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Synthesis, Structure, and Reactivity of Kinetically Stabilized Divalent Organolead Compounds (Plumbylenes)

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Divalent organolead compounds (plumbylenes; Tip_2Pb (**6**; Tip = 2,4,6-triisopropylphenyl) and Tbt(R)Pb (**7a**, R = Tbt; **7b**, R = Ttm; **7c**, R = Tip; **7d**, R = Dis; Tbt = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl, Ttm = 2,4,6-tris[(trimethylsilyl)methyl]phenyl, and Dis = bis(trimethylsilyl)methyl)) were synthesized by taking advantage of kinetic stabilization afforded by bulky substituents and characterized by UV/vis and ^{207}Pb NMR spectroscopy. X-ray structural analysis revealed that plumbylene **7a** has a V-shaped, monomeric structure. Reactions of these plumbylenes with methyl iodide, carbon tetrabromide, diphenyl disulfide, diphenyl diselenide, and elemental sulfur are described. New methods for the synthesis of plumbylenes from tetravalent organolead compounds, by reductive debromination of dibromoplumbanes and exhaustive desulfurization of tetrathiaplumbolanes, were developed.

Introduction

Remarkable progress has been made in the chemistry of divalent organic compounds of silicon, germanium, and tin, R_2M (M = Si, Ge, Sn), the heavier homologues of carbenes, in recent decades.[1] Although these compounds had once been thought to exist only as highly reactive intermediates, examples of stable R_2M compounds have been reported in recent years. However, divalent organolead compounds (plumbylenes), the heaviest carbene analogues, are less well-known. They usually occur as reactive intermediates in the preparation of plumbanes R_4Pb and polymerize and undergo disproportionation in the absence of suitable stabilizing groups on the lead atom.[2]

Dicyclopentadienyllead(II) compounds, formally also plumbylenes, have been known since 1956.[3] Since dicyclopentadienyllead(II) compounds are stabilized by η^5-coordination of cyclopentadienyl ligands, they are not the congeners of carbenes.

The first stable diaminoplumbylene, $[(Me_3Si)_2N]_2Pb$ (**1**), was synthesized by Lappert and co-workers in 1974.[4] Other stable plumbylenes with heteroatom substituents, such as phosphanyl and silyl groups, bonded to the lead atom have also been reported.[5,6] The electronic or photoelectron spectra of these compounds indicate that their frontier orbitals were perturbed by their heteroatom substituents to such an extent that they are different from those of an intrinsic singlet carbene analogue.

A few stable heteroleptic plumbylenes are also known. They form oligomers in most cases,[7−9] but we recently reported a stable aryl(arylthio)plumbylene which exists in monomeric form.[10] Another monomeric and heteroleptic plumbylene is known, but this is not a two-coordinate but rather three-coordinate divalent organolead compound.[11]

A few plumbylenes bearing only carbon substituents have also been reported. Some of them, however, are stabilized by intramolecular coordination of the lone pair of a donor group in the organic substituent, thus giving

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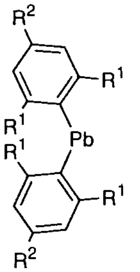
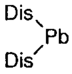
the lead a coordination number greater than 2. For example, an X-ray diffraction study of the first stable diarylplumbylene R^f_2Pb (**2**; R^f = bis[2,4,6-tris(trifluoromethyl)phenyl]) showed that four CF_3 fluorine atoms were coordinated to the lead atom.[12] Four-coordinate divalent organolead compounds were also reported recently,[13−15] in which intramolecular coordination of nitrogen atoms is responsible for their stability. Similar interactions were also observed in the first alkylarylplumbylene.[9]

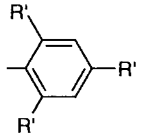


2 $R^1 = R^2 = CF_3$
4 R^1 = 2,4,6-$Me_3C_6H_2$, R^2 = H
5 $R^1 = R^2 = CMe_3$



3
Dis = $CH(SiMe_3)_2$

Because of such intramolecular coordination by heteroatoms these diorganolead compounds may not show the intrinsic nature of plumbylenes in terms of their physical properties and reactivities. Kinetically stabilized plumbylenes bearing only organic substituents that do not contain donor groups are scarce, and their structures and reactivities are almost unexplored. The first dialkylplumbylene, Dis_2Pb (**3**; Dis = bis(trimethylsilyl)methyl), was obtained in only 3% yield, and its structure was not determined by X-ray crystallographic analysis.[16] Another dialkylplumbylene with the lead atom in a seven-membered-ring system was synthesized and crystallographically characterized recently.[17] There are only two examples of structurally characterized two-coordinated diarylplumbylenes: [2,6-(mesityl)$_2C_6H_3$]$_2$Pb (**4**), which bears bulky terphenyl substituents to provide steric stabilization,[18] and R_2Pb (R = 2-*tert*-butyl-4,5,6-Me_3C_6H).[9]



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

Dis = $CH(SiMe_3)_2$

All of the stable plumbylenes reported to date have been synthesized by nucleophilic substitution of a lead(II) compound.[4−9,11−18] Other divalent group 14 element compounds have been prepared by various other methods from tetravalent precursors.[1] It seemed desirable, therefore, to develop new synthetic methods for plumbylenes other than those based on Pb(II) precursors.

Little is known about the reactivity of R_2Pb-type plumbylenes. A few reactions of Dis_2Pb (**3**) have been reported; it reacts with $Mo(CO)_6$ to give the complex $Dis_2PbMo(CO)_5$, but it gives no adducts in attempted reactions with methyl iodide, hydrogen chloride, or DisCl.[16] Another example is the reaction of diarylplumbylene R^f_2Pb (**2**) with the arenethiol R^fSH, affording the bis(arylthio)plumbylene $(R^fS)_2Pb$.[12]

We previously reported some kinetically stabilized diarylplumbylenes in preliminary communications.[19,20] We describe here the full details of this work: development of new synthetic methods, spectroscopic properties, crystal structure, and reactivities of these diaryl- and alkylarylplumbylenes. The following bulky substituents were used: Tbt = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl, Ttm = 2,4,6-tris[(trimethylsilyl)methyl]phenyl, Tip = 2,4,6-triisopropylphenyl, and Dis = bis(trimethylsilyl)methyl.

Results and Discussion

Synthesis. (a) From Lead(II) Amide. Since our attempted synthesis of the diarylplumbylene Mes^*_2Pb (**5**; Mes* = 2,4,6-tri-*tert*-butylphenyl) resulted in the formation of an unexpected rearranged product,[21,22] we tried to synthesize the less hindered diarylplumbylene Tip_2Pb (**6**) by the sequential nucleophilic substitution of a divalent lead compound with TipLi. Lead(II) amide **1** was selected as a starting material because of its stability and good solubility in organic solvents together with the low nucleophilicity of the resulting lithium hexamethyldisilazide with respect to the plumbylene produced. The addition of TipLi to a diethyl ether solution of lead(II) amide **1** at −40 °C afforded the less hindered plumbylene Tip_2Pb (**6**), the ether solution of which was intensely purple (Scheme 1).[19,20,23]

More hindered plumbylenes Tbt(R)Pb (R = Ttm, Tip, Dis; **7b**−**d**) also were prepared by essentially the same method, addition of 1 molar equiv of TbtLi to **1** at −40 °C, followed by addition of 1 molar equiv of RLi in ether at −30 °C.[20]

Plumbylene Tbt_2Pb (**7a**) was prepared similarly. However, the second step required a higher reaction

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[23] After we had finished writing this paper, Weidenbruch and coworkers very recently reported that the reaction of TipMgBr with $PbCl_2$ at −110 °C gave the first stable diplumbene, $Tip_2Pb{=}PbTip_2$: Stürmann, M.; Saak, W.; Marsmann, H.; Weidenbruch, M. *Angew. Chem., Int. Ed.* **1999**, *38*, 187.

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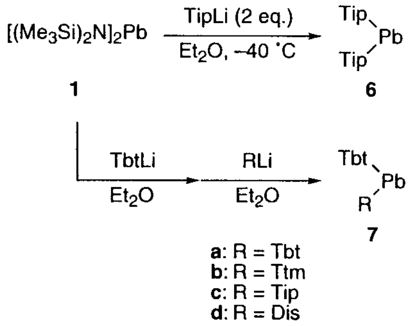
Scheme 1



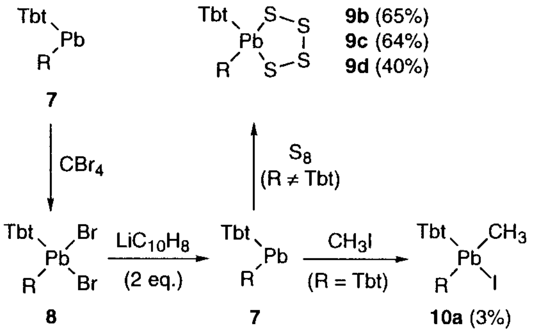
temperature (−10 °C). It is noteworthy that the introduction of two Tbt groups on the same element was achieved for the first time in the case of the lead compound. We were unable to prepare analogous Tbt$_2$M compounds of silicon, germanium, and tin despite much effort, very likely because the larger lead atom allows introduction of two such large substituents. This preparation of **7a** makes clear that in the synthesis of Tbt(R)Pb the initial addition of TbtLi should be effected below −10 °C; otherwise, some **7a** might be formed as a second product.

These kinetically stabilized plumbylenes **6** and **7b**−**d** are sensitive to both air and moisture, but we succeeded in the isolation of the pure symmetrically substituted plumbylene **7a**. It was synthesized as described above, and the solvent was changed to hexane after evaporation of ether in vacuo. Removal of insoluble materials by passing the crude hexane solution through glass wool, followed by repeated recrystallization from hexane in an inert-atmosphere box, allowed the isolation of plumbylene **7a** in 40% yield as blue crystals. Plumbylene **7a** also was synthesized from lead(II) chloride (39%). Plumbylene **7a** is stable at room temperature under argon both in the crystalline state and in solution; it is stable in benzene-d_6 at 80 °C for 42 h without any appreciable change but decomposes in benzene-d_6 at 100 °C within 48 h, giving quantitatively TbtD and lead metal.

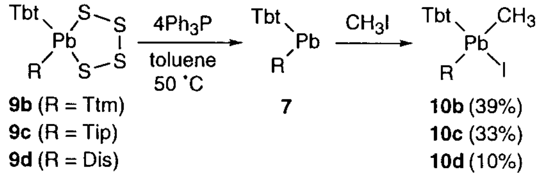
(b) From Tetravalent Organolead Compounds. Although divalent group 14 element compounds containing Si, Ge, and Sn have been synthesized by various methods from tetravalent derivatives as mentioned earlier, no stable plumbylenes have been synthesized from tetravalent organolead compounds.

Since we previously succeeded in generating stable overcrowded germylenes and stannylenes by the reductive debromination of the corresponding dibromogermane and dibromostannane, respectively, with lithium naphthalenide,[24] dibromoplumbanes **8** were expected to be suitable precursors for the corresponding plumbylenes **7**. The reaction of dibromoplumbanes **8b**−**d**, prepared by the reaction of **7** with carbon tetrabromide (see Scheme 2), with 2 equiv of lithium naphthalenide at low temperature followed by treatment with an excess of elemental sulfur gave tetrathiaplumbolanes **9** in moderate yields as expected. The successful formation of **9** evidently indicates the generation of the corresponding plumbylenes **7** as intermediates in these reactions.

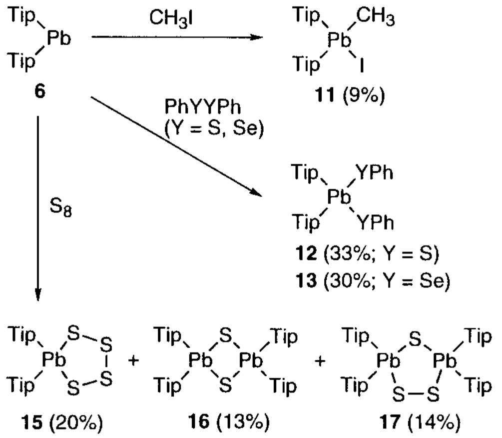
Scheme 2



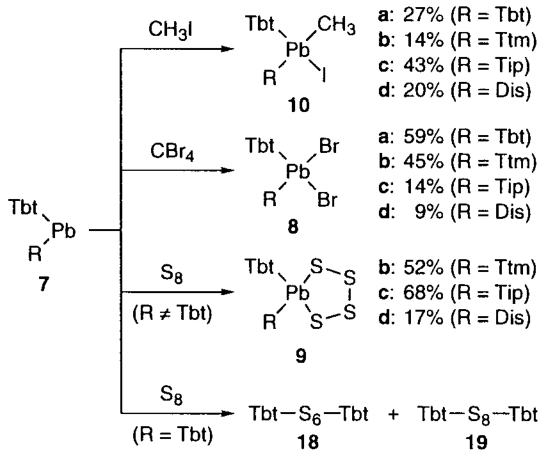
Scheme 3



Scheme 4



Scheme 5



Since the reaction of plumbylene **7a** with elemental sulfur did not provide the expected adduct, tetrathiaplumbolane **9a**, methyl iodide was added after treatment of **8a** with lithium naphthalenide in the dark to verify the generation of plumbylene **7a**. As will be discussed later (Scheme 5), methyl iodide can trap **7a** to give insertion product **10a**. Although **10a** was obtained in this experiment, the yield was very low, probably because of the extreme instability of the **8a** intermediate in THF.[25]

Table 1. Spectroscopic Data of Plumbylenes Tbt(R)Pb (7)

Tbt(R)Pb	color[a]	λ_{max}/nm	$\delta(^{207}Pb)$[b]
Tbt_2Pb	blue	610	9751
Tbt(Ttm)Pb	violet	560	8873
Tbt(Tip)Pb	purple	550	8888
Tbt(Dis)Pb	purple	531	8884

[a] In hexane. [b] In toluene-d_8.

Tetrathiaplumbolanes **9** were also expected to be plumbylene precursors. We previously showed that overcrowded stannylenes can be formed by exhaustive desulfurization of the corresponding tetrathiastannolanes with an excess of a tertiary phosphine.[26] Thus, when a toluene solution of tetrathiaplumbolane **9** was reacted with 4 equiv of triphenylphosphine at 50 °C, the resulting mixture turned violet or purple, suggesting the formation of plumbylene **7** (Scheme 3). The formation of **7** was confirmed by a trapping reaction with methyl iodide, affording the corresponding iodoplumbanes **10** in low to moderate yields. The formation of **7** was also confirmed by the extremely low field chemical shifts in the ^{207}Pb NMR spectra (see Table 1).

Spectroscopic Properties. The characterization of plumbylenes **7** was performed by electronic and ^{207}Pb NMR spectroscopy. Each of the four **7** species has its own characteristic intense color. The colors and spectroscopic data of plumbylenes are summarized in Table 1. The absorption maxima of **7** are most likely attributable to the n−p transition of plumbylenes. In ^{207}Pb NMR spectra, characteristic broad signals due to the central lead atoms are observed as a singlet at extremely low field, which are unambiguously attributable to the kinetically stabilized monomeric plumbylenes. These chemical shift values are rather close to those of other kinetically stabilized monomeric dialkylplumbylenes(δ 10 050 and 9110).[17,27] These values are much greater than those of plumbylenes in which the lead has a coordination number greater than 2 (δ 1981−4878)[7,12−15] and diaminoplumbylene (δ 4916).[27] Since diarylplumbylene **4** (δ 3870) bearing bulky terphenyl substituents resonates at much higher field than **7** and other kinetically stabilized plumbylenes,[18] there might be some interaction between the π electrons of the mesityl rings and the vacant p orbital on the lead atom in **4**.

Reactivities. The successful formation of the kinetically stabilized plumbylenes **6** and **7** prompted us to examine their reactivities, because very little is known about the reactivities of plumbylenes to date. Since Lappert and co-workers have reported that an attempted reaction of dialkylplumbylene **3** with methyl iodide resulted in the formation of lead(II) iodide instead of the expected insertion product,[16] we first investigated the reaction of our plumbylenes with methyl iodide.

The reaction of less hindered plumbylene **6** with methyl iodide resulted in the formation of iodoplumbane **11** (Scheme 4) which can be interpreted in terms of the insertion of plumbylene **6** into the carbon (CH_3)−iodine bond.[19] Formation of lead(II) iodide was not observed. Plumbylene **6** also reacted with diphenyl disulfide and diphenyl diselenide to give adducts **12** and **13**, respectively, very likely by insertion of plumbylene **6** into the chalcogen−chalcogen bonds. These results show that plumbylenes have reactivities similar to those of a carbene.

Reactions of more hindered plumbylenes **7a**−**d** with methyl iodide also gave the corresponding iodoplumbanes **10a**−**d**.[20] On the other hand, we previously reported that the diaryldibromoplumbane was formed instead of an insertion product in the reaction of plumbylene **7a** with an excess of carbon tetrabromide.[25] When plumbylenes **7b**−**d** were treated with an excess of carbon tetrabromide, the corresponding diorganodibromoplumbanes **8b**−**d** were produced in low to moderate yield.

The successful insertion reactions of plumbylene **6** into chalcogen−chalcogen bonds inspired us to examine the reactivities of the plumbylenes with elemental sulfur. The reaction of the less hindered plumbylene **6** with an excess of elemental sulfur afforded 1,2,3,4,5-tetrathiaplumbolane **15** together with two other heterocycles bearing two plumbylene units, 1,3,2,4-dithiadiplumbetane **16** and 1,2,4,3,5-trithiadiplumbolane **17** (Scheme 4).[20] Interestingly, the treatment of **7b**−**d** with elemental sulfur proceeded in a slightly different way, leading to the formation of the corresponding tetrathiaplumbolanes **9b**−**d** as the sole Pb-containing product in moderate yields. The most hindered plumbylene **7a** behaved in quite a different way under similar reaction conditions, giving two polysulfides, Tbt-S_6-Tbt (**18**; 25%) and Tbt-S_8-Tbt (**19**; 25%), together with TbtH (19%) instead of the expected tetrathiaplumbolane **9a**. This difference most likely results from the steric hindrance due to the two Tbt groups around the lead atom, which are too large to provide the space required to form a Pb-containing polysulfide ring. The formation mechanism of polysulfides **18** and **19** is not clear at present. It is interesting that the bulkiness of a plumbylene plays an important role in controlling the reaction pathways.

It should be noted that tetrathiaplumbolanes **15** and **9b**−**d** here described are the first examples of novel Pb-containing cyclic polysulfides. They are crystalline compounds stable in the open air and can be separated by routine silica gel chromatography. The molecular structures of **15** and **9c** were established by X-ray crystallographic analysis, the results of which have already been reported.[20]

X-ray Crystal Structure of 7a. Only three examples have been reported for the crystallographic structures of kinetically stabilized plumbylenes,[9,17,18] despite their structural importance. The molecular structure of **7a** was established by X-ray crystallographic analysis (Figure 1). Crystal data for **7a** are summarized in Table 2. Plumbylene **7a** has a V-shaped geometry with the nearest Pb···Pb intermolecular separation of 11.60 Å, indicating the monomeric nature of **7a**.

The structural features of **7a** are fairly different from those of the usual tetravalent organolead compounds. The Pb−C bond length (2.327(13) Å) is notably longer than that (2.19(3) Å) in tetrahedrally coordinated Ph_4Pb[28] as well as the sum of the covalent radii of Pb and C (2.23 Å).[29] Furthermore, the C−Pb−C angle (116.3(7)°)

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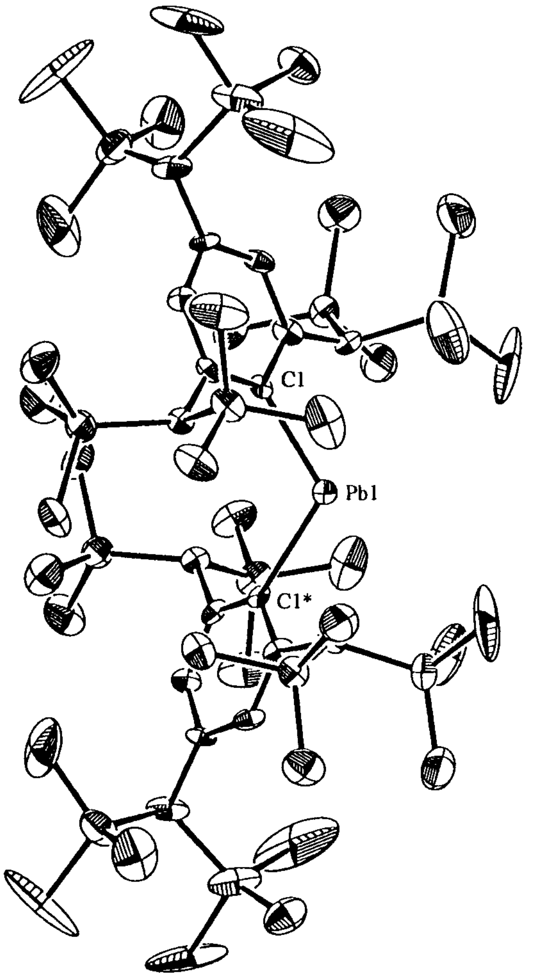

Figure 1. ORTEP drawing of Tbt_2Pb (**7a**) with thermal ellipsoid plot (30% probability). Selected bond length (Å) and angle (deg); Pb(1)−C(1) 2.327(13), C(1)−Pb(1)−C(1*) 116.3(7).

Table 2. Crystallographic Data for 7a

empirical formula	$C_{54}H_{118}PbSi_{12}$
fw	1311.75
cryst size/mm	0.45 × 0.35 × 0.05
temp/K	296
cryst syst	monoclinic
space group	*C*2/*c* (No. 15)
a/Å	29.74(2)
b/Å	11.601(6)
c/Å	22.71(1)
β/deg	97.44(6)
V/Å^3	7768(7)
Z	4
D_{calcd}/g cm^{-3}	1.121
R	0.059
R_w	0.070
goodness of fit	1.50

is much wider than the typical value of a tetravalent compound (109.5°).

In this connection, the results of ab initio calculation on the structure of dimethylplumbylene by Kaupp and Schleyer should be noted.[30] The calculation indicates reduction of C−Pb−C bond angle (97.3°) and elongation of Pb−C bond length (2.323 Å) compared with those for tetramethylplumbane (109.5° and 2.238 Å).[31] The Pb−C bond length calculated for Me_2Pb fits well with the experimental result (2.327(13) Å) of **7a**. Since these structural features may partly be due to the large steric repulsion of two bulky Tbt groups on the lead atom, the structure of **7a** is better compared to that of dibromoplumbane Tbt_2PbBr_2 (**8a**), bearing two Tbt groups on the lead atom, as does **7a**. The angle of C−Pb−C in **7a** (116.3(7)°) is much smaller than that of **8a** (135.8(3)°) despite bearing the same two Tbt ligands on the lead atom.[25] Meanwhile, the Pb−C bond length (2.327(13) Å) in **7a** is longer than that of **8a** (2.274(6) Å). Such structural features are also observed for other stable plumbylenes which have been structurally analyzed; the Pb−C bond lengths of the previously reported diaryl- and dialkylplumbylenes (2.334(12)−2.476(14) Å) are close to that of plumbylene **7a**, while the C−Pb−C bond angle ranges from 88.2(2) to 117.1(2)°.[9,12,14,15,17,18] The degree of its widening may depend on the steric repulsion between the substituents on the lead atom, though it centers around 103°. The C−Pb−C angle in plumbylene **7a** (116.3(7)°) is one of the widest among the reported stable plumbylenes, indicating the extremely large steric repulsion between the two Tbt groups.

Judging from these overall results, the Pb−C bond lengths are longer and the C−Pb−C bond angle is smaller in divalent organolead compounds (plumbylenes) than in the tetravalent organolead compounds. These structural features of plumbylenes may be attributable not only to the steric congestion between the substituents on the lead atom but also to the intrinsic nature of a plumbylene.

Conclusion

We have succeeded in the synthesis of several kinetically stabilized plumbylenes by the nucleophilic substitution of lead(II) amide with the corresponding aryl/alkyllithium reagents. Furthermore, the debromination of dibromoplumbanes and exhaustive desulfurization of tetrathiaplumbolanes also gave the corresponding stable plumbylenes. The last two procedures are new as methods for the preparation of plumbylenes from the tetravalent organolead compounds and are useful for the synthesis of overcrowded plumbylenes. Plumbylene **7a** exhibits a monomeric, V-shaped molecular structure, as predicted by theoretical calculations. The reaction of plumbylenes thus synthesized with some substrates gave the corresponding oxidation Pb(IV) products, just as in the cases of other divalent group 14 element counterparts. In this study we have shown that stable plumbylenes are good precursors for various kinds of organolead compounds which are otherwise difficult to obtain. These results give new insight into organolead compounds and the properties of the heavier homologues of carbenes. The next target in the future would be the application of a plumbylene to the formation of the novel organolead compounds such as double-bonded compounds between lead and another element.

Experimental Section

All experiments were performed under an argon atmosphere otherwise noted. ^1H (500 MHz), ^{13}C (125 MHz), ^{77}Se (95 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 (δ 0) for ^1H and ^{13}C NMR spectra and tetramethylplumbane (δ 0) for ^{207}Pb NMR spectra as external standards, respectively, and with diphenyl diselenide (δ 480) for ^{77}Se NMR spectra as internal standard.

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[30] Kaupp, M.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1993**, *115*, 1061.

[31] Oyamada, T.; Iijima, T.; Kimura, M. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 2638.

High-resolution mass spectral data were obtained on a JEOL SX-102 mass spectrometer. Electronic spectra were measured on a JASCO U_{best}-50 UV/vis spectrometer. Preparative gel permeation liquid chromatography (GPLC) with a recycling system was performed on an LC-908 (Japan Analytical Industry Co., Ltd.) equipped with JAI-gel 1H and 2H columns (eluent $CHCl_3$ or toluene). All melting points were determined on a Yanaco micro melting point apparatus and are uncorrected. Elemental analyses were carried out at the Microanalytical Laboratory of the Department of Chemistry, Faculty of Science, The University of Tokyo.

Materials. 1-Bromo-2,4,6-tris[bis(trimethylsilyl)methyl]-benzene (TbtBr),[32] 1-bromo-2,4,6-tris[(trimethylsilyl)methyl]-benzene (TtmBr),[33] 1-bromo-2,4,6-triisopropylbenzene (TipBr),[34] and bis[bis(trimethylsilyl)amino]lead(II) ($[(Me_3Si)_2N]_2Pb$, **1**)[4b] were prepared according to procedures reported in the literature. Bis(trimethylsilyl)chloromethane (DisCl) was purchased from Aldrich Chemical Co., Inc. Solvents and methyl iodide were dried by standard methods and freshly distilled prior to use. Carbon tetrabromide was purchased from Wako Pure Chemical Industries, Ltd., and used as such.

Preparation of an Ether Solution of ArLi (Ar = Tbt, Ttm, Tip). To an ether solution (5 mL) of ArBr (0.50 mmol) was added *t*-BuLi (1.60 M pentane solution, 0.66 mL, 1.05 mmol) at −72 °C. The resulting suspension was stirred for 1 h at −72 °C and for 1 h at −40 °C. The resulting solution was used as such in the following reactions with lead compounds.

Preparation of an Ether Solution of DisLi. To a refluxing ether suspension (3 mL) of lithium (31 mg, 4.5 mmol) was added DisCl (0.33 mL, 1.5 mmol), and the reaction mixture was refluxed for 23 h. After the reaction mixture had cooled to room temperature, ether (5 mL) was added, and the excess lithium was filtered through a sintered-glass filter. The resulting solution was used as such in the following reactions with lead compounds.

Preparation of Plumbylene 6. To an ether solution (50 mL) of bis[bis(trimethylsilyl)amino]lead(II) (**1**; 1.32 g, 2.50 mmol) was added slowly an ether solution (25 mL) of TipLi (5.00 mmol) prepared as described above at −40 °C. After it had been stirred for 2 h at −40 °C, the purple reaction mixture was warmed gradually to room temperature. The resulting purple ether suspension of Tip_2Pb (**6**) was used in subsequent reactions.

Preparation of Plumbylene 7a. To an ether solution (50 mL) of **1** (1.32 g, 2.50 mmol) was added slowly an ether solution (25 mL) of TbtLi (2.50 mmol) prepared as described above at −40 °C. After the resulting red-brown reaction mixture had been stirred for 2 h at −30 °C, an ether solution (25 mL) of TbtLi (2.50 mmol), prepared as described above, was added slowly to the reaction mixture at −10 °C. After further stirring for 1 h at −10 °C, the blue reaction mixture was warmed gradually to room temperature. The resulting blue ether suspension of Tbt_2Pb (**7a**) was used in subsequent reactions.

Preparation of Plumbylenes 7b and 7c. To an ether solution (10 mL) of **1** (264 mg, 0.500 mmol) was added at −40 °C an ether suspension (5 mL) of TbtLi, prepared from TbtBr (316 mg, 0.500 mmol) as described above. After the resulting red-brown suspension had been warmed to −25 °C, an ether suspension (5 mL) of TtmLi (prepared from TtmBr (208 mg, 0.500 mmol)) or TipLi (prepared from TipBr (128 mL, 0.500 mmol)) was added to give a violet suspension of Tbt(Ttm)Pb (**7b**) or Tbt(Tip)Pb (**7c**), respectively. After the reaction mixture had been warmed to room temperature, the ether suspension of Tbt(Ttm)Pb (**7b**) or Tbt(Tip)Pb (**7c**) was used in subsequent reactions.

Preparation of Plumbylene 7d. To an ether solution (30 mL) of **1** (797 mg, 1.51 mmol) was added at −40 °C an ether suspension (15 mL) of TbtLi, prepared from TbtBr (984 mg, 1.56 mmol) as described above. After the resulting red-brown suspension had been warmed to −25 °C, an ether solution (8 mL) of DisLi, prepared from DisCl (0.33 mL, 1.51 mmol), was added to give a purple suspension. After the reaction mixture had been warmed to room temperature, the ether suspension of Tbt(Dis)Pb (**7d**) was used in subsequent reactions.

Preparation of Samples of Plumbylene 7 for Electronic Spectroscopy. Plumbylene **7**, prepared from **1** (264 mg, 0.500 mmol) as described above, was evaporated in vacuo to remove volatile components. To the residue was added 10 mL of dry, degassed hexane, and the volatile portion was again removed in vacuo. After repetition of this procedure for solvent exchange four times followed by exhaustive evaporation of hexane, 10 mL of hexane was added to the residue to give a hexane solution of plumbylene **7**. A small amount of the solution (0.25 mL) was transferred to a quartz UV cell ($l = 10$ mm), and hexane was introduced into the UV cell until the total amount of hexane became 3 mL. The electronic spectrum was measured of this solution. Absorption maxima of plumbylenes **7** are summarized in Table 1.

Preparation of ^{207}Pb NMR Samples of Plumbylene 7. Plumbylene **7**, prepared from **1** (264 mg, 0.500 mmol) as described above, was evaporated in vacuo to remove volatile components. To the residue was added 5 mL of dry degassed hexane, and the volatile portion was again removed in vacuo. After repetition of this procedure for solvent exchange four times followed by exhaustive evaporation of hexane, 0.7 mL of toluene-d_8 was added to the residue to give a saturated solution of plumbylene **7**. After insoluble materials were filtered through a sintered-glass filter, the filtrate was transferred to and sealed in a 5 mm i.d. NMR tube with degassing to give the ^{207}Pb NMR sample of plumbylene **7**. Broad signals attributable to the plumbylenes **7** in the ^{207}Pb NMR spectrum are summarized in Table 1.

Synthesis and Isolation of Plumbylene 7a from 1. After removal of the solvent from an ether suspension of plumbylene **7a**, prepared from **1** (531 mg, 1.01 mmol) as described above, hexane (50 mL) was added to the reaction mixture. After the reaction mixture had been filtered through glass wool in the glovebox to remove insoluble material, the filtrate was evaporated under reduced pressure to give a blue solid, recrystallization of which from hexane afforded bis{2,4,6-tris[bis-(trimethylsilyl)methyl]phenyl}plumbylene (**7a**; 529 mg, 40%). **7a**: blue crystals (hexane); mp 165 °C dec; ^{1}H NMR (C_6D_6, 500 MHz) δ 0.27 (s, 36H), 0.31 (s, 36H), 0.37 (s, 36H), 1.46 (s, 2H), 1.52 (s, 2H), 1.56 (s, 2H), 7.60 (s, 2H), 7.64 (s, 2H); ^{13}C NMR (C_6D_6, 125 MHz) δ 1.3 (q), 2.3 (q), 2.6 (q), 31.2 (d), 33.2 (d), 36.1 (d), 132.3 (d), 137.6 (d), 141.4 (s), 143.2 (s), 151.5 (s), 152.9 (s); ^{207}Pb NMR (toluene-d_8, 106 MHz) δ 8971 (br s). Anal. Calcd for $C_{54}H_{118}PbSi_{12}$: C, 49.44; H, 9.07. Found: C, 49.14; H, 8.99.

Synthesis and Isolation of Plumbylene 7a from Lead(II) Chloride. To an ether suspension (40 mL) of lead(II) dichloride (556 mg, 2.00 mmol) was added slowly an ether solution (40 mL) of TbtLi (4.00 mmol) prepared as described above, at 0 °C. After the resulting reaction mixture had been stirred for 1 h at 0 °C, the blue reaction mixture was warmed to room temperature. After removal of the solvent from the ether suspension of plumbylene **7a**, hexane was added to the reaction mixture. The reaction mixture was filtered through glass wool in the glovebox to remove insoluble material, and the filtrate was evaporated under reduced pressure to give a blue solid, recrystallization of which from hexane afforded blue crystals of plumbylene **7a** (1.02 g, 39%), having NMR spectra identical with those previously described.

X-ray Data Collection for Plumbylene 7a. A dark blue platelike crystal of **7a** having dimensions 0.45 × 0.35 × 0.05 mm was mounted in a glass capillary. The data set was

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(32) (a) Auner, A.; Klingebiel, U. In *Synthetic Methods of Organometallic and Inorganic Chemistry*; Herrmann, W. A., Ed.; Georg Thieme Verlag: Stuttgart, Germany, 1996; Vol. 2, p 260. (b) Okazaki, R.; Unno, M.; Inamoto, N. *Chem. Lett.* **1987**, 2293.

(33) Kano, N.; Tokitoh, N.; Okazaki, R. Unpublished results.

(34) Whitesides, G. M.; Eisenhut, M.; Bunting, W. M. *J. Am. Chem. Soc.* **1974**, *96*, 5406.

collected on a Rigaku AFC5R diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.710 69 Å) at 296 K and a rotating-anode generator. The structure was solved by direct methods with SHELXS-86.[35] 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 2384 observed reflections ($I > 3.00\sigma(I)$) and 303 variable parameters and converged (largest parameter shift was 0.05 times its esd) at R (R_w) = 0.059 (0.070) with GOF = 1.50. The crystal data are summarized in Table 2.

Reaction of Plumbylene 6 with Methyl Iodide. After an ether solution (30 mL) of plumbylene **6**, prepared from **1** (264 mg, 0.500 mmol) as described above, was treated with 0.12 mL (2.0 mmol) of methyl iodide at −30 °C, the reaction mixture was warmed to room temperature. After the reaction mixture had been filtered through Celite, the filtrate was evaporated to leave an oil. Purification of the crude oil by preparative GPLC (eluent toluene) afforded iodomethyl{bis(2,4,6-triisopropylphenyl)}plumbane (**11**; 2.7 mg, 9%) as a pale yellow oil, which could not be completely purified because of the instability of the plumbane. **11**: ^{1}H NMR (CDCl$_3$, 500 MHz) δ 1.10 (d, 12H, $^3J_{HH}$ = 6.7 Hz), 1.11 (d, 12H, $^3J_{HH}$ = 6.7 Hz), 1.19 (d, 12H, $^3J_{HH}$ = 6.9 Hz), 2.18 (s, 3H, $^2J_{PbH}$ = 59.7 Hz), 2.82 (sept, 4H, $^3J_{HH}$ = 6.7 Hz), 7.03 (s, 4H, $^4J_{PbH}$ = 48.6 Hz); ^{13}C NMR (CDCl$_3$, 125 MHz) δ 24.0 (q), 24.5 (q), 24.6 (q), 24.9 (q), 34.2 (d), 37.4 (d, $^3J_{PbC}$ = 75.3 Hz), 122.9 (d, $^3J_{PbC}$ = 80.5 Hz), 150.1 (s, $^4J_{PbC}$ = 17.7 Hz), 153.3 (s, $^2J_{PbC}$ = 80.8 Hz), 155.5 (s, $^1J_{PbC}$ = 487.0 Hz); ^{207}Pb NMR (CDCl$_3$, 105 MHz) δ −234 (s); HRMS (FAB) found m/z 629.3617, calcd for $C_{31}H_{49}Pb$ ([M − I]$^+$) 629.3601.

Reaction of Plumbylene 6 with Diphenyl Disulfide. Similarly, the reaction of plumbylene **6**, prepared from **1** (264 mg, 0.500 mmol), with diphenyl disulfide (437 mg, 2.00 mmol) at −40 °C in ether (30 mL) gave bis(phenylthio)bis{(2,4,6-triisopropylphenyl)}plumbane (**12**; 138 mg, 33%) as a yellow oil. **12**: yellow viscous oil; ^{1}H NMR (CDCl$_3$, 500 MHz) δ 0.97 (d, 24H, $^3J_{HH}$ = 6.7 Hz), 1.19 (d, 12H, $^3J_{HH}$ = 7.0 Hz), 2.80 (sept, 4H, $^3J_{HH}$ = 6.7 Hz), 2.81 (sept, 2H, $^3J_{HH}$ = 6.7 Hz), 6.98 (s, 4H, $^4J_{PbH}$ = 57.7 Hz), 7.03 (m, 6H), 7.33 (m, 4H); ^{13}C NMR (CDCl$_3$, 125 MHz) δ 24.0 (q), 24.4 (q), 34.1 (d), 37.6 (d, $^3J_{PbC}$ = 70.3 Hz), 123.2 (d, $^3J_{PbC}$ = 96.1 Hz), 126.7 (d), 127.9 (d), 135.6 (s, $^2J_{PbC}$ = 35.8 Hz), 135.9 (d), 150.4 (s, $^4J_{PbC}$ = 21.4 Hz), 153.4 (s, $^2J_{PbC}$ = 91.3 Hz), 161.2 (s, $^1J_{PbC}$ = 502.5 Hz); ^{207}Pb NMR (CDCl$_3$, 105 MHz) δ 69 (s); HRMS (FAB) found m/z 723.3538, calcd for $C_{36}H_{51}PbS$ ([M − Tip]$^+$) 723.3478.

Reaction of Plumbylene 6 with Diphenyl Diselenide. Similarly, the reaction of plumbylene **6**, prepared from **1** (132 mg, 0.250 mmol), with diphenyl diselenide (312 mg, 1.00 mmol) at −78 °C in ether (30 mL) gave bis(phenylseleno)bis{(2,4,6-triisopropylphenyl)}plumbane (**13**; 69 mg, 30%) as an orange oil. **13**: orange oil; ^{1}H NMR (CDCl$_3$, 500 MHz) δ 0.95 (d, 24H, $^3J_{HH}$ = 6.8 Hz), 1.19 (d, 12H, $^3J_{HH}$ = 6.8 Hz), 2.82 (sept, 6H, $^3J_{HH}$ = 6.8 Hz), 6.94 (s, 4H, $^4J_{PbH}$ = 56.8 Hz), 7.01 (dd, 4H, $^3J_{HH}$ = 7 Hz, $^4J_{HH}$ = 7 Hz), 7.07 (tt, 2H, $^3J_{HH}$ = 7 Hz, $^4J_{HH}$ = 1 Hz), 7.40 (dd, 4H, $^3J_{HH}$ = 7 Hz, $^4J_{HH}$ = 1 Hz); ^{13}C NMR (CDCl$_3$, 125 MHz) δ 24.0 (q), 24.4 (q), 34.4 (d), 37.8 (d, $^3J_{PbC}$ = 70.3 Hz), 123.0 (d, $^3J_{PbC}$ = 86.2 Hz), 127.1 (d), 128.1 (d), 128.7 (s), 137.3 (d), 150.1 (s, $^4J_{PbC}$ = 19.8 Hz), 153.3 (s, $^2J_{PbC}$ = 84.8 Hz), 159.0 (s, $^1J_{PbC}$ = 430.6 Hz); ^{77}Se NMR (CDCl$_3$, 95 MHz) δ 303 (s, $^1J_{PbSe}$ = 1367 Hz);[36] ^{207}Pb NMR (CDCl$_3$, 105 MHz) δ −261 (s, $^1J_{SePb}$ = 1367 Hz); HRMS (FAB) found m/z 771.2933, calcd for $C_{36}H_{51}PbSe$ ([M − Tip]$^+$) 771.2922.

Reaction of Plumbylene 6 with Elemental Sulfur. After an ether solution (30 mL) of plumbylene **6**, prepared from **1** (264 mg, 0.500 mmol), was treated with elemental sulfur (390 mg, 1.52 mmol as S_8) at −40 °C, the reaction mixture was warmed to room temperature. After the reaction mixture had been filtered through Celite, the filtrate was evaporaed to leave a brown solid. Purification of the crude solid by preparative GPLC (eluent CHCl$_3$) followed by silica gel chromatography (hexane/CH$_2$Cl$_2$ 5:1) gave three lead-containing cyclic sulfides, 5,5-bis(2,4,6-triisopropylphenyl)-1,2,3,4,5-tetrathiaplumbolane (**15**; 74.4 mg, 20%), 2,2,4,4-tetrakis(2,4,6-triisopropylphenyl)-1,3,2,4-dithiadiplumbetane (**16**; 42.0 mg, 13%), and 2,2,5,5-tetrakis(2,4,6-triisopropylphenyl)-1,3,4,2,5-trithiadiplumbolane (**17**; 46.3 mg, 14%). **15**: orange yellow crystals (CH$_2$Cl$_2$/ethanol); mp 151−153 °C dec; ^{1}H NMR (CDCl$_3$, 500 MHz) δ 1.16 (d, $^3J_{HH}$ = 6.7 Hz, 24H), 1.20 (d, $^3J_{HH}$ = 6.9 Hz, 12H), 2.83 (sept, $^3J_{HH}$ = 6.9 Hz, 2H), 3.13 (sept, $^3J_{HH}$ = 6.7 Hz, 4H), 7.12 (s, $^4J_{PbH}$ = 58.0 Hz, 4H); ^{13}C NMR (CDCl$_3$, 125 MHz) δ 23.9 (q), 24.8 (q), 34.2 (d), 38.6 (d, $^3J_{PbC}$ = 73.1 Hz), 123.7 (d, $^3J_{PbC}$ = 89.9 Hz), 150.9 (s), 152.9 (s, $^2J_{PbC}$ = 92.4 Hz), 164.6 (s, $^1J_{PbC}$ = 351.8 Hz); ^{207}Pb NMR (CDCl$_3$, 105 MHz) δ 288.6 (s); HRMS (FAB) found m/z 742.2318, calcd for $C_{30}H_{46}PbS_4$ ([M]$^+$) 742.2249. Anal. Calcd for $C_{30}H_{46}PbS_4$: C, 48.55; H, 6.25; S, 17.28. Found: C, 48.54; H, 6.14; S, 17.63. **16**: yellow crystals (CH$_2$Cl$_2$/ethanol); mp 226−228 °C dec; ^{1}H NMR (CDCl$_3$, 500 MHz) δ 1.04 (d, $^3J_{HH}$ = 6.7 Hz, 48H), 1.18 (d, $^3J_{HH}$ = 6.9 Hz, 24H), 2.80 (sept, $^3J_{HH}$ = 6.9 Hz, 4H), 3.50 (sept, $^3J_{HH}$ = 6.7 Hz, 8H), 6.99 (s, $^4J_{PbH}$ = 57.9 Hz, 8H); ^{13}C NMR (CDCl$_3$, 125 MHz) δ 24.0 (q), 24.8 (q), 34.2 (d), 35.9 (d, $^3J_{PbC}$ = 83.9 Hz), 123.1 (d, $^3J_{PbC}$ = 94.6 Hz), 149.8 (s, $^4J_{PbC}$ = 21.1 Hz), 153.8 (s, $^2J_{PbC}$ = 92.6 Hz), 161.5 (s, $^1J_{PbC}$ = 569.2 Hz); ^{207}Pb NMR (CDCl$_3$, 105 MHz) δ 81.6 (s); HRMS (FAB) found m/z 1089.4369, calcd for $C_{45}H_{69}Pb_2S_2$ [M − Tip]$^+$ 1089.4374. Anal. Calcd for $C_{60}H_{92}Pb_2S_2$: C, 55.78; H, 7.18; S, 4.96. Found: C, 55.49; H, 7.01; S, 5.34. **17**: orange crystals (CH$_2$Cl$_2$/ethanol); mp 193−194 °C(dec); ^{1}H NMR (CDCl$_3$, 500 MHz) δ 0.99 (d, $^3J_{HH}$ = 6.6 Hz, 24H), 1.03 (d, $^3J_{HH}$ = 6.6 Hz, 24H), 1.16 (d, $^3J_{HH}$ = 6.9 Hz, 24H), 2.78 (sept, $^3J_{HH}$ = 6.9 Hz, 4H), 3.30 (sept, $^3J_{HH}$ = 6.6 Hz, 8H), 7.01 (s, $^4J_{PbH}$ = 54.9 Hz, 8H); ^{13}C NMR (CDCl$_3$, 125 MHz) δ 23.9 (q), 24.7 (q), 24.9 (q), 34.2 (d), 37.5 (d, $^3J_{PbC}$ = 71.3 Hz), 123.3 (d, $^3J_{PbC}$ = 91.6 Hz), 149.8 (s, $^4J_{PbC}$ = 20.9 Hz), 153.4 (s, $^2J_{PbC}$ = 92.8 Hz), 164.9 (s, $^1J_{PbC}$ = 449.8 Hz); ^{207}Pb NMR (CDCl$_3$, 105 MHz) δ 130.0 (s); HRMS (FAB) found m/z 1121.4084, calcd for $C_{45}H_{69}Pb_2S_3$ ([M − Tip]$^+$) 1121.4094. Anal. Calcd for $C_{60}H_{92}Pb_2S_3$: C, 54.43; H, 7.00; S, 7.27. Found: C, 54.15; H, 6.83; S, 7.22.

Reaction of Plumbylene 7a with Methyl Iodide. Similarly, the reaction of plumbylene **7a**, prepared from **1** (152 mg, 0.288 mmol), with methyl iodide (0.18 mL, 2.9 mmol) at room temperature in THF (4 mL) gave bis{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}iodomethylplumbane (**10a**; 115.0 mg, 27%). **10a**: pale yellow crystals (hexane/ethanol); mp 161.0−165.0 °C dec; ^{1}H NMR (C$_6$D$_6$, 500 MHz) δ 0.24 (s, 27H), 0.26 (s, 36H), 0.38 (s, 18H), 0.44 (s, 18H), 0.50 (s, 9H), 1.28 (s, 2H), 2.46 (s, $^3J_{PbH}$ = 35.2 Hz, 3H), 4.15 (br s, 4H), 6.63 (s, 1H), 6.74 (s, 1H), 6.83 (s, 1H), 6.92 (s, 1H); ^{13}C NMR (CDCl$_3$, 125 MHz) δ 0.6 (q), 1.1 (q), 1.2 (q), 1.5 (q), 2.7 (q), 3.2 (q), 29.6 (d), 30.0 (d), 30.2 (d), 32.3 (q, $^1J_{PbC}$ = 103.5 Hz), 124.2 (d), 125.3 (d), 129.7 (d), 130.3 (d), 142.0 (s), 142.6 (s), 143.1 (s), 143.6 (s), 148.1 (s), 149.9 (s), 150.4 (s), 151.6 (s); ^{207}Pb NMR (CDCl$_3$, 105 MHz) δ −191 (s); HRMS (FAB) found: m/z 1325.6420, calcd for $C_{55}H_{121}{}^{208}PbSi_{12}$ ([M − I]$^+$) 1325.6466. Anal. Calcd for $C_{55}H_{121}IPbSi_{12}$: C, 45.44; H, 8.39. Found: C, 45.57; H, 8.40.

Reaction of Plumbylene 7b with Methyl Iodide. Similarly, the reaction of plumbylene **7b**, prepared from **1** (90 mg, 0.17 mmol), with methyl iodide (0.31 mL, 5.0 mmol) at room temperature in ether gave {2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}iodomethyl[2,4,6-tris(trimethylsilylmethyl)phenyl]plumbane (**10b**; 28.6 mg, 14%). **10b**: yellow crystals (CH$_2$Cl$_2$/ethanol); mp 187.0−192.0 °C dec; ^{1}H NMR (CDCl$_3$, 500 MHz) δ −0.02 (br s, 18H), 0.01 (s, 9H), 0.02 (s, 9H), 0.03 (br s, 18H), 0.04 (s, 9H), 0.11 (s, 18H), 1.28 (s, 1H), 1.94 (s, 2H), 2.00

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[35] Sheldrick, G. M. SHELXS-86, Program for Crystal Structure Determination; University of Göttingen, Göttingen, Germany, 1986.

[36] Compound **13** was reported in our previous preliminary communication,[19] but its ^{77}Se (δ 931.4) and ^{207}Pb NMR (δ −268.6) chemical shifts were erroneous. The correct values are δ 303 (s, $^1J_{PbSe}$ = 1367 Hz) and δ −261 (s, $^1J_{PbSe}$ = 1367 Hz), respectively.

(s, 1H), 2.12 (s, $^2J_{\rm PbH} = 47.7$ Hz, 3H), 2.13 (br s, 2H), 2.18 (s, 1H), 2.55 (br s, 2H), 6.39 (s, 1H), 6.50 (s, 1H), 6.64 (s, $^4J_{\rm PbH} = 51.8$ Hz, 2H); ^{13}C NMR (CDCl$_3$, 125 MHz) δ −1.4 (q), −0.5 (q), 0.7 (q), 0.8 (q), 1.1 (q), 1.2 (q), 1.4 (q), 26.7 (t), 26.8 (t), 29.4 (q, $^1J_{\rm PbC} = 206.2$ Hz), 30.2 (d), 30.7 (d), 31.2 (d), 123.0 (d), 126.5 (d), 127.9 (d), 139.9 (s), 141.2 (s), 144.0 (s), 150.3 (s), 150.8 (s), 154.6 (s), 156.5 (s); ^{207}Pb NMR (CDCl$_3$, 105 MHz) δ −176 (s); HRMS (FAB) found *m/z* 1235.4235, calcd for $C_{46}H_{96}I^{208}PbSi_9$ ([M − H]$^+$) 1235.4247. Anal. Calcd for $C_{46}H_{97}IPbSi_9$: C, 44.66; H, 7.90. Found: C, 45.20; H, 8.12.

Reaction of 7c with Methyl Iodide. Similarly, the reaction of plumbylene **7c**, prepared from **1** (106 mg, 0.200 mmol), with methyl iodide (0.25 mL, 4.0 mmol) at room temperature in ether gave {2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}iodomethyl(2,4,6-triisopropylphenyl)plumbane (**10c**; 194.1 mg, 43%). **10c**: pale yellow solid (hexane); mp 193.0−195.0 °C dec; ^{1}H NMR (CDCl$_3$, 500 MHz) δ −0.07 (s, 9H), −0.01 (s, 9H), 0.03 (s, 18H), 0.06 (s, 9H), 0.11 (s, 9H), 1.20 (d, $^3J_{\rm HH} = 6.7$ Hz, 6H), 1.24 (d, $^3J_{\rm HH} = 6.1$ Hz, 6H), 1.29 (s, 1H), 1.34 (d, $^3J_{\rm HH} = 6.1$ Hz, 6H), 1.97 (s, 1H), 2.21 (s, 1H), 2.26 (s, $^2J_{\rm PbH} = 50.2$ Hz, 3H), 2.84 (sept, $^3J_{\rm HH} = 6.7$ Hz, 1H), 3.05 (sept, $^3J_{\rm HH} = 6.1$ Hz, 2H), 6.36 (s, 1H), 6.52 (s, 1H), 7.09 (s, $^4J_{\rm PbH} = 49.5$ Hz, 2H); ^{13}C NMR (CDCl$_3$, 125 MHz) δ 0.7 (q), 0.9 (q), 1.1 (q), 1.3 (q), 1.4 (q), 1.6 (q), 23.96 (q), 24.01 (q), 26.2 (q), 29.7 (q, $^1J_{\rm PbC} = 234.2$ Hz), 30.1 (d), 31.1 (d), 31.6 (d), 34.2 (d), 37.6 (d), 123.2 (d), 123.5 (d), 128.2 (d), 143.8 (s), 149.4 (s), 149.9 (s), 150.3 (s), 153.3 (s), 158.2 (s); ^{207}Pb NMR (CDCl$_3$, 105 MHz) δ −195 (s); HRMS (FAB) found *m/z* 1104.4098, calcd for $C_{43}H_{85}I^{208}PbSi_6$ ([M]$^+$) 1104.4078. Anal. Calcd for $C_{43}H_{85}IPbSi_6$: C, 46.75; H, 7.75. Found: C, 46.86; H, 7.98.

Reaction of 7d with Methyl Iodide. Similarly, the reaction of plumbylene **7d**, prepared from **1** (114 mg, 0.216 mmol), with methyl iodide (0.13 mL, 2.1 mmol) at room temperature in hexane gave {2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}[bis(trimethylsilyl)methyl]iodomethylplumbane (**10d**; 45.5 mg, 20%). **10d**: pale yellow crystals (CH$_2$Cl$_2$/ethanol); mp 165.0−170.0 dec; ^{1}H NMR (CDCl$_3$, 500 MHz) δ 0.04 (s, 9H), 0.05 (s, 9H), 0.11 (s, 9H), 0.13 (s, 27H), 0.17 (s, 9H), 0.33 (s, 9H), 1.31 (s, 1H), 1.46 (s, 1H), 1.78 (s, 1H), 2.01 (s, 1H), 2.02 (s, $^2J_{\rm PbH} = 44.0$ Hz, 3H), 6.39 (s, 1H), 6.51 (s, 1H); ^{13}C NMR (CDCl$_3$, 125 MHz) δ 0.8 (q), 0.9 (q), 1.4 (q), 1.7 (q), 1.8 (q), 3.7 (q), 4.3 (q), 27.0 (q), 28.4 (q), 30.4 (d), 31.2 (d), 31.5 (d), 123.1 (d), 127.9 (d), 144.6 (s), 150.1 (s), 150.5 (s), 153.8 (s); ^{207}Pb NMR (CDCl$_3$, 105 MHz) δ −10 (s); HRMS (FAB) found *m/z* 1059.3254, calcd for $C_{35}H_{80}I^{208}PbSi_8$ ([M − H]$^+$) 1059.3225. Anal. Calcd for $C_{35}H_{81}IPbSi_8$: C, 39.63; H, 7.70; I, 11.96. Found: C, 39.09; H, 7.29; I, 11.94.

Reaction of 7a with Elemental Sulfur. To an ether solution of **7a**, prepared from **1** (264 mg, 0.500 mmol), was added elemental sulfur (640 mg, 2.50 mmol as S$_8$) in portions at room temperature. Immediately the reaction mixture turned brown. After it had been stirred for 30 min, the reaction mixture was filtered through Celite, and the filtrate was concentrated under reduced pressure to afford a yellow solid, which was purified by preparative GPLC (eluent CHCl$_3$) to give TbtH (103.3 mg, 19%) and a 1:1 mixture of bis{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl} hexasulfide (**18**) and bis{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl} octasulfide (**19**) (115.9 mg, 50%). Further separation by preparative GPLC and successive repeated recrystallization gave small amounts of **18** and **19**, respectively, as pure crystalline compounds. **18**: pale yellow crystals (CHCl$_3$/ethanol); mp 265.0−268.5 °C dec; ^{1}H NMR (CDCl$_3$, 500 MHz) δ 0.05 (s, 36H), 0.07 (s, 72H), 1.37 (s, 2H), 2.99 (s, 2H), 3.10 (s, 2H), 6.41 (s, 2H), 6.54 (s, 2H); ^{13}C NMR (CDCl$_3$, 125 MHz) δ 0.7 (q), 0.9 (q), 28.0 (d), 31.0 (d), 122.0 (d), 126.8 (d), 129.0 (s), 145.8 (s), 150.2 (s); HRMS (FAB) found *m/z* 583.2990, calcd for $C_{27}H_{59}SSi_6$ ([Tbt + S]$^+$) 583.2953. Anal. Calcd for $C_{54}H_{118}S_6Si_{12}$: C, 50.01; H, 9.17; S, 14.83. Found: C, 49.95; H, 8.65; S, 14.78. **19**: yellow crystals (CHCl$_3$/ethanol); mp 270.0−271.5 °C; ^{1}H NMR (CDCl$_3$, 500 MHz) δ 0.04 (s, 108H), 1.35 (s, 2H), 2.86 (s, 2H), 2.99 (s, 2H), 6.38 (s, 2H), 6.52 (s, 2H); ^{13}C NMR (CDCl$_3$, 125 MHz) δ 0.7 (q), 0.9 (q), 28.0 (d), 31.0 (d), 122.1 (d), 126.9 (d), 128.2 (s), 146.0 (s), 150.4 (s); HRMS (FAB) found *m/z* 583.2911. Calcd for $C_{27}H_{59}SSi_6$ ([Tbt + S]$^+$) 583.2953. Anal. Calcd for $C_{54}H_{118}S_8Si_{12}$: C, 47.65; H, 8.74; S, 18.84. Found: C, 47.82; H, 8.63; S, 18.71.

Reaction of 7b with Elemental Sulfur. To an ether suspension of **7b**, prepared from **1** (1.32 g, 2.50 mmol), was added elemental sulfur (1.92 g, 7.51 mmol as S$_8$) in portions at room temperature. Immediately the reaction mixture turned yellow. After it had been stirred for 10 min, the reaction mixture was filtered through Celite. The filtrate was concentrated under reduced pressure to afford a brown solid, which was purified by preparative GPLC (eluent CHCl$_3$) followed by silica gel chromatography to give 5-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-5-[2,4,6-tris(trimethylsilylmethyl)phenyl]-1,2,3,4,5-tetrathiaplumbolane (**9b**; 1.58 g, 52%). **9b**: orange crystals (CH$_2$Cl$_2$/ethanol); mp 180.0−183.0 °C dec; ^{1}H NMR (CDCl$_3$, 500 MHz) δ −0.02 (s, 18H), 0.00 (br s, 27H), 0.02 (s, 18H), 0.03 (s, 18H), 1.31 (s, 1H), 1.57 (s, 1H), 1.61 (s, 1H), 1.93 (s, 2H), 2.47 (br s, 4H), 6.50 (s, $^4J_{\rm PbH} = 65.0$ Hz, 1H), 6.58 (s, $^4J_{\rm PbH} = 65.0$ Hz, 1H), 6.71 (s, $^4J_{\rm PbH} = 60.0$ Hz, 2H); ^{13}C NMR (CDCl$_3$, 125 MHz) δ −1.5 (q), −0.6 (q), 0.7 (q), 1.0 (q), 1.3 (q), 26.8 (t, $^5J_{\rm PbC} = 14.3$ Hz), 30.5 (d, $^5J_{\rm PbC} = 12.7$ Hz), 31.7 (d, $^3J_{\rm PbC} = 55.0$ Hz), 32.2 (t, $^3J_{\rm PbC} = 62.5$ Hz), 123.5 (d, $^3J_{\rm PbC} = 90.8$ Hz), 126.7 (d, $^3J_{\rm PbC} = 89.0$ Hz), 128.6 (d, $^3J_{\rm PbC} = 88.8$ Hz), 141.8 (s, $^4J_{\rm PbC} = 20.6$ Hz), 144.4 (s, $^2J_{\rm PbC} = 95.0$ Hz), 145.2 (s, $^4J_{\rm PbC} = 20.8$ Hz), 150.0 (s, $^2J_{\rm PbC} = 107.2$ Hz), 150.2 (s, $^2J_{\rm PbC} = 108.0$ Hz), 164.7 (s, $^1J_{\rm PbC} = 384.9$ Hz), 167.7 (s, $^1J_{\rm PbC} = 371.6$ Hz); ^{207}Pb NMR (CDCl$_3$, 105 MHz) δ 312 (s); HRMS (FAB) found *m/z* 1222.3862, calcd for $C_{45}H_{94}{}^{208}PbS_4Si_9$ ([M]$^+$) 1222.3928. Anal. Calcd for $C_{45}H_{94}PbS_4Si_9$: C, 44.18; H, 7.85; S, 10.19. Found: C, 44.43; H, 7.97; S, 10.02.

Reaction of 7c with Elemental Sulfur. A similar reaction of **7c**, prepared from **1** (1.39 g, 5.0 mmol), with elemental sulfur (3.85 g, 15.0 mmol as S$_8$) gave 5-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-5-(2,4,6-triisopropylphenyl)-1,2,3,4,5-tetrathiaplumbolane (**9c**; 3.69 g, 68%). **9c**: orange crystals (CH$_2$Cl$_2$/ethanol); mp 189.0−192.0 °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, $^3J_{\rm HH} = 6.9$ Hz, 6H), 1.23 (d, $^3J_{\rm HH} = 6.5$ Hz, 12H), 1.32 (s, 1H), 1.66 (s, $^4J_{\rm PbH} = 13.1$ Hz, 1H), 1.71 (s, $^4J_{\rm PbH} = 14.7$ Hz, 1H), 2.83 (sept, $^3J_{\rm HH} = 6.9$ Hz, 1H), 3.28 (sept, $^3J_{\rm HH} = 6.5$ Hz, 2H), 6.48 (s, $^4J_{\rm PbH} = 65.6$ Hz, 1H), 6.59 (s, $^4J_{\rm PbH} = 64.8$ Hz, 1H), 7.16 (s, $^4J_{\rm PbH} = 55.6$ 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, $^3J_{\rm PbC} = 70.6$ Hz), 124.1 (d, $^3J_{\rm PbC} = 89.7$ Hz), 128.8 (d, $^3J_{\rm PbC} = 87.8$ Hz), 145.2 (s, $^4J_{\rm PbC} = 20.7$ Hz), 149.6 (s), 149.8 (s), 150.7 (s, $^4J_{\rm PbC} = 19.5$ Hz), 152.4 (s, $^2J_{\rm PbC} = 89.7$ Hz), 165.2 (s, $^1J_{\rm PbC} = 368.6$ Hz), 167.6 (s, $^1J_{\rm PbC} = 307.6$ Hz); ^{207}Pb NMR (CDCl$_3$, 105 MHz) δ 314 (s); HRMS (FAB) found *m/z* 1091.3604, calcd for $C_{42}H_{83}{}^{208}PbS_4Si_6$ ([M + H]$^+$) 1091.3760. 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.

Reaction of 7d with Elemental Sulfur. A similar reaction of **7d**, prepared from **1** (2.61 g, 4.94 mmol), with elemental sulfur (3.79 g, 14.8 mmol as S$_8$) gave 5-{2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-5-[bis(trimethylsilyl)methyl]-1,2,3,4,5-tetrathiaplumbolane (**9d**; 869.0 mg, 17%). **9d**: yellow-orange crystals (CH$_2$Cl$_2$/ethanol); mp 176.0−179.0 °C dec; ^{1}H NMR (CDCl$_3$, 500 MHz) δ 0.02 (s, 18H), 0.11 (s, 36H), 0.22 (s, 18H), 1.34 (s, 1H), 1.65 (s, 1H), 1.73 (s, 1H), 1.87 (s, $^2J_{\rm PbH} = 67.9$ Hz, 1H), 6.50 (s, 1H), 6.61 (s, 1H); ^{13}C NMR (CDCl$_3$, 125 MHz) δ 0.8 (q), 1.3 (q), 1.4 (q), 1.6 (q), 4.4 (q), 30.6 (d), 32.1 (d), 32.4 (d), 47.6 (d, $^1J_{\rm PbC} = 170.5$ Hz), 123.9 (d, $^3J_{\rm PbC} = 88.5$ Hz), 129.0 (d, $^3J_{\rm PbC} = 85.8$ Hz), 145.3 (s, $^4J_{\rm PbC} = 20.7$ Hz), 149.3 (s), 149.8 (s), 165.4 (s, $^1J_{\rm PbC} = 297.5$ Hz); ^{207}Pb NMR (CDCl$_3$, 105 MHz) δ 499 (s); HRMS (FAB) found *m/z* 1046.2899, calcd for $C_{34}H_{78}{}^{208}PbS_4Si_8$ ([M]$^+$) 1046.2907. Anal. Calcd for $C_{34}H_{78}PbS_4Si_8$: C, 39.00; H, 7.51; S, 12.25. Found: C, 38.84; H, 7.21; S, 12.00.

Synthesis of Dibromoplumbane 8b. To an ether suspension (60 mL) of plumbylene **7b** (1.00 mmol), prepared from **1** (528 mg, 1.00 mmol), was added carbon tetrabromide (994 mg, 3.00 mmol) at 0 °C. After the reaction mixture had been stirred for 5 min, insoluble materials were filtered through Celite. After removal of the volatile substances under reduced pressure, the residue was subjected to preparative GPLC (eluent toluene) to yield {2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-[2,4,6-tris(trimethylsilylmethyl)phenyl]dibromoplumbane (**8b**; 570.5 mg, 45%). **8b**: yellow crystals (hexane); mp 212.0−218.0 °C dec; ^{1}H NMR (CDCl$_3$, 500 MHz) δ 0.02 (s, 27H), 0.04 (s, 18H), 0.07 (s, 18H), 0.12 (s, 18H), 1.33 (s, 1H), 1.97 (s, 2H), 2.13 (s, 1H), 2.35 (s, 1H), 2.56 (br s, 4H), 6.43 (br s, 1H), 6.55 (br s, 1H), 6.66 (s, $^4J_{\mathrm{PbH}} = 84$ Hz, 2H); ^{13}C NMR (CDCl$_3$, 125 MHz) δ −1.5 (q), −0.9 (q), 0.7 (q), 0.9 (q), 1.2 (q), 26.9 (t), 29.3 (t), 30.3 (d), 30.66 (d), 30.70 (d), 124.0 (d), 127.7 (d), 128.5 (d), 142.9 (s), 144.9 (s), 146.3 (s), 149.2 (s), 149.9 (s), 163.4 (s), 163.5 (s); ^{207}Pb NMR (CDCl$_3$, 105 MHz) δ −137 (s); HRMS (FAB) found *m/z* 1254.3414, calcd for $C_{45}H_{94}Br_2PbSi_9$ ([M]$^+$) 1254.3349. Anal. Calcd for $C_{45}H_{94}Br_2PbSi_9$: C, 43.07; H, 7.55. Found: C, 43.18; H, 7.27.

Synthesis of Dibromoplumbane 8c. Similarly, the reaction of plumbylene **7c**, prepared from **1** (264 mg, 0.500 mmol), with carbon tetrabromide (332 mg, 1.00 mmol) at −30 °C in ether (20 mL) gave {2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}-(2,4,6-triisopropylphenyl)dibromoplumbane (**8c**; 78.9 mg, 14%). **8c**: yellow crystals (hexane); mp 181.0−186.0 °C dec; ^{1}H NMR (CDCl$_3$, 500 MHz) δ 0.06 (s, 36H), 0.16 (s, 18H), 1.22 (d, $^3J_{\mathrm{HH}} = 6.6$ Hz, 6H), 1.36 (d, $^3J_{\mathrm{HH}} = 6.3$ Hz, 12H), 2.21 (s, 1H), 2.42 (s, 1H), 2.87 (sept, $^3J_{\mathrm{HH}} = 6.6$ Hz, 1H), 3.37 (sept, $^3J_{\mathrm{HH}} = 6.3$ Hz, 2H), 6.42 (s, 1H), 6.57 (s, 1H), 7.17 (s, 2H, $^4J_{\mathrm{PbH}} = 81.5$ Hz); ^{13}C NMR (CDCl$_3$, 125 MHz) δ 0.8 (q), 1.0 (q), 1.2 (q), 23.9 (q), 25.8 (q), 30.6 (d), 31.1 (d), 31.3 (d), 34.2 (d), 36.7 (d), 124.3 (d), 124.8 (d), 129.0 (d), 146.1 (s), 148.6 (s), 148.9 (s), 151.7 (s), 152.4 (s), 163.7 (s), 164.9 (s); ^{207}Pb NMR (CDCl$_3$, 105 MHz) δ −143 (s); HRMS (FAB) found *m/z* 1041.3942, calcd for $C_{42}H_{82}{}^{81}BrPbSi_6$ ([M − Br]$^+$) 1041.3940. Anal. Calcd for $C_{42}H_{82}Br_2PbSi_6$: C, 44.94; H, 7.36. Found: C, 44.72; H, 7.08.

Synthesis of Dibromoplumbane 8d. Similarly, the reaction of plumbylene **7d**, prepared from **1** (228 mg, 0.432 mmol), with carbon tetrabromide (425 mg, 1.28 mmol) at room temperature in hexane (10 mL) gave {2,4,6-tris[bis(trimethylsilyl)methyl]phenyl}[bis(trimethylsilyl)methyl]dibromoplumbane (**8d**; 40.6 mg, 9%). **8d**: pale yellow crystals (hexane); mp 176.5−179.0 °C dec; ^{1}H NMR (CDCl$_3$, 500 MHz) δ 0.05 (s, 18H), 0.14 (s, 18H), 0.16 (s, 18H), 0.37 (s, 18H), 1.35 (s, 1H), 2.12 (s, 1H), 2.17 (s, 1H), 2.40 (s, 1H), 6.43 (s, 1H), 6.57 (s, 1H); ^{13}C NMR (CDCl$_3$, 125 MHz) δ 0.8 (q), 1.2 (q), 1.4 (q), 3.6 (q), 30.62 (d), 30.64 (d), 30.7 (d), 52.7 (d), 124.4 (d), 128.9 (d), 146.5 (s), 148.9 (s), 149.5 (s), 163.7 (s); ^{207}Pb NMR (CDCl$_3$, 105 MHz) δ 82 (s); HRMS (FAB) found *m/z* 1077.2069, calcd for $C_{34}H_{77}{}^{79}Br^{81}BrPbSi_8$ ([M]$^+$) 1077.2292. Anal. Calcd for $C_{34}H_{78}Br_2PbSi_8$: C, 37.86; H, 7.29. Found: C, 38.65; H, 7.42.

Reaction of Dibromoplumbane 8a with Lithium Naphthalenide. To a solution of dibromoplumbane **8a** (73.8 mg, 0.0501 mmol) in THF (1 mL) was added lithium naphthalenide (0.098 M in THF, 1.0 mL, 0.098 mmol) at −72 °C in the dark. The reaction mixture was warmed to 0 °C over 2 h in the dark. Subsequently, methyl iodide (0.31 mL, 5.0 mmol) was added at 0 °C and the reaction mixture was stirred for 7 h, during which time it was warmed to room temperature. Filtration through Celite was followed by concentration of the filtrate under reduced pressure to afford a pale yellow solid, which was purified by preparative GPLC (eluent toluene) to give iodoplumbane **10a** (2.3 mg, 3%) and TbtH (49.7 mg, 90%).

Reaction of Dibromoplumbane 8b with Lithium Naphthalenide. To a solution of dibromoplumbane **8b** (75.6 mg, 0.0602 mmol) in THF (3 mL) was added lithium naphthalenide (0.64 M in THF, 0.19 mL, 0.12 mmol) at −72 °C. The mixture was stirred for 2 h, and then elemental sulfur (46.5 mg, 0.181 mmol as S_8) was added. The reaction mixture was stirred for 10 min at −72 °C and for 10 min at room temperature. After the reaction mixture had been filtered through Celite, the filtrate was concentrated under reduced pressure to afford a pale yellow solid, which was purified by preparative GPLC (eluent CHCl$_3$) to give tetrathiaplumbolane **9b** (47.7 mg, 65%) and TbtH (3.1 mg, 9%).

Reaction of Dibromoplumbane 8c with Lithium Naphthalenide. To a solution of dibromoplumbane **8c** (66.4 mg, 0.0590 mmol) in THF (3 mL) was added lithium naphthalenide (0.65 M in THF, 0.19 mL, 0.12 mmol) at −72 °C. The same procedure as above, using 46.0 mg (0.180 mmol as S_8) of elemental sulfur, gave a pale yellow solid, which was purified by preparative GPLC (eluent CHCl$_3$) to give tetrathiaplumbolane **9c** (41.2 mg, 64%) and TbtH (7.4 mg, 23%).

Reaction of Dibromoplumbane 8d with Lithium Naphthalenide. To a solution of dibromoplumbane **8d** (25.2 mg, 0.0234 mmol) in THF (1 mL) was added lithium naphthalenide (0.29 M in THF, 0.16 mL, 0.046 mmol) at −72 °C, and the mixture was stirred at −72 °C for 2 h. To this mixture was added elemental sulfur (18.2 mg, 0.0709 mmol as S_8) at −72 °C, and the reaction mixture was stirred for 4 h, during which time it was warmed to room temperature. Workup as above gave tetrathiaplumbolane **9d** (9.7 mg, 40%) and TbtH (4.8 mg, 37%).

Exhaustive Desulfurization of Tetrathiaplumbolane 9b with Triphenylphosphine. A toluene solution (2 mL) of tetrathiaplumbolane **9b** (93.1 mg, 0.0761 mmol) and triphenylphosphine (79.9 mg, 0.305 mmol) was sealed in a glass tube after five freeze−pump−thaw cycles. After the solution had been heated at 50 °C for 21 h, the sealed tube was opened in the glovebox filled with argon. The purple reaction solution was transferred to another flask, and methyl iodide (0.46 mL, 7.4 mmol) was added at room temperature. The reaction mixture was filtered through Celite, and the filtrate was concentrated under reduced pressure to afford a pale yellow solid, which was purified by preparative GPLC (eluent CHCl$_3$) to give iodoplumbane **10b** (36.4 mg, 39%).

Exhaustive Desulfurization of Tetrathiaplumbolane 9c with Triphenylphosphine. A toluene solution (3.6 mL) of tetrathiaplumbolane **9c** (109 mg, 0.100 mmol) and triphenylphosphine (106 mg, 0.403 mmol) sealed in a glass tube was heated at 50 °C for 6.5 h. The resulting purple reaction solution was treated with methyl iodide (0.60 mL, 9.0 mmol) at room temperature and then was filtered through Celite. The filtrate was concentrated under reduced pressure to afford a pale yellow solid, which was purified by preparative GPLC (eluent CHCl$_3$) to give iodoplumbane **10c** (36.9 mg, 33%).

Exhaustive Desulfurization of Tetrathiaplumbolane 9d with Triphenylphosphine. A similar procedure using tetrathiaplumbolane **9d** (57.5 mg, 0.0549 mmol), triphenylphosphine (57.9 mg, 0.221 mmol), and methyl iodide (0.13 mL, 2.1 mmol) gave a pale yellow solid, which was purified by preparative GPLC (eluent CHCl$_3$) to give iodoplumbane **10d** (5.9 mg, 10%).

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Supporting Information Available: Tables of all bond lengths and angles, atomic coordinates, and positional and thermal parameters for **7a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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