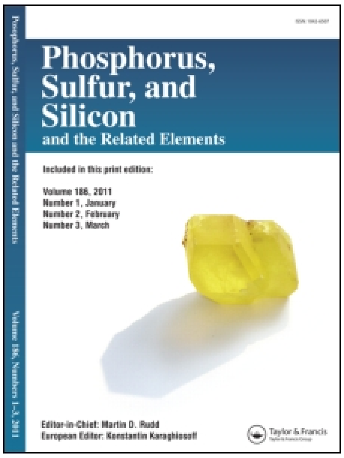

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Formation and Reactions of Novel Arylsulfido-Bridged Cyclic Organolead Compounds

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FORMATION AND REACTIONS OF NOVEL ARYLSULFIDO-BRIDGED CYCLIC ORGANOLEAD COMPOUNDS

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Desulfurization of tetrathiaplumbolane **2** at 50 °C with three equivalent of triphenylphosphine afforded stable aryl(arylthio)-plumbylene and dithiadiplumbetane. The formation of these products is most likely interpreted in terms of generation of a novel arylsulfido bridged cyclic organolead compounds.

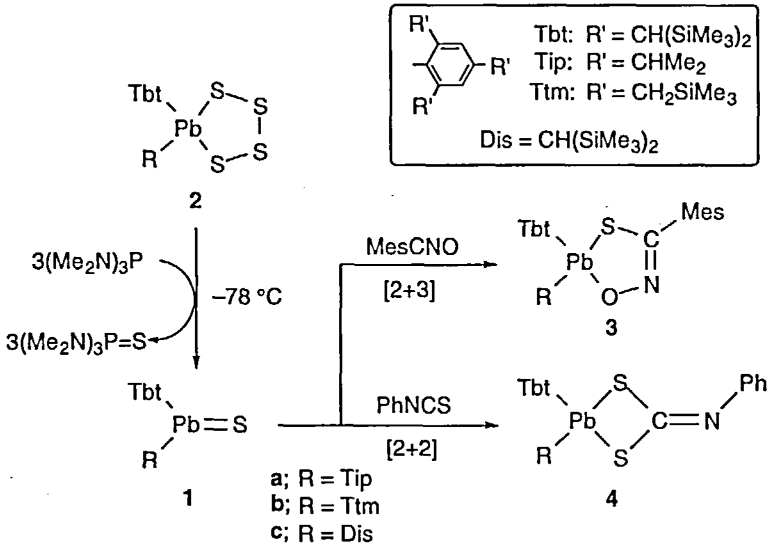
Keywords: arylsulfido-bridged organolead compounds; plumbylene; plumbanethione; steric protection; aryl-migration

INTRODUCTION

We recently reported the first lead–sulfur double-bond compounds, *plumbanethiones*, which are kinetically stabilized by an efficient steric protection group, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (denoted as Tbt hereafter) and another bulky substituent. Plumbanethiones are anticipated to be good precursors for the heterocycles containing lead and sulfur. Here, we present the generation of novel arylsulfido-bridged cyclic organolead compounds derived from plumbanethiones **1** ($R^1R^2Pb{=}S$).

RESULTS AND DISCUSSION

The plumbanethiones **1** were generated by desulfurization of tetrathiaplumbolanes **2** at –78 °C with 3 equiv of a phosphine reagent. Their generation was confirmed by trapping reactions with mesitonitrile oxide and phenyl isothiocyanate giving the corresponding cycloadducts **3** and **4** (SCHEME 1)[1].



SCHEME 1

The structure of **3 b** and **4b** was finally determined by the X-ray crystallographic analyses. ORTEP drawing of **4b** is shown in Figure 1. Both Pb-containing heterocycles are planar, and surrounded by bulky aromatic substituents.

In contrast to the above desulfurization at low temperature, desulfurization of **2a** at 50 °C with 3 equivalent of triphenylphosphine afforded stable aryl(arylthio)plumbylene Tbt(TbtS)Pb: **5** along with dithiadiplumbetane, $[Tip_2Pb{=}S]_2$ **6** (SCHEME 2).

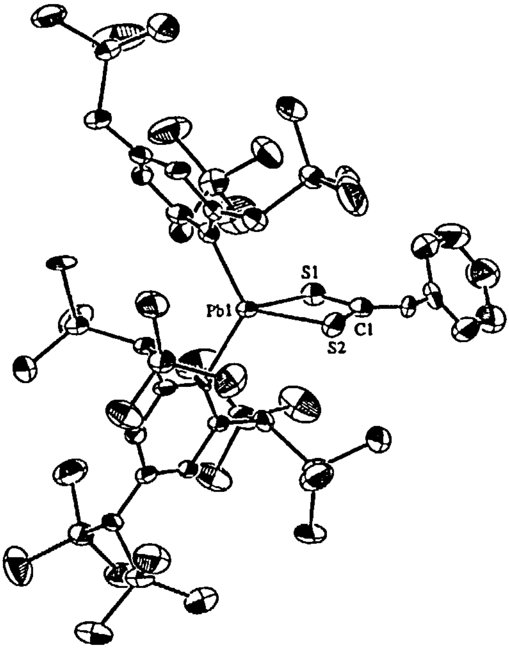
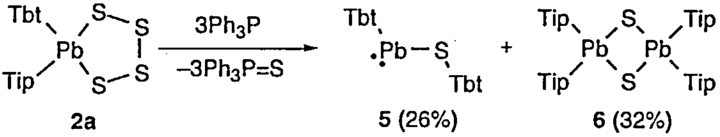


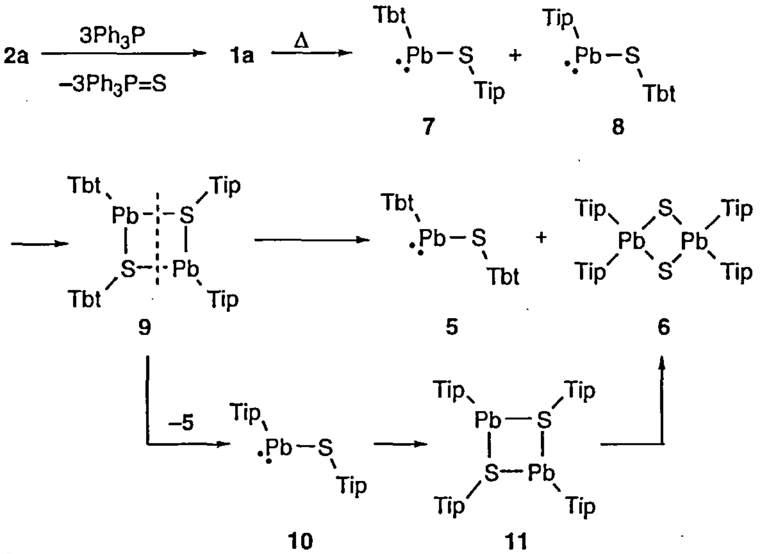
FIGURE 1

Such a type of reaction has never been observed in the case of other metallanethiones, [Tbt(Tip)M=S]; (M = Si, Ge, Sn).[3,4,5] The structure of 5 was established by the X-ray crystallography.



SCHEME 2

The fact that 4 and 5 bear only Tbt and Tip groups, respectively, indicates the presence of some comproportionation process in their formation. Thus, we propose a mechanism shown in SCHEME 3 for the formation of 4 and 5. As in the case of the desulfurization at low temperature, plumbanethione 1 is generated at the initial stage, but 1,2-migration of aryl gruop from Pb to S in **1a** occurs with the thermal conditions to form plumbylenes **7** and **8**. As an arylthioplumbylene is known to tend to oligomerise,[2] plumbylenes **7** and **8** might generate a novel arylsulfido bridged cyclic organolead compounds **9**. The formation of the plumbylene **5** can be most likely interpreted in terms of the retro [2+2]cycloaddition of **9**. Plumbylene **10**, another product from **9**, might form a self-dimerization product **11** in a manner similar to the formation of **9**. The formation of dithiadiplumbetane **6** can be rationalized by the aryl-migration in an arylsulfido-bridged Pb-containing heterocycle **11**.



SCHEME 3

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