Synthesis and X-ray Crystal Structure of Bis{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}dibromoplumbane: The First Monomeric Diorganodihaloplumbane in the Crystalline State

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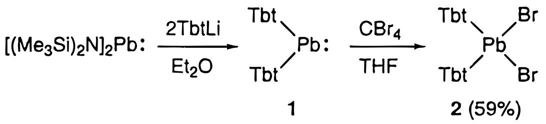
*Summary: Reaction of a plumbylene Tbt_2Pb: (**1**) with carbon tetrabromide in THF gave the first crystallographically characterized dibromoplumbane Tbt_2PbBr_2 (**2**) bearing two 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (Tbt) groups. The X-ray crystallographic analysis revealed that **2** has a monomeric structure with a distorted tetrahedral lead center.*

Diorganodihaloplumbanes are one of the most important and fundamental compounds in the organic chemistry of lead.[1] Although they have been known for many years, very little has been studied about their structures. Diphenyldihaloplumbanes Ph_2PbX_2 (X = Cl, Br, and I) have been reported to have a polymeric structure from vibrational spectoscopic analysis,[2] but the X-ray crystallographic structure of diorganodihaloplumbanes is known only for Ph_2PbCl_2,[3] which indicates the presence of symmetrical chlorine bridgings giving rise to polymeric chains of octahedrally coordinated lead atoms. There have been no reports of the X-ray crystallographic analysis for the monomeric diorganodihaloplumbanes with a tetrahedral lead center, in contrast to the well-known tetrahedral counterparts of silicon, germanium, and tin.[1c]

We have been studying the synthesis and isolation of various kinds of highly reactive chemical species, which tend to dimerize or polymerize, as stable monomeric compounds by taking advantage of steric protection due to the 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl group (denoted as Tbt hereafter).[4] We recently succeeded in the kinetic stabilization of divalent organolead species, i.e. plumbylenes, by introduction of the Tbt group and another bulky group on the lead atom.[5] There have been only few reports on the reactivities of plumbylenes, although they are expected to be potentially useful for the synthesis of various organolead compounds.[6] In the course of our study on the reactions of plumbylenes, we have found that a plumbylene Tbt_2Pb: (**1**) reacts with an excess amount of carbon tetrabromide to give an extremely hindered dibromoplumbane, Tbt_2PbBr_2 (**2**). Here, we present the synthesis and X-ray crystallographic analysis of the dibromoplumbane **2**, which is the first example of a crystallographically characterized monomeric diorganodihaloplumbane.

Scheme 1



Results and Discussion

We recently reported the synthesis of plumbylenes Tbt(Ar)Pb: [Ar = 2,4,6-triisopropylphenyl (Tip) or 2,4,6-tris(trimethylsilylmethyl)phenyl (Ttm)] by sequential substitution of $Pb[N(SiMe_3)_2]_2$ with TbtLi and ArLi.[5] The plumbylene Tbt_2Pb: (**1**) bearing two Tbt groups on a lead atom was synthesized by almost the same procedure, though the substitution reaction required a higher temperature (−10 °C) than for those plumbylenes (−40 °C) (Scheme 1). Plumbylene **1** is stable at room temperature under an argon atmosphere, though sensitive to the air and moisture. The reaction of **1** with an excess amount of carbon tetrabromide in THF gave dibromoplumbane **2** in a moderate yield (59%). This is in a remarkable contrast with the reaction of methyl iodide with plumbylenes Tip_2Pb:, Tbt(Tip)Pb:, and Tbt(Ttm)Pb:, which gives the carbon−iodine insertion products,[5, 6] or that with a plumbylene $[(Me_3Si)_2CH]_2Pb$: , which gives lead diiodide.[7] Dibromoplumbane **2** can be purified even by silica gel chromatography and is stable in the open air. In the solid state, **2** is stable to the light, though slightly sensitive in solution, especially in THF, giving TbtH. It is readily soluble in common organic solvents such as THF, ether, chloroform, dichloromethane, and toluene, but hardly soluble in ethanol, hexane, and ethyl acetate.

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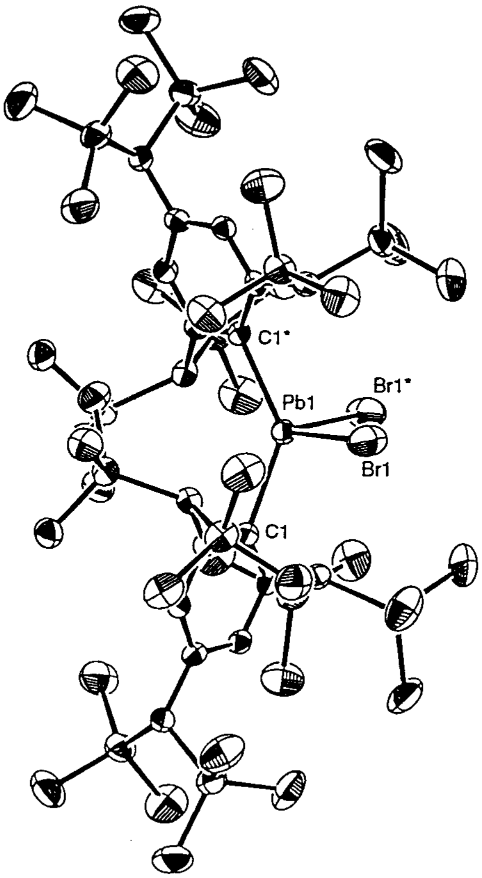

Figure 1. ORTEP drawing of Tbt_2PbBr_2 (**2**) with thermal ellipsoid plots (30% probability). Selected bond lengths (Å) and angles (deg): Pb−C(1) 2.274(6), Pb−Br(1) 2.623(1); C(1)−Pb−C(1*) 135.8(3), C(1)−Pb−Br(1) 95.4(2), C(1)−Pb−Br(1*) 114.4(2), Br(1)−Pb−Br(1*) 95.29(7).

Diorganodibromoplumbanes are generally synthesized by bromination of tetravalent organolead compounds with brominating reagents, such as bromine and hydrogen bromide.[1] The synthesis of **2** is the first example where a dibromoplumbane was synthesized by oxidative bromination of a plumbylene. The reaction mechanism is most likely explained by a two times repetition of the bromine radical abstraction process, as has been shown in the reaction of dimethylgermylene with halocarbons.[8]

Dibromoplumbane **2** showed satisfactory spectral and analytical data. The ^1H and ^{13}C NMR spectra indicated that the two bulky Tbt groups in **2** are equivalent in solution in spite of their steric hindrance. The molecular structure of **2** was finally determined by X-ray crystallographic analysis. This is the first example of a crystallographically characterized diorganodibromoplumbane. The ORTEP drawing of **2** is shown in Figure 1. The lead atom is bound to two Tbt groups and two bromine atoms with a geometry best described as distorted tetrahedral. The two Tbt groups and two bromine atoms are both equivalent in the crystal.

The Pb−C bond, 2.274(6) Å, is notably longer than that [2.19(3) Å] in tetrahedrally coordinated Ph_4Pb[9] and that [2.12(2) Å] in octahedrally coordinated Ph_2PbCl_2[3] and slightly longer than the sum of the covalent radii of Pb and C, 2.23 Å,[10] suggesting steric repulsion between two Tbt groups. The Pb−Br bond length [2.623(1) Å] is shorter than those in Ph_3PbBr [2.852(1) Å][11] and tris{2-[3,5-bis(1,1-dimethylethyl)phenyl]-2-methylpropyl}bromoplumbane [2.656(7) Å][12] and in the range of those [2.60−2.82 Å] in $(Ph_2PbBr)_4C$.[13] This value slightly exceeds the sum of the covalent radii of the two atoms, 2.60 Å,[10] suggesting that the Pb−Br bond in **2** is not ionic but covalent, as has been seen in the other group 14 element analogues. This is the first successful isolation of a compound carrying two of the very bulky Tbt groups attached geminally on one element. Since we have been unable to synthesize such a type of compound in the case of the other group 14 elements, it is conceivable that the long Pb−C bonds enable the two Tbt groups to bind to one element for a steric reason.

The nearest distance between intermolecular lead and bromine atoms is 9.664(1) Å, showing the absence of intermolecular contacts which have sometimes been seen in triorganolead halides[11,13] and Ph_2PbCl_2.[3]

The angles of C(1)−Pb−C(1*) [135.8(3)°] and C(1)−Pb−Br(1*) [114.4(2)°] are larger, and those of Br(1)−Pb−Br(1*) [95.29(7)°] and C(1)−Pb−Br(1) [95.4(2)°] are smaller than the usual tetrahedral angle, 109.5°. The lead center is best regarded as distorted tetrahedral rather than octahedral as has been seen in Ph_2PbCl_2.[3] The enlarged C−Pb−C bond angle and Pb−C bond length are most likely interpreted in terms of steric repulsion between two bulky Tbt groups. Thus, we have shown that a diorganodihaloplumbane, which tends to form an octahedral polymer, can be synthesized as a tetrahedral monomer by taking advantage of steric protection due to bulky substituents.

Experimental Section

General Methods. All reactions were carried out under an atmosphere of dry argon. Solvents were dried by standard methods and freshly distilled prior to use. ^1H (500 MHz), ^{13}C (125 MHz), and ^{207}Pb (105 MHz) NMR spectra were recorded on a JEOL α-500 MHz spectrometer at 27 °C. Chemical shifts were measured with tetramethylsilane ($\delta = 0$) for ^1H and ^{13}C NMR and tetramethylplumbane ($\delta = 0$) for ^{207}Pb NMR as external standards, respectively. Preparative HPLC was performed on an LC-908 (Japan Analytical Industry Co., Ltd.) equipped with JAI-gel 1H and 2H columns (eluent: toluene). High-resolution mass spectral data were obtained on a JEOL SX-102 mass spectrometer. The melting point was determined by differential scanning calorimetry using a SHIMADZU DSC-50 differential scanning calorimeter. Elemental analyses were carried out at the Microanalytical Laboratory of Department of Chemistry, Faculty of Science, The University of Tokyo. 1-Bromo-2,4,6-tris[bis(trimethylsilyl)methyl]benzene (TbtBr)[14] and bis[*N*,*N*-bis(trimethylsilyl)amino]lead(II)[15] were prepared according to procedures reported in the literature. Carbon

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tetrabromide was purchased from Wako Pure Chemical Ind., Ltd., and used as such.

Synthesis of Tbt_2PbBr_2, (2). To an ether suspension (25 mL) of TbtLi prepared from TbtBr (1.58 g, 2.50 mmol) and *t*-BuLi (1.60 M in pentane; 1.60 mL, 2.05 equiv) at −40 °C was added slowly an ether solution (50 mL) of bis[*N*,*N*-bis(trimethylsilyl)amino]lead(II) (1.32 g, 2.50 mmol) at −30 °C. After further stirring of the red reaction mixture for 2 h at −30 °C, an ether suspension (25 mL) of TbtLi (2.50 mmol), prepared in a way similar to the above, was slowly added to the reaction mixture at −10 °C. After further stirring of the reaction mixture for 1 h at −10 °C, the reaction mixture turned green-blue. After further stirring of the reaction mixture for 1 h at 25 °C, the volatile substances were removed under reduced pressure. After 25 mL of THF was added, the solution was stirred at 25 °C for 30 min, and then carbon tetrabromide (2.49 g, 7.50 mmol) was added to the reaction mixture at 25 °C. After the reaction mixture was stirred for 3 min, insoluble materials were filtered out through Celite. After removal of the volatile substances under reduced pressure, the residue was subjected to HPLC to yield bis{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}dibromoplumbane (**2**) (2.19 g, 59%). **2**: mp 139.4 °C dec; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.08 (s, 72H), 0.20 (s, 36H), 1.33 (s, 2H), 1.95 (s, 2H), 3.77 (s, 2H), 6.45 (s, 2H), 6.66 (s, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 1.06 (q), 1.28 (q), 2.07 (q), 3.01 (q), 3.14 (q), 28.40 (d), 30.51 (d), 31.51 (d), 126.30 (d), 130.62 (d), 145.16 (s), 147.66 (s), 150.15 (s), 167.21 (s); ^{207}Pb NMR ($CDCl_3$, 105 MHz) δ −83. HRMS (FAB): found, *m*/*z* 1390.5555; calcd for $C_{54}H_{119}{}^{79}Br^{208}PbSi_{12}$, $[M - Br + H]^+$, 1390.5493. Anal. Calcd for $C_{54}H_{118}Br_2PbSi_{12}$: C, 44.08; H, 8.08; Br, 10.86. Found: C, 43.82; H, 8.14; Br, 10.67.

X-ray Data Collection and Structure Refinement of Tbt_2PbBr_2 (2). Single crystals of **2** were grown by the slow evaporation of its saturated solution in ethanol and dichloromethane at room temperature. Crystal data for **2**: $C_{54}H_{118}PbBr_2Si_{12}$, fw = 1471.56, monoclinic, space group *C*2/c, $a = 25.49(1)$ Å, $b = 11.23(1)$ Å, $c = 26.74(2)$ Å, $\beta = 91.01(5)°$, $V = 7656(8)$ Å^3, $Z = 4$, $D_c = 1.276$ g cm^{-3}, μ(Mo Kα) = 34.71 cm^{-1}, $F(000) = 3048$. A yellow prismatic crystal of **2** having dimensions of 0.50 × 0.50 × 0.40 mm was mounted on a glass fiber. The data set was collected on a Rigaku AFC5R diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,69$ Å) at 296 K and a rotating anode generator. The structure was solved by direct methods with SHELXS-86.[16] The intensities were corrected for Lorentz and polarization effects. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on 3830 observed reflections ($I > 3.00\sigma(I)$) and 312 variable parameters and converged (largest parameter was 0.02 times its esd) at R (R_w) = 0.043 (0.037) with a GOF = 1.28. All calculations were performed using the TEXSAN crystallographic software package of the Molecular Structure Corp. Atomic coodinates, bond lengths and angles, and thermal parameters have been deposited at Cambridge Crystallographic Data Centre.

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Supporting Information Available: Text giving experimental details of the crystallographic study, tables of complete crystal and refinement data, bond lengths and angles, and positional and thermal parameters for **2**, and the packing view along the *b* axis and a drawing showing the atomic numbering of **2** (26 pages). Ordering information is given on any current masthead page.

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