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The First Pb-Containing Cyclic Polysulfides, 1,2,3,4,5-Tetrathiaplumbolanes, Derived from Kinetically Stabilized Plumbylenes

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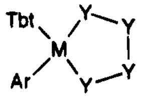
Summary: The first examples of Pb-containing cyclic polysulfides, 1,2,3,4,5-tetrathiaplumbolanes ($R^1R^2PbS_4$: **2** (R^1 = Tbt, R^2 = Tip), **3** (R^1 = Tbt, R^2 = Ttm), *and* **4** ($R^1 = R^2$ = Tip); *Tbt = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl, Tip = 2,4,6-triisopropylphenyl, and Ttm = 2,4,6-tris[(trimethylsilyl)methyl]phenyl), were synthesized and isolated as stable crystalline compounds by sulfurization of the corresponding kinetically stabilized diarylplumbylenes Tbt(Tip)Pb: (**6**), Tbt(Ttm)Pb: (**7**), and* Tip_2Pb*: (**10**). The molecular structures of the novel lead-containing metallacycles **2** and **4** were determined by X-ray crystallographic analysis.*

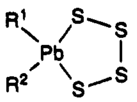
In contrast to the wide chemistry of the transition-metal polychalcogenido complexes,[1] cyclic polychalcogenides containing a main-group element had been unknown until we recently succeeded in the synthesis of novel tetrachalcogenolanes containing a group 14 element, $Tbt(Ar)MY_4$ (**1**: M = Si, Ge, Sn; Y = S, Se; Ar = mesityl, 2,4,6-triisopropylphenyl (Tip)),[2] by taking advantage of a new steric protection group, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (noted as Tbt hereafter).[3]

Furthermore, we have found that these overcrowded cyclic polychalcogenides are good precursors of stable group 14 element–chalcogen double-bond compounds, Tbt(Ar)M=Y.[4] Here, we present the synthesis of novel Pb-containing cyclic tetrasulfides, 1,2,3,4,5-tetrathiaplumbolanes ($R^1R^2PbS_4$: **2** (R^1 = Tbt, R^2 = Tip), **3** (R^1 = Tbt, R^2 = Ttm), and **4** ($R^1 = R^2$ = Tip); Ttm = 2,4,6-tris[(trimethylsilyl)methyl]phenyl), the heaviest congener of tetrathiolanes containing a group 14 element, together with their crystallographic structure analysis.

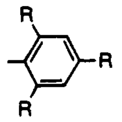


1

M = Si, Ge, Sn
Y = S, Se



2 (R^1 = Tbt, R^2 = Tip)
3 (R^1 = Tbt, R^2 = Ttm)
4 ($R^1 = R^2$ = Tip)



Tbt: R = $CH(SiMe_3)_2$
Ttm: R = CH_2SiMe_3
Tip: R = $CHMe_2$

We employed kinetically stabilized diarylplumbylenes[5] as starting materials for the preparation of the lead-containing cyclic polysulfides **2**–**4**. Ligand ex-

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[⊗] Abstract published in *Advance ACS Abstracts*, June 15, 1995.

(1) Reviews of polychalcogenido complexes: (a) Draganjac, M.; Rauchfuss, T. B. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 742. (b) Müller, A.; Diemann, E. *Adv. Inorg. Chem.* **1987**, *31*, 89. (c) Ansari, M. A.; Ibers, J. A. *Coord. Chem. Rev.* **1990**, *100*, 223. (d) Kolis, J. W. *Coord. Chem. Rev.* **1990**, *105*, 195.

(2) (a) Tokitoh, N.; Suzuki, H.; Matsumoto, T.; Matsuhashi, Y.; Okazaki, R.; Goto, M. *J. Am. Chem. Soc.* **1991**, *113*, 7047. (b) Tokitoh, N.; Matsuhashi, Y.; Okazaki, R. *Tetrahedron Lett.* **1991**, *32*, 6151. (c) Tokitoh, N.; Matsumoto, T.; Okazaki, R. *Tetrahedron Lett.* **1992**, *33*, 2531. (d) Matsuhashi, Y.; Tokitoh, N.; Okazaki, R.; Goto, M.; Nagase, S. *Organometallics* **1993**, *12*, 1351. (e) Matsumoto, T.; Tokitoh, N.; Okazaki, R.; Goto, M. *Organometallics* **1995**, *14*, 1008. Although cyclic polysulfides containing silicon and germanium were prepared by Steudel et al., they are reportedly stable only below −20 °C. See: Albertsen, J.; Steudel, R. *Phosphorus, Sulfur, Silicon Relat. Elem.* **1992**, *65*, 165. Steudel, R. In *The Chemistry of Inorganic Ring Systems*; Steudel, R., Ed.; Elsevier: Amsterdam, 1992; p 233.

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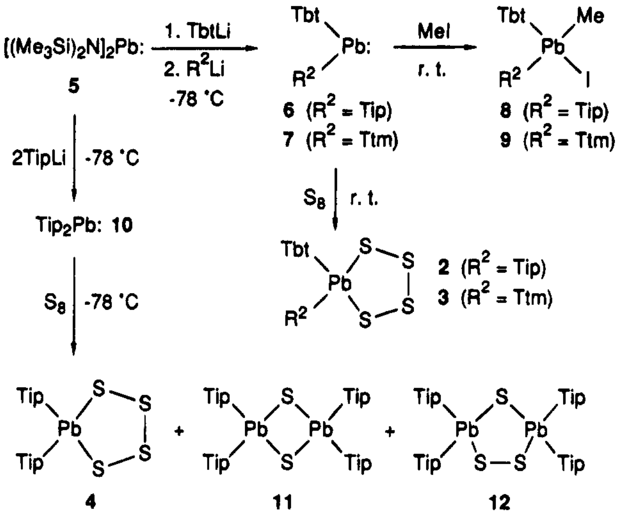
Scheme 1



change of bis[bis(trimethylsilyl)amino]plumbylene (**5**)[7a] by sequential nucleophilic substitution with TbtLi and R^2Li (R^2 = Tip, Ttm) in ether at −78 °C afforded the overcrowded diarylplumbylenes **6** and **7**, respectively. Plumbylenes **6** and **7** were found to be stable in solution even at room temperature, showing a characteristic purple color. They were readily trapped with methyl iodide at room temperature to afford the corresponding iodoplumbanes **8** and **9**[9] in 43 and 33% yields, respectively.[10] In ^{207}Pb NMR, characteristic signals for **6** and **7** were observed as singlets in an extremely downfield region (δ_{Pb} (in toluene-d_8 relative to external Me_4Pb) +8888 for **6** and +8873 for **7**), which were unambiguously attributable to those for base-free monomeric plumbylenes.[11]

The successful formation and the promising reactivity of the kinetically stabilized diarylplumbylenes **6** and **7** prompted us to examine their sulfurization with elemental sulfur, which was reported to be a useful synthetic method for the lower homologues of tetrachalcogenolanes **1** containing a group 14 element.[3a,4a] Thus, treatment of **6** and **7** with an excess amount of elemental sulfur gave the corresponding tetrathiaplumbolanes **2** and **3** as stable orange crystals in 68 and 52% yield, respectively.[9] On the other hand, the reaction of the less hindered plumbylene Tip_2Pb: (**10**)[12] with sulfur in ether at −40 °C afforded the expected tetrathiaplumbolane **4** (20%)[9] together with byproducts having two plumbylene units, *i.e.* 1,3,2,4-dithiadiplumbetane **11** (13%) and 1,3,4,2,5-trithiadiplumbolane **12** (14%),[9] suggesting that the Tip group is less effective for steric protection than the Tbt group. All tetrathiaplumbolanes **2**−**4** here obtained were found to be stable toward air and moisture and could be purified by HPLC followed by silica gel chromatography. In ^{207}Pb NMR the tetrathiaplumbolanes **2**−**4** showed singlet signals at 313.9, 311.6, and 288.6 ppm (relative to external Me_4Pb in $CDCl_3$), which are reasonably assigned to those for tetravalent lead compounds.

The tetrathiaplumbolanes **2**−**4** should be noted as the first examples of Pb-containing cyclic polysulfides, and the molecular structures of **2** and **4** were finally determined by X-ray crystallographic analysis.[13] The con-

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(3) We have recently found that the Tbt group is a useful steric protection group for the kinetic stabilization of a variety of highly reactive chemical species containing heavier typical elements: (a) Tokitoh, N.; Saito, M.; Okazaki, R. *J. Am. Chem. Soc.* **1993**, *115*, 2065. (b) Tokitoh, N.; Matsuhashi, Y.; Okazaki, R. *J. Chem. Soc., Chem. Commun.* **1993**, 407. (c) Tokitoh, N.; Suzuki, H.; Okazaki, R.; Ogawa, K. *J. Am. Chem. Soc.* **1993**, *115*, 10428. See also refs 2 and 4.

(4) (a) Tokitoh, N.; Matsumoto, T.; Manmaru, K.; Okazaki, R. *J. Am. Chem. Soc.* **1993**, *115*, 8855. (b) Matsuhashi, Y.; Tokitoh, N.; Okazaki, R. *Organometallics* **1993**, *12*, 2573. (c) Suzuki, H.; Tokitoh, N.; Nagase, S.; Okazaki, R. *J. Am. Chem. Soc.* **1994**, *116*, 11578. (d) Matsumoto, T.; Tokitoh, N.; Okazaki, R. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2316.

(5) Although Lappert et al. have already described the stable overcrowded dialkylplumbylene $[(Me_3Si)_2CH]_2Pb$:,[6] most of the other stable plumbylenes reported so far are restricted to the examples thermodynamically stabilized by the heteroatom-containing substituents.[7] As for the aryl-substituted counterparts, there have been no stable plumbylenes except for the only isolable example, bis[2,4,6-tris(trifluoromethyl)phenyl]plumbylene, stabilized by the intramolecular coordination of the fluorine atoms of its four *o*-trifluoromethyl groups.[8]

(6) Cotton, J. D.; Davidson, P. J.; Lappert, M. F. *J. Chem. Soc., Dalton Trans.* **1976**, 2275.

(7) (a) Harris, D. H.; Lappert, M. F. *J. Chem. Soc., Chem. Commun.* **1974**, 895. (b) Gynane, M. J. S.; Harris, D. H.; Lappert, M. F.; Power, P. P.; Rivière, P.; Rivière-Baudet, M. *J. Chem. Soc., Dalton Trans.* **1977**, 2004. (c) Fjeldberg, T.; Hope. H.; Lappert, M. F.; Power, P. P.; Thorne, A. J. *J. Chem. Soc., Chem. Commun.* **1983**, 639. (d) Çetinkaya, B.; Gümrükçü, I.; Lappert, M. F.; Atwood, J. L.; Rogers, R. D.; Zaworotko, M. J. *J. Am. Chem. Soc.* **1980**, *102*, 2088. (e) Hitchcock, P. B.; Lappert, M. F.; Samways, B. J.; Weinberg, E. L. *J. Chem. Soc., Chem. Commun.* **1983**, 1492.

(8) Brooker, S.; Buijink, J. -K.; Edelmann, F. T. *Organometallics* **1991**, *10*, 25.

(9) All the new organolead compounds here obtained showed satisfactory spectral and analytical data, which are described in the supporting information together with the experimetal details for their preparation. In the following the preparation of diarylplumbylene **6** and its reaction with elemental sulfur are described as representative examples. *Preparation of **6**:* To an ether solution (200 mL) of $[(Me_3Si)_2N]_2Pb$ (**5**), synthesized from $PbCl_2$ (1.39 g, 5.0 mmol) and lithium hexamethyldisilazide (10.0 mmol) according to the reported method,[7a] was added at −40 °C an ether suspension (50 mL) of TbtLi, prepared by the treatment of TbtBr (3.16 g, 5.0 mmol) with *t*-BuLi (1.60 M pentane solution, 6.6 mL, 10.5 mmol) at −40 °C, by means of a transfer tube. To the resulting red-brown suspension was added, after gradual warming to −25 °C, an ether suspension (50 mL) of TipLi (prepared from TipBr (1.28 mL, 5.0 mmol) as in the case of TbtLi) to give the dark purple solution of Tbt(Tip)Pb: (**6**). *Reaction of **6** with elemental sulfur:* To the ether solution of **6** thus prepared was added 3.85 g (15.0 mmol as S_8) of elemental sulfur in portions at room temperature. Immediately after the addition of sulfur the reaction mixture turned yellow, and it was stirred for 10 min. After the filtration of insoluble materials with Celite, the filtrate was concentrated under reduced pressure to afford a brown oil, which was purified by GPLC followed by column chromatography (SiO_2/hexane) to give 3.69 g (68%) of **2** as orange crystals. **2**: mp 189−192 °C dec; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.01 (s, 18H), 0.02 (s, 18H), 0.03 (s, 18H), 1.19 (d, J = 6.9 Hz, 6H), 1.23 (d, J = 6.5 Hz, 12H), 1.32 (s, 1H), 1.66 (s, $^4J_{PbH}$ = 13.1 Hz, 1H), 1.71 (s, $^4J_{PbH}$ = 14.7 Hz, 1H), 2.83 (sept, J = 6.9 Hz, 1H), 3.28 (sept, J = 6.5 Hz, 2H), 6.48 (s, $^4J_{PbH}$ = 65.6 Hz, 1H), 6.59 (s, $^4J_{PbH}$ = 64.8 Hz, 1H), 7.16 (s, $^4J_{PbH}$ = 55.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 0.8 (q), 1.3 (q), 1.6 (q), 24.0 (q), 25.9 (q), 30.5 (d), 32.1 (d), 32.7 (d), 34.3 (d), 39.5 (d, $^3J_{PbC}$ = 70.6 Hz), 124.1 (d, $^3J_{PbC}$ = 89.7 Hz), 128.8 (d, $^3J_{PbC}$ = 87.8 Hz), 145.2 (s, $^4J_{PbC}$ = 20.7 Hz), 149.6 (s), 149.8 (s), 150.7 (s, $^4J_{PbC}$ = 19.5 Hz), 152.4 (s, $^2J_{PbC}$ = 89.7 Hz), 165.2 (s, $^1J_{PbC}$ = 368.6 Hz), 167.6 (s, $^1J_{PbC}$ = 307.6 Hz); ^{207}Pb NMR ($CDCl_3$, 56.4 MHz) δ 313.9; high-resolution FABMS *m/z* calcd for $C_{42}H_{83}{}^{208}PbS_4Si_6$ 1091.3760, found 1091.3604 (MH^+). Anal. Calcd for $C_{42}H_{82}PbS_4Si_6$: C, 46.23; H, 7.57; S, 11.76. Found: C, 46.25; H, 7.70; S, 12.14.

(10) Among the carbene analogues of heavier group 14 elements, a plumbylene is most difficult to trap, since it easily polymerizes accompanying disproportionation. Attempted reaction of the Lappert plumbylene $[(Me_3Si)_2CH]_2Pb$: with methyl iodide gave no expected insertion product but resulted in the formation of PbI_2.[7a] The successful isolation of the insertion products **8** and **9** in the present reactions is in sharp contrast to the case of the Lappert plumbylene.

(11) δ_{Pb} of $[(Me_3Si)_2CH]_2Pb$: (in benzene-d_6) was reportedly +9110 relative to external Me_4Pb: Wrackmeyer, B.; Horchler, K.; Zhou, H. *Spetctrochim. Acta* **1990**, *46A*, 809. ^{207}Pb NMR resonances of the heteroatom-substituted plumbylenes appear in a rather upfield region (δ_{Pb} +4916 for $[(Me_3Si)_2N]_2Pb$: (in benzene-d_6) and +4260 for $^tBuNSiMe_2N(^tBu)Pb$: (in toluene-d_8)). (a) Wrackmeyer, B. *J. Magn. Reson.* **1985**, *61*, 536. (b) Stader, C.; Wrackmeyer, B. *J. Magn. Reson.* **1987**, *72*, 544. For the ^{207}Pb NMR resonance of bis[2,4,6-tris(trifluoromethyl)phenyl]plumbylene, see ref 8.

(12) We have recently reported the formation and several reactions of bis(2,4,6-triisopropylphenyl)plumbylene (**10**), which was found to be stable only below −40 °C: Shibata, K.; Tokitoh, N.; Okazaki, R. *Tetrahedron Lett.* **1993**, *34*, 1495.

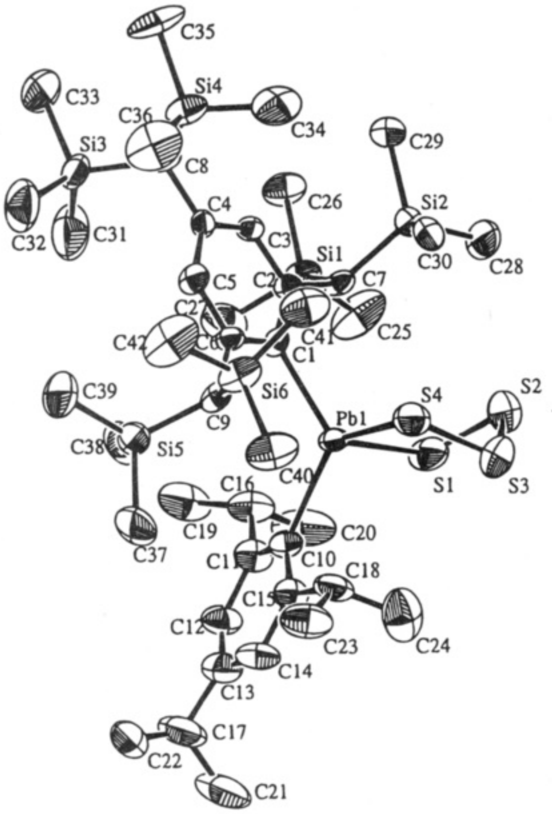

Figure 1. ORTEP drawing of Tbt(Tip)PbS_4 (**2**) with thermal ellipsoid plot (30% probability). Selected bond lengths (Å) and angles (deg): Pb(1)–S(1), 2.553(4); Pb(1)–S(4), 2.564(5); Pb(1)–C(1), 2.28(1); Pb(1)–C(10), 2.29(1); S(1)–S(2), 2.058(8); S(2)–S(3), 2.011(9); S(3)–S(4), 2.020(7); S(1)–Pb(1)–S(4), 92.7(2); S(1)–Pb(1)–C(1), 122.2(3); S(1)–Pb(1)–C(10), 97.5(3); S(4)–Pb(1)–C(1), 97.7(3); S(4)–Pb(1)–C(10), 120.5(4); C(1)–Pb(1)–C(10), 123.6(5); Pb(1)–S(1)–S(2), 99.6(2); S(1)–S(2)–S(3), 103.5(3); S(2)–S(3)–S(4), 102.4(3); Pb(1)–S(4)–S(3), 100.7(3).

formations of their tetrathiaplumbolane rings have almost half-chair geometry in contrast to the previously reported tetrachalcogenolanes **1** containing a group 14 element, the MS_4 rings of which were all found to have highly distorted half-chair (*i.e.*, nearly envelope) conformations.[2,15]

In Figure 1 is shown an ORTEP drawing of **2** together with some selected bond lengths and angles. The central two sulfur atoms, S(2) and S(3), in the PbS_4 ring lie at almost equal distances (0.60 Å for S(2) and 0.63 Å for S(3)) on both sides of the plane that contains the central lead atom and the two coordinated sulfur atoms S(1) and S(4).[11] Since the bond lengths between the central lead atom and the surrounding four atoms (two ipso carbons and two sulfur atoms in α-positions) are longer than those for the other group 14 element analogues of tetrathiolanes **1**, the conformation of the tetrathiaplumbolane ring is considered to be less affected by the bulky substituents than those of the other group 14 element analogues. It is quite interesting that the borderline for such noticeable conformational change lies between the tin and lead systems.

Since the plumbylenes and tetrathiaplumbolanes here obtained are potentially good precursors for the synthesis of plumbanethiones, a novel class of lead–sulfur double-bond compounds, as in the cases of other group 14 element analogues,[4] investigation on their further transformation is currently in progress.

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Supporting Information Available: Text giving experimental details for the preparation of **2**–**12** together with their spectral and analytical data and tables of crystal data and structural refinement details, positional and thermal parameters, and bond lengths and angles for **2** and **4** (68 pages). Ordering information is given on any current masthead page.

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(13) Crystal data for **2**: $C_{42}H_{82}PbS_4Si_6$, $M_r = 1091.06$, triclinic, space group $P\bar{1}$, $a = 11.653(6)$ Å, $b = 24.207(4)$ Å, $c = 10.690(2)$ Å, $\alpha = 98.26(1)°$, $\beta = 107.39(2)°$, $\gamma = 79.54(2)°$, $V = 2817(3)$ Å^3, $Z = 2$, $D_c = 1.286$ g cm^{-3}, $\mu = 33.10$ cm^{-1}, R (R_w) = 0.056 (0.053). Crystal data for **4**: $C_{30}H_{46}PbS_4$, $M_r = 742.13$, orthorhombic, space group $Pna2_1$, $a = 22.875(6)$ Å, $b = 14.26(1)$ Å, $c = 10.351(7)$ Å, $\alpha = \beta = \gamma = 90°$, $V = 3377(6)$ Å^3, $Z = 4$, $D_c = 1.460$ g cm^{-3}, $\mu = 52.89$ cm^{-1}, R (R_w) = 0.048 (0.049). The intensity data were collected on a Rigaku AFC5R diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,69$ Å). The structures were solved by direct methods with *SHELXS-86*.[14] All non-hydrogen atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement was based on 4211 (**2**) and 2139 (**4**) observed reflections ($I > 3.00\sigma(I)$) and 478 (**2**) and 315 (**4**) variable parameters, respectively. Full details for the crystallographic analysis of **2** and **4** are described in the supporting information.

(14) Sheldrick, G. M. *SHELXS-86*; University of Göttingen: Göttingen, Germany, 1986.

(15) The central two sulfur atoms in the MS_4 ring of the analogous tetrathiolanes containing a group 14 element, Tbt(Ar)MS_4 (**1**; M = Si, Ge, Sn), are considerably apart from their M–S(1)–S(4) planes (0.21 and 1.02 Å for **1a** (M = Si, Ar = Mes), 0.26 and 0.99 Å for **1b** (M = Ge, Ar = Mes), and 0.31 and 0.93 Å for **1c** (M = Sn, Ar = Mes)).

(16) Also in the case of **4** the central two sulfur atoms S(2) and S(3) in the PbS_4 ring lie at about the same distances (0.59 Å for S(2) and 0.68 Å for S(3)) from the Pb(1)–S(1)–S(4) plane.