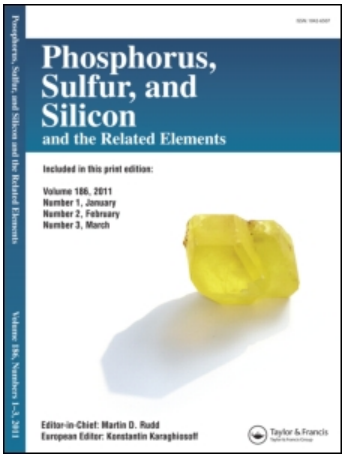

Phosphorus, Sulfur, and Silicon and the Related Elements

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Norihiro Tokitoh[a]; Naokazu Kano[a]; Kazusato Shibata[a]; Renji Okazaki[a]
[a] Department of Chemistry, Graduate School of Science, The University of Tokyo, Tokyo 113, Japan

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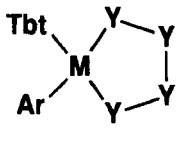
SYNTHESIS AND STRUCTURE OF 1,2,3,4,5-TETRATHIAPLUMBOLANES, THE FIRST STABLE Pb-CONTAINING CYCLIC POLYSULFIDES

NORIHIRO TOKITOH, NAOKAZU KANO, KAZUSATO SHIBATA, AND RENJI OKAZAKI*
Department of Chemistry, Graduate School of Science, The University of Tokyo
7-3-1 Hongo, Bunkyo-ku, Tokyo 113, Japan

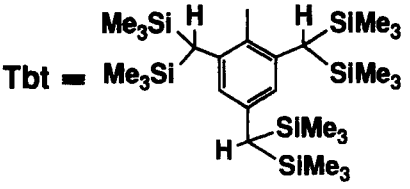
Abstract The first examples of Pb-containing cyclic tetrasulfides, R(Tip)PbS_4 [**4** (R=Tip) and **5** (R=Tbt); Tip=2,4,6-triisopropylphenyl, Tbt=2,4,6-tris[bis(trimethylsilyl)methyl]phenyl], were synthesized and isolated as stable crystalline compounds by the sulfurization of the corresponding overcrowded diarylplumbylenes, Tip_2Pb: (**6**) and Tbt(Tip)Pb: (**10**). Molecular structures of **4** and **5** were determined by X-ray crystallographic analysis. Desulfurization reactions of the tetrathiaplumbolanes **4** and **5** leading to the foramtion of plumbanethiones R(Tip)Pb=S, novel lead–sulfur double bond compounds, are also described.

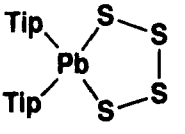
INTRODUCTION

In contrast to the wide chemistry of the transition metal polychalcogenido complexes, cyclic polychalcogenides containing main group metals had been unknown until we recently succeeded in the synthesis of novel tetrachalcogenametallolanes of group 14 metals, Tbt(Ar)MY_4 **1–3** [M=Si, Ge, or Sn; Y=S or Se; Ar=mesityl or 2,4,6-triisopropylphenyl (Tip)],[1] by taking advantage of a new steric protection group, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (denoted as Tbt hereafter). These cyclic polychalcogenides were found to be good precursors of stable metal-chalcogen double bond com-



1a; M=Si, Y=S
2a; M=Ge, Y=S
2b; M=Ge, Y=Se
3a; M=Sn, Y=S
3b; M=Sn, Y=Se





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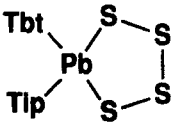

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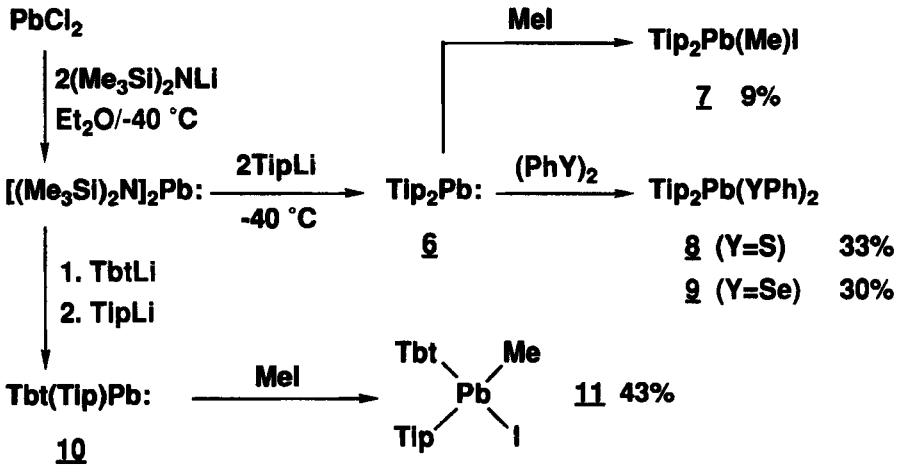
pounds, Tbt(Ar)M=Y.[2] Here, we present the synthesis of novel Pb-containing heterocycles, 1,2,3,4,5-tetrathiaplumbolanes **4** and **5**, *i. e.* the heavier congeners of **1–3**.

RESULTS AND DISCUSSION

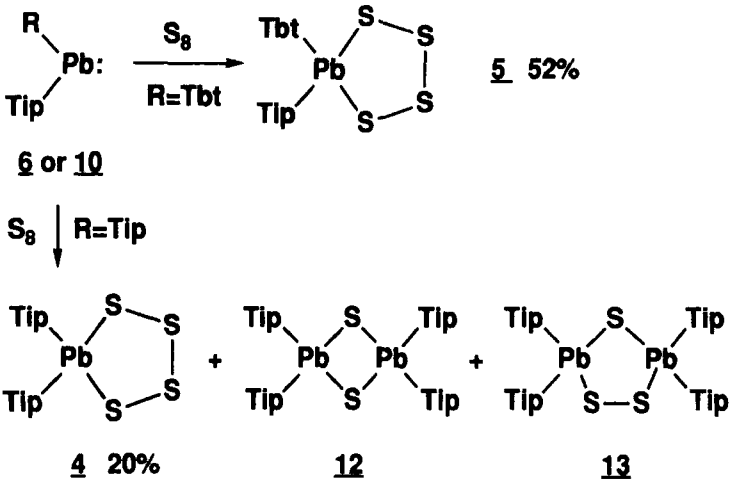
Although an attempt at introducing Tbt group onto a lead atom by the reactions of TbtLi with lead dichloride or iodide has failed due to inevitable electron-transfer reactions, ligand exchange of bis[bis(trimethylsilyl)amino]plumbylene by nucleophilic substitution with TipLi, a less hindered aryllithium than TbtLi, resulted in the formation of a new kinetically stabilized diarylplumbylene **6**. Plumbylene **6** was found to be stable only in solution at low temperature (-40 °C) and underwent ready insertion reactions with methyl iodide, diphenyl disulfide, and diphenyl diselenide to give the expected products **7**, **8**, and **9**. On the other hand, sequential treatment of $[(Me_3Si)_2N_2]_2Pb$: with TbtLi and



TipLi in ether afforded a more hindered diarylplumbylene **10**, which showed a characteristic absorption maxima at 640 nm (hexane, r. t.) and readily trapped with methyl iodide at room temperature to afford the corresponding iodoplumbane **11** in 43% yield. Among the heavier group 14 element carbene analogues it is most difficult to trap a plumbylene, since it easily polymerizes to undergo disproportionation. Although Lappert et al. reported the sole example of a kinetically stabilized dialkyl substituted plumbylene, $[(Me_3Si)_2CH]_2Pb$:,[3] its attempted reaction with methyl iodide gave no expected insertion products but resulted in the formation of only PbI_2.[4] The successful isolation of the insertion products in the reactions of diarylplumbylenes **6** and **10** is in sharp contrast with the case of the Lappert's plumbylene.

The remarkable stability and the promising reactivity of the diarylplumbylenes **6** and **10** prompted us to examine their sulfurization with elemental sulfur, which is one of the useful synthetic methods for tetrachalcogenametallolanes **1**–**3**.[2,5] Treatment of plumbylene **6** with an excess amount of elemental sulfur afforded the expected tetrathiaplumbolane **4** (20%) as stable yellow crystals along with small amounts of 1,3,2,4-dithiaplumbetane **12** and 1,3,4,2,5-trithiadiplumbetane **13**, while the reaction of more

hindered plumbylene **10** with elemental sulfur under the reaction conditions similar to **6** gave only tetrathiaplumbolane **5** (stable orange crystals) as sulfurized products in 52%



yield. The formation of tetrathiaplumbolanes **4** and **5** is worthy of note as the first example of the synthesis and isolation of a Pb-containing cyclic polychalcogenide, and their final molecular structures were determined by X-ray crystallographic analysis. In Figure 1 is shown an ORTEP drawing of Tbt(Tip)PbS_4 (**5**) together with some selected bond lengths and angles.

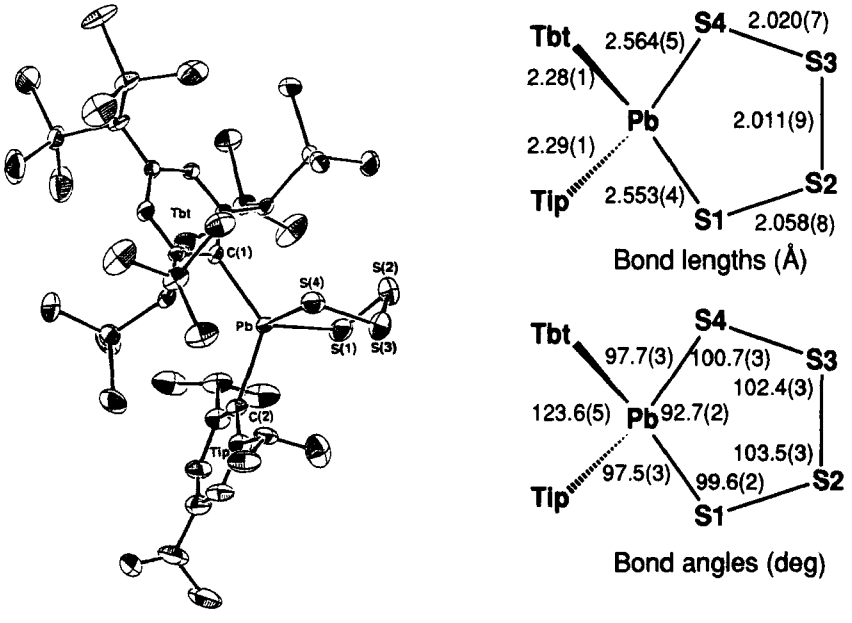
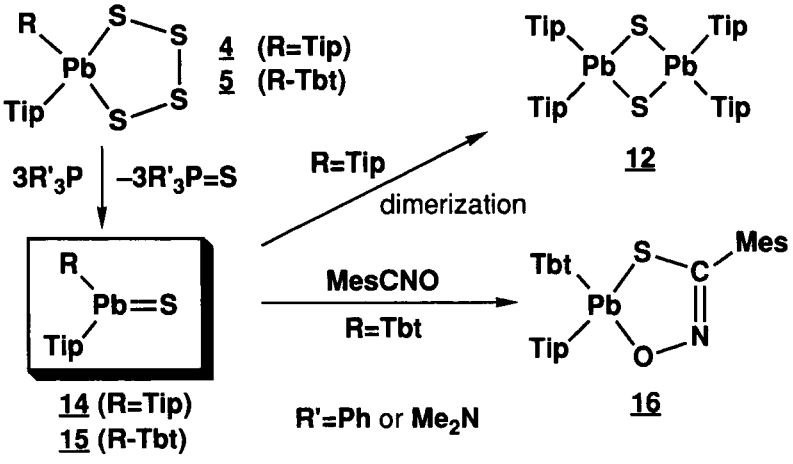


Figure 1. Molecular Structure of Tbt(Tip)PbS_4 (**5**).

The conformation of the tetrathiaplumbolane ring of both **4** and **5** was found to be of almost half-chair geometry as in the case of the previously reported tetrachalcogenametallolanes **1**–**3**.[1]

Since tetrathiaplumbolanes **4** and **5** are considered to be good precursors of plumbanethiones, novel lead–sulfur double bond compounds hetherto unknown, we have examined their desulfurization reactions with trivalent phosphorus compounds. When **4** was treated with 3 equivalents of Ph_3P in hexane at room temperature, 1,3,2,4-dithiadiplumbetane **12**, a self-dimerization product of an intermediary plumbanethione $Tip_2Pb{=}S$ (**14**), was obtained in more than 70% yield regardless in the presence or absence of the trapping reagents such as mesitonitrile oxide. On the other hand, a similar treatment of the more hindered tetrathiaplumbolane **5** with hexamethylphosphorus triamide (3 equiv) in THF gave a dark-red solution (λ_{max}=530 nm) suggesting the formation of plumbanethione, Tbt(Tip)Pb=S **15**. Chemical evidence for the formation of **15** was obtained by the trapping experiment using mesitonitrile oxide, which afforded the corresponding [2+3]cylcoadduct **16** in 35% yield.



The successful isolation and remarkable stability of tetrathiaplumbolanes **4** and **5** are obviously due to the steric demand of the bulky aryl groups (Tbt and Tip), which also enable us to demonstrate the first example of the cycloaddition reaction of plumbanethione.

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