Synthesis and Reactions of the First Lead–Sulfur Double-Bond Compounds, Plumbanethiones

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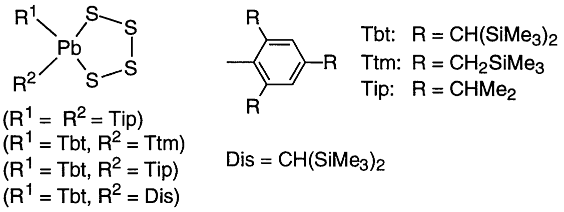
Desulfurization of 1,2,3,4,5-tetrathiaplumbolanes **1** by a phosphine reagent gives the first lead–sulfur double-bond compounds, plumbanethiones **2**. The cycloaddition reactions of plumbanethiones with MesCNO and PhNCS provide novel Pb-containing heterocycles.

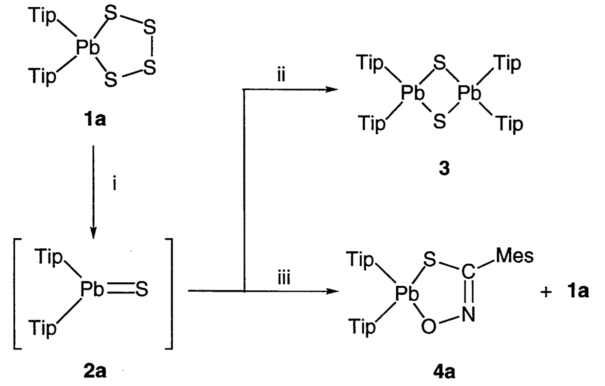
The chemistry of doubly bonded compounds between heavier group 14 elements and chalcogen atoms has been a fascinating subject of considerable attention in recent years.[1] There have been some examples of doubly bonded compounds of such type for silicon,[2] germanium,[3] and tin,[4] though they are thermodynamically stabilized by intramolecular coordination of neighboring nitrogen atoms to electron-deficient group 14 atoms. We have recently reported the synthesis of heavier congeners of ketones ($R^1R^2M{=}X$; M = Si, Ge and Sn; X = O, S and Se) , which we refer to as "heavy ketones", by taking advantage of kinetic stabilization of an efficient steric protection group, 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl (denoted as Tbt hereafter).[5] By contrast, neither thermodynamically nor kinetically stabilized analogues with a lead–sulfur double bond have been synthesized so far.

Here, we wish to present the synthesis of the first kinetically stabilized plumbanethiones **2** ($R^1R^2Pb{=}S$) by desulfurization of 1,2,3,4,5-tetrathiaplumbolanes **1** previously reported by us.[6] We also report that the plumbanethiones thus obtained are stable in solution and undergo some cycloaddition reactions.



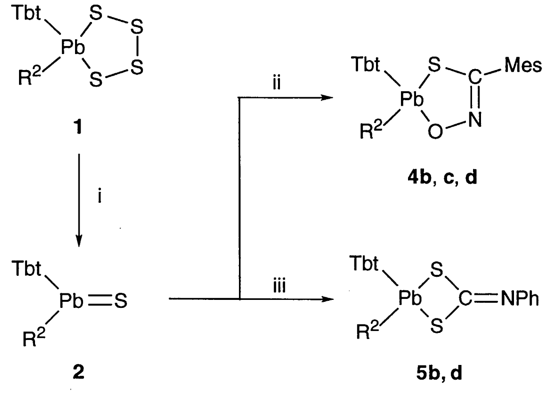
1a (R^1 = R^2 = Tip)
b (R^1 = Tbt, R^2 = Ttm)
c (R^1 = Tbt, R^2 = Tip)
d (R^1 = Tbt, R^2 = Dis)

When tetrathiaplumbolane **1a** (R^1 = R^2 = Tip; Tip = 2,4,6-triisopropylphenyl) was reacted with 3 equiv of triphenylphosphine in hexane at –78 °C, 1,3,2,4-dithiadiplumbetane **3** was obtained in 72% yield. The product **3** is thought to be formed by ready head-to-tail self-dimerization of transient plumbanethione **2a** because the substituents are not bulky enough.[7] In an attempt to trap **2a**, phenyl isothiocyanate or 2,3-dimethyl-1,3-butadiene, which is an effective reagent for trapping other heavy ketones,[5] was added to the reaction solution at –78 °C. In both cases, however, only dimerization product **3** was obtained as a Pb-containing product with a small amount of TipH, no adduct of plumbanethione **2a** being obtained. The trapping of transient plumbanethione **2a** was successful in the desulfurization of **1a** in the presence of mesitonitrile oxide, giving a [3+2] cycloaddition product **4a** in 12% yield, but most of **1a** was recovered (86%) because triphenylphosphine reacted faster with mesitonitrile oxide than with **1a**.



Scheme 1. *Reagents and conditions:* i, Ph_3P (3 equiv.), hexane, –78 °C; ii, –78 to 25 °C, **3**; 72%; iii, MesCNO, –78 to 25 °C, **4a**; 12%, **1a**; 86%.

In anticipation of further stabilization for plumbanethiones, more hindered tetrathiaplumbolanes [**1b** (R^1 = Tbt, R^2 = Ttm), **1c** (R^1 = Tbt, R^2 = Tip), **1d** (R^1 = Tbt, R^2 = Dis); Ttm = 2,4,6-tris(trimethylsilylmethyl)phenyl, Dis = bis(trimethylsilyl)methyl] were desulfurized with a more reactive phosphine reagent. When a yellow THF solution of **1b**, **1c** or **1d** was treated with 3 equiv of hexamethylphosphorous triamide at –78 °C, the color of the reaction solution turned red for **1b** and **1c** or orange for **1c**, indicating the generation of plumbanethiones **2b**, **2c** or **2d**, respectively. Subsequent addition of mesitonitrile oxide to this solution at –78 °C gave the corresponding oxathiazaplumbole **4**, a [3+2] cycloadduct of plumbanethione **2**, in a moderate yield in each case. Plumbanethiones **2b** and **2d** were also trapped with phenyl isothiocyanate to give [2+2] cycloaddition products **5b** and **5d**, respectively, though **2c** did not give such an adduct. The



b: R^2 = Ttm, c: R^2 = Tip, d: R^2 = Dis

Scheme 2. *Reagents and conditions:* i, $(Me_2N)_3P$ (3 equiv.), THF, –78 °C; ii, MesCNO, –78 to 25 °C, **b**; 64%, **c**; 35%, **d**; 31%; iii, PhNCS, –78 to 25 °C, **b**; 37%, **d**; 5%.

newly obtained Pb-containing heterocycles (**4** and **5**) showed satisfactory spectral and analytical data.[8, 9] The formation of new Pb-containing heterocycles **4** and **5** is worthy of note as the first examples of the trapping of plumbanethiones.

The thermal stability of plumbanethiones, **2b** and **2c**, was examined by UV/vis spectroscopy. The red color of the reaction solution due to plumbanethiones **2b** and **2c** remained up to –20 °C, but gradually turned pale yellow with raising temperature. Unlike **2a** described above, no self-dimerization products of **2b** and **2c** were obtained as the result of effective steric protection by Tbt group.[10] These results suggest that plumbanethiones with suitable steric protection groups on the lead atom are stable in solution at least below –20 °C. Attempts at further stabilization of plumbanethiones are in progress.

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7 We have reported that the thioketone analogues of group 14 elements dimerize when they do not bear a sufficiently bulky group on their group 14 elements. See ref. 5.

8 Selected analytical and spectroscopic data for **4c**: yellow crystals; mp 219–220.5 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ=0.03 (s, 9H), 0.060 (s, 9H), 0.062 (s, 9H), 0.07 (s, 9H), 0.08 (s, 9H), 0.10 (s, 9H), 1.22 (d, 6H, J = 6.9 Hz), 1.25 (s, 1H), 1.32 (d, 6H, J = 6.2 Hz), 1.34 (d, 6H, J = 6.2 Hz), 1.83 (s, 1H), 2.02 (brs, 6H), 2.04 (s, 1H), 2.23 (s, 3H), 2.86 (sept, 1H, J = 6.9 Hz), 2.93 (brs, 2H), 6.56 (s, 1H), 6.67 (s, 1H), 6.76 (s, 2H), 7.15 (s, 2H, $^{4}J_{PbH}$ = 63.8 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ=0.70 (q), 0.78 (q), 0.82 (q), 0.9 (q), 1.0 (q), 19.8 (q), 21.0 (q), 23.88 (q), 23.94 (q), 25.5 (q), 26.1 (q), 30.6 (d), 33.8 (d), 33.9 (d), 34.2 (d), 38.6 (d), 124.5 (d, $^{3}J_{PbH}$ = 99 Hz), 128.1 (d), 129.1 (d), 131.9 (s), 137.2 (s), 137.6 (s), 143.7 (s), 145.4 (s), 148.7 (s), 149.0 (s), 150.8 (s), 152.6 (s), 165.2 (s), 166.3 (s); ^{207}Pb NMR (56.4 MHz, $CDCl_3$) δ=390; Calcd for $C_{52}H_{93}NOPbSSi_6$: C, 54.02; H, 8.11; N, 1.21; S, 2.77%. Found: C, 53.87; H, 8.11; N, 1.50; S, 2.70%.; HRMS (FAB): Found: *m/z* 1156.5422. Calcd for $C_{52}H_{94}NOPbSSi_6$: $[M+H]^+$ 1156.5438.

9 The molecular structures for **4b** and **5b** were also determined by preliminary X-ray crystallographic analysis. The results of the X-ray crystallographic analysis will be published elsewhere.

10 The main product is TbtH. The minor products are an unidentifiable complex mixture.