesize an alkylthallium(I) derivative in an analogous way to the corresponding indium compound by treating freshly sublimed TlBr with the THF adduct of LiC- $(SiMe_3)_3$ .<sup>[13]</sup> However, we obtained HC $(SiMe_3)_3$  as the main product; the brief appearance of a red color possibly indicates the formation of an alkylthallium compound. In contrast, in addition to insoluble lithium cyclopentadienide, deep red-violet, almost black crystals of the alkylthallium(I) compound 1, were obtained from cyclopentadienylthallium(I) and the organolithium compound in toluene under mild conditions, followed by rapid workup [Eq. (a)]. The product 1 decomposes at 65 °C,

Postfach 2503, D-26111 Oldenburg (Germany) Fax: Int. code +(441)7983329

Dr. K. W. Klinkhammer, Dr. W. Schwarz

Institut für Anorganische Chemie der Universität Stuttgart (Germany)

 $TIC_5H_5 + LiC(SiMe_3)_3 \cdot 2THF$  —

$$TI[C(SiMe_3)_3] + LiC_5H_5 + 2 THF$$

(a)

and thallium deposits even at -50 °C from the red-violet solutions in pentane. The organothallium compound is thus considerably less stable than the corresponding gallium<sup>[5]</sup> and indium derivatives.<sup>[7]</sup> According to the cryoscopic determination of the molar mass, 1 is present as a monomer in benzene, whereas the indium analog remains tetrameric in solution.<sup>[7]</sup> Because of the steric demand of the voluminous substituents and the shorter element–element distances than in the tretraindium derivative, the gallium compound forms monomers on increasing the dilution of its solutions in benzene.<sup>[5]</sup> In the <sup>1</sup>H and <sup>13</sup>C NMR spectra of 1 singlets are observed for the SiMe<sub>3</sub> groups regardless of the temperature, and the most bathochromically shifted absorption band in the UV/Vis spectra appears similarly as for the In<sub>4</sub> derivative at 515 nm.

The crystal structure analysis of 1 (Figure 1)<sup>[14]</sup> reveals a tetramer, in which the thallium atoms are in a distorted tetrahedral arrangement with remarkably different Tl-Tl distances.



Figure 1. Molecular structure of 1; methyl groups are omitted for clarity. Important bond lengths [pm] and angles [°]: T11 – T12 332.2(1), T11 – T13 335.1(1), T12 – T13 335.1(1), T12 – T14 346.1(1), T13 – T14 363.8(1), T11 – C1 238(1), T12 – C2 238(1), T13 – C3 238(1), T14 – C4 233(1); T12 – T11 - T13 59.89(2), T12 – T11 - T14 59.54(2), T13 – T12 – T14 64.62(2), T13 – T12 – T14 64.62(2), T13 – T12 – T14 64.74(2), T13 – T12 59.62(2), T11 – T13 – T14 59.35(2), T13 – T14 59.35(2), T11 – T14 – T13 55.84(2), T11 – T14 – T13 54.94(2), T12 – T14 – T13 55.91(2).

An average Tl–Tl distance of 333.5 pm is observed in the plane (Tl1,Tl2,Tl3), but the distances to the atom Tl4 are significantly longer (346.1–363.8 pm), and lie in the range of weak interactions in pentabenzylcyclopentadienylthallium(I);<sup>[11]</sup> the significance of these interactions has been discussed controversially.<sup>[12]</sup> A length of approximately 294 pm was established for a Tl–Tl single bond;<sup>[4, 15]</sup> thus even the shortest Tl–Tl distance in 1 is 13% longer than this value. In contrast, in the analogous compounds with Ga<sub>4</sub> and In<sub>4</sub> tetrahedra we observed almost indistinguishable Ga–Ga and In–In distances, respectively, which are less than 6% longer than the respective single bonds in organoelement compounds. Intermetallic phases with Tl clusters show Tl–Tl distances of greater than 300 pm.<sup>[16]</sup>

In contrast to the Ga<sub>4</sub> and In<sub>4</sub> compounds, in the Tl<sub>4</sub> cluster the E-C vectors (E = Tl) do not point away from the center of the terahedron, but rather a paddle wheel arrangement of the substituents is observed; thus, the deviation from the ideal arrangement on projection on a triangular face of the cluster is close to 35°, and one almost linear Tl-Tl-C group (155 to 174°)

<sup>[\*]</sup> Prof. Dr. W. Uhl, S. U. Keimling Fachbereich Chemie der Universität

<sup>[\*\*]</sup> We are grateful to the Deutschen Forschungsgemeinschaft and the Fonds der Chemischen Industrie for generous financial support.