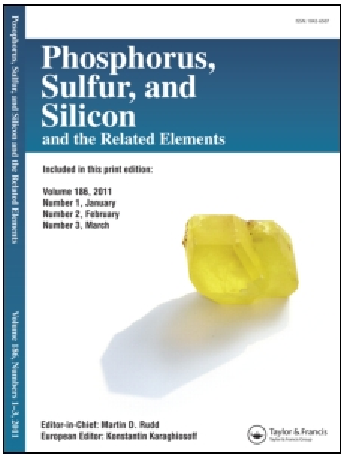

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Novel Reactions of Extremely Hindered Plumbylenes with Elemental Sulfur and Carbon Disulfide

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Synthesis, structure, and some reactivities of kinetically stabilized plumbylenes are described. The reaction of an extremely hindered plumbylene Tbt_2Pb: (Tbt = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl with elemental sulfur gave Tbt(TbtS)Pb: via an interesting 1,2-aryl migration of the intermediary plumbanethione, $Tbt_2Pb{=}S$. 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 (Tbt). As an extension of this chemistry to that of the heaviest group 14 element (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$[(Me_3Si)_2N]_2Pb$ (**1**) with TbtLi resulted in the formation of stable diarylplumbylene, Tbt_2Pb: (**2**), the structure of which was definitively determined by X-

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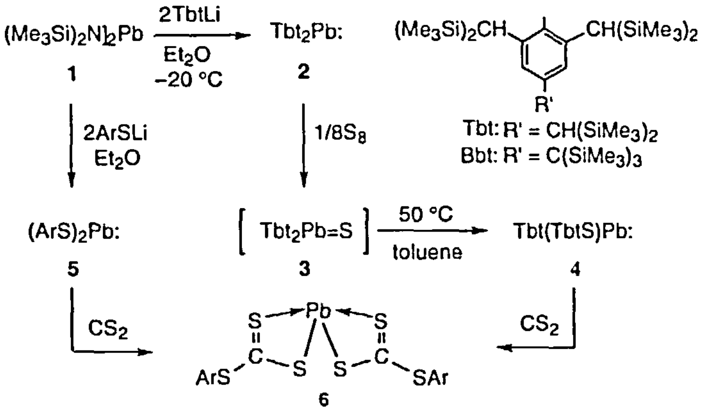
ray diffraction analysis. Treatment of **2** with elemental sulfur afforded a novel heteroleptic plumbylene [Tbt(TbtS)Pb: (**4**)] via the rearrangement of the intermediary plumbanethione, $Tbt_2Pb{=}S$ (**3**) [1,2]. The facile isomerization of the plumbanethione **3** into **4** is in sharp contrast 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 plumbylenes {**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**). Plumbylenes **4** and **5** showed a quite unique reactivity towards carbon disulfide to give the first lead(II) bis(aryl trithiocarbonate) compounds, $(ArSCS_2)_2Pb$ (**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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