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## Novel Reactions of Extremely Hindered Plumbylenes with Elemental Sulfur and Carbon Disulfide

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Synthesis, structure, and some reactivities of kinetically stabilized plumbylenes are described. The reaction of an extremely hindered plumbylene  $\text{Tbt}_2\text{Pb}$ : ( $\text{Tbt} = 2,4,6\text{-tris}[\text{bis}(\text{trimethylsilyl})\text{methyl}]\text{phenyl}$ ) with elemental sulfur gave  $\text{Tbt}(\text{TbtS})\text{Pb}$ : via an interesting 1,2-aryl migration of the intermediary plumbanethione,  $\text{Tbt}_2\text{Pb}=\text{S}$ . The reactions of overcrowded aryl(arylthio)plumbylenes and bis(arylthio)-plumbylenes with carbon disulfide are also described.

**Keywords:** plumbylenes; kinetic stabilization; elemental sulfur; 1,2-aryl migration; plumbanethione; carbon disulfide

### INTRODUCTION

Recently, we have succeeded in the synthesis and isolation of a variety of doubly bonded compounds between heavier group 14 and 16 elements by taking advantage of an extremely bulky and efficient steric protection group ( $\text{Tbt}$ ). As an extension of this chemistry to that of the heaviest group 14 element ( $\text{Pb}$ ), we present here the synthesis, structure, and some unique reactions of extremely hindered divalent organolead compounds (plumbylenes).

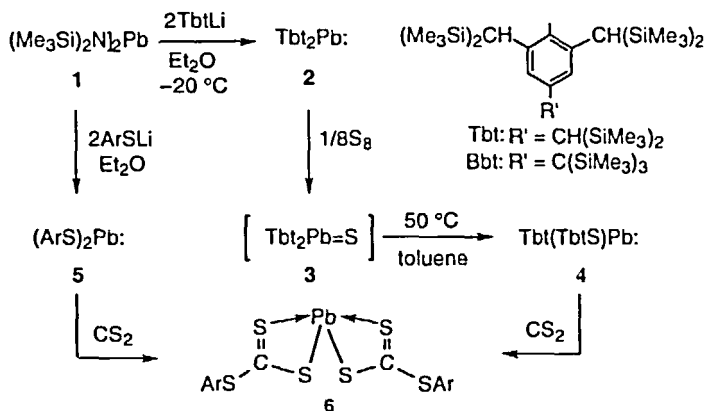
### RESULTS AND DISCUSSION

The nucleophilic substitution of lead(II) diamide $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Pb}$  (**1**) with  $\text{TbtLi}$  resulted in the formation of stable diarylplumbylene,  $\text{Tbt}_2\text{Pb}$ : (**2**), the structure of which was definitively determined by X-

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ray diffraction analysis. Treatment of **2** with elemental sulfur afforded a novel heteroleptic plumblylene [Tbt(TbtS)Pb: (**4**)] via the rearrangement of the intermediary plumbanethione, Tbt<sub>2</sub>Pb=S (**3**) [1,2]. The facile isomerization of the plumbanethione **3** into **4** is in sharp contrast to the high stability of its lighter congeners [Tbt(R)M=S; M = Si, Ge, and Sn; R = 2,4,6-triisopropylphenyl or 2,2''-diisopropyl-*m*-terphenyl-2'-yl] which are synthesized as stable crystalline compounds.



A new type of homoleptic plumblylenes (**5a**, Ar = Tbt; **5b**, Ar = 2,6-bis[bis(trimethylsilyl)methyl]-4-[tris(trimethylsilyl)methyl]phenyl (Bbt)), were also prepared starting from lead(II) diamide (**1**). Plumblylenes **4** and **5** showed a quite unique reactivity towards carbon disulfide to give the first lead(II) bis(aryl trithiocarbonate) compounds, (ArSCS<sub>2</sub>)<sub>2</sub>Pb (**6a**; Ar = Tbt, **6b**; Ar = Bbt), the formation of which can be most likely interpreted in terms of double insertion of carbon disulfide into two lead–sulfur bonds of **5**. The structure of **6b** was also determined by X-ray crystallographical analysis.

## References

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