

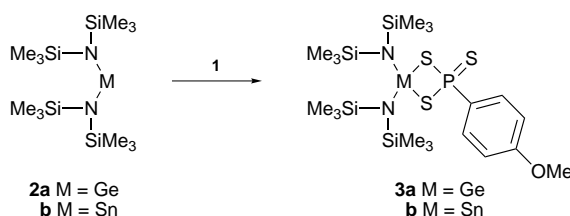
# Germylene and stannylene cleavage of Lawesson's reagent

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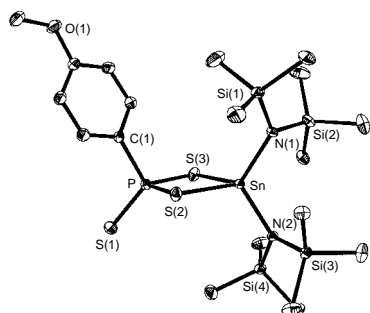
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Lawesson's reagent undergoes cleavage reactions with bis[bis(trimethylsilyl)amino]germanium(II) and bis[bis(trimethylsilyl)amino]tin(II) whilst with 1,3-di-*tert*-butyl-1,3,2-diazagermol-2-ylidene the product is a novel spirocyclic germanium derivative.

Lawesson's reagent **1** is one of the most versatile thiation reagents available and is highly effective, for example, for the conversion of aldehydes and ketones to the corresponding thio derivatives.<sup>1</sup> However, much less information is available regarding the interaction of **1** with transition metal<sup>2</sup> or main group reagents. Herein we describe the unusual reactions of **1** with some coordinatively unsaturated group 14 compounds.

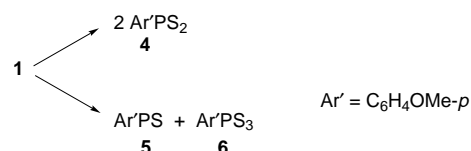


The reaction of **1** with stannylene **2b**<sup>3</sup> in THF solution resulted in a >90% isolated yield of **4b**.<sup>†</sup> Interestingly, the corresponding reaction of **1** with **2a**<sup>3</sup> produced a much smaller yield (*ca.* 10%) of the Ge analogue **3a**. <sup>31</sup>P NMR and HRMS(CI<sup>+</sup>) data were consistent with the formulae proposed above for both compounds, and <sup>1</sup>H and <sup>13</sup>C NMR spectra indicated the presence of one *p*-MeOC<sub>6</sub>H<sub>4</sub> and two (non-equivalent) N(SiMe<sub>3</sub>)<sub>2</sub> groups.<sup>‡</sup> However, in order to ascertain the atom connectivity, it was necessary to appeal to X-ray crystallography. Suitable single crystals of **3b** were obtained from CH<sub>2</sub>Cl<sub>2</sub> solution. The central feature of the molecular structure of **3b**<sup>§</sup> (Fig. 1) comprises a planar PS<sub>2</sub>Sn ring [sum of angles = 360.00(3)°]. Such rings are rare as indicated by a search of the Cambridge Data Base which revealed only one previous example.<sup>4</sup> As expected, the average P–S<sub>ring</sub> bond

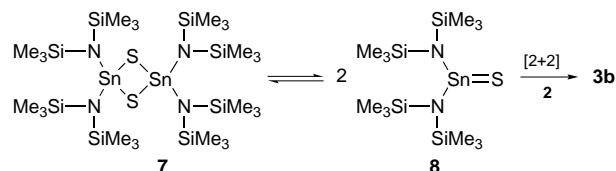


**Fig. 1** Molecular structure of **3b** showing the atom numbering scheme. Selected distances (Å) and angles (°): P–C(1) 1.804(2), P–S(1) 1.9315(9), P–S(2) 2.1168(9), P–S(3) 2.1018(9), Sn–S(2) 2.4188(6), Sn–S(3) 2.4358(6), N(1)–Sn 2.015(2), N(2)–Sn 2.023(2), N–Si(1) 1.764(2), N–Si(2) 1.757(2), N(2)–Si(3) 1.757(2), N(2)–Si(4) 1.761(2); C(1)–P–S(1) 112.05(8), S(2)–P–S(3) 101.32(3), P–S(2)–Sn 87.17(3), P–S(3)–Sn 87.06(3), N(1)–Sn–N(2) 116.07(7), Sn–N(1)–Si(1) 122.83(10), Sn–N(1)–Si(2) 115.15(9), Sn–N(2)–Si(3) 116.33(9), Sn–N(2)–Si(4) 120.37(10), Si(1)–N(1)–Si(2) 120.73(10), Si(3)–N(2)–Si(4) 121.35(10).

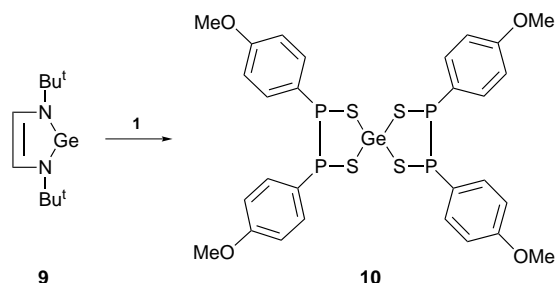
distance [2.1125(9) Å] is longer than that of the external P–S bond [1.9315(9) Å]. Although the phosphorus and tin centres are four-coordinate, there is considerable deviation of the bond angles from the ideal tetrahedral value and the N–Sn–N angle in **3b** [116.07(7)°] is larger than that in **2b** [104.7(2)°].<sup>5</sup>



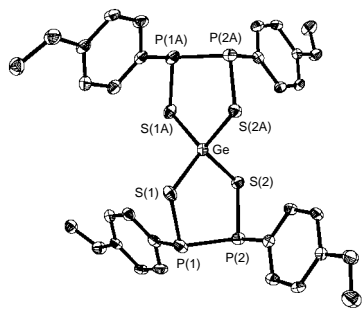
The mechanism of formation of **3a,b** is not clear, but plausible routes to these products include (i) oxidative addition of **2a,b** to **4**, which results from symmetrical cleavage of **1**, followed by addition of sulfur to phosphorus, (ii) addition of **2a,b** to an Ar'PS<sub>3</sub> (**6**) fragment resulting from unsymmetrical cleavage of **1**, and (iii) addition of sulfur to **2a,b** followed by reaction of the resulting germa- or stanna-thione with **4**. In an attempt to clarify this point, **7**,<sup>6</sup> which can be viewed as a cyclic dimer of the requisite stanna-thione **8**, was treated with an equimolar quantity of **1** in CD<sub>2</sub>Cl<sub>2</sub> or C<sub>6</sub>D<sub>6</sub> solution at 25 °C. NMR (<sup>31</sup>P and <sup>1</sup>H) assay indicated quantitative conversion to **3b**. This observation is consistent with route (iii), and as such would represent a novel formal [2 + 2] cycloaddition involving P=S and Sn=S bonds.<sup>7</sup>



In sharp contrast to the results obtained with **2a**, the cyclic germylene **9**<sup>8</sup> undergoes a completely different type of reaction with **1** and affords **10** as the major product. Whilst not appropriate as a mechanism, one way of thinking of this reaction is to consider that the cyclic germylene **9** serves as a source of Ge atoms for transfer to four Ar'PS (**5**) moieties. As pointed out above, **5** could arise *via* unsymmetrical cleavage of **1**.



The X-ray crystal structure of **10** revealed an interesting spirocyclic geometry (Fig. 2). Individual molecules of **10** reside on a crystallographic twofold axis. The GeS<sub>2</sub>P<sub>2</sub> rings are slightly puckered and the dihedral angle between the S–Ge–S planes is 81.7°. The geometry at Ge is essentially tetrahedral;



**Fig. 2** Molecular structure of **10** showing the atom numbering scheme. Selected distances (Å) and angles (°): Ge–S(1) 2.222(1), Ge–S(2) 2.223(1), P(1)–S(1) 2.103(2), P(2)–S(2) 2.098(2), P(1)–P(2) 2.220(2); S(1)–Ge–S(2) 105.89(4), P(1)–S(1)–Ge 104.69(5), S(1)–P(1)–P(2) 104.46(6), S(2)–P(2)–P(1) 103.50(6), P(2)–S(2)–Ge 105.07(5).

however, the endocyclic S–Ge–S angles [ $105.89(4)^\circ$ ] are more acute than the exocyclic angles [ $117.10(6)^\circ$ ]. The average Ge–S [2.222(1) Å], P–S [2.100(2) Å] and P–P [2.220(2) Å] distances each correspond to a bond order of unity. Finally, the  $R_2P_2S_2$  ligand does not appear to have been described previously; although a phosphorus–sulfur heterocycle is known<sup>9</sup> in which the  $Ph_2P_2S_2$  ligand is associated with a  $PhP(S)$  moiety, *i.e.* ( $PhPS$ )<sub>3</sub>.

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## Footnotes and References

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† *Experimental procedure*: **3a**: compound **2a** (0.81 g, 2.1 mmol) in 50 cm<sup>3</sup> of THF was added to a stirred slurry of **1** (0.80 g, 2.0 mmol) in 10 cm<sup>3</sup> of THF. The solution was warmed to 60 °C for 20 min. The solvent was removed *in vacuo* and the resulting yellow residue was dissolved in 30 cm<sup>3</sup> of CH<sub>2</sub>Cl<sub>2</sub>. After filtration through Celite the filtrate was concentrated and stored at –25 °C to afford a small quantity of yellow powder **3a** (0.09 g, 0.15 mmol, 8%), mp 132–136 °C.

**3b**: compound **2b** (1.25 g, 2.8 mmol) in 50 cm<sup>3</sup> of THF was added to a stirred slurry of **1** (1.15 g, 2.8 mmol) in 10 cm<sup>3</sup> of THF. The solution was warmed to 60 °C for 20 min. The solvent was removed *in vacuo* and the resulting pale yellow powder was dissolved in 30 cm<sup>3</sup> of CH<sub>2</sub>Cl<sub>2</sub>. After filtration through Celite the filtrate was concentrated and stored at –25 °C to afford pale yellow crystals of **3b** (0.90 g, 1.3 mmol, 92% yield based on **1**), mp 140–143 °C.

**10**: compound **9** (0.67 g, 2.80 mmol) was dissolved in 30 cm<sup>3</sup> of toluene and added to a stirred suspension of **1** (0.78 g, 1.94 mmol) in 40 cm<sup>3</sup> of toluene at 25 °C. Over a 20 min period, the originally yellowish solution turned red as the solids dissolved. After 4 h a precipitate formed and the reaction mixture was allowed to stir for an additional 12 h. After filtration, the solvent and volatiles were removed from the filtrate and the residue was dissolved in CH<sub>2</sub>Cl<sub>2</sub> and this solution was covered with a layer of hexane. Colourless crystals of **10** formed over a period of several days (0.15 g, 20%

yield based on **1**), mp 200 °C (becomes opaque at 170 °C). HRMS: calculated for C<sub>28</sub>H<sub>28</sub>GeO<sub>4</sub>P<sub>4</sub>S<sub>4</sub> (M<sup>+</sup>), 754.9111; found 754.9125.

‡ *Selected spectroscopic data*: **3a**: NMR (C<sub>6</sub>D<sub>6</sub>): <sup>31</sup>P{<sup>1</sup>H} δ 42.0; <sup>1</sup>H δ 8.02–8.08 (m, 2 H, aryl), 6.80–6.82 (m, 2 H, aryl), 8.85 (s, 3 H, OCH<sub>3</sub>), 0.47 [s, 18 H, Si(CH<sub>3</sub>)<sub>3</sub>], 0.34 [s, 18 H, Si(CH<sub>3</sub>)<sub>3</sub>]; <sup>13</sup>C δ 162.6 (s, *p*-C<sub>aryl</sub>), 132.2 (d, <sup>3</sup>J<sub>PC</sub> 14 Hz, *m*-C<sub>aryl</sub>), 114.3 (d, <sup>2</sup>J<sub>PC</sub> 16 Hz, *o*-C<sub>aryl</sub>), 54.9 (s, OCH<sub>3</sub>), 6.5 (s, SiCH<sub>3</sub>), 5.5 (s, SiCH<sub>3</sub>), *ipso*-C<sub>aryl</sub> not observed. HRMS (CI<sup>+</sup>): calc. for C<sub>19</sub>H<sub>43</sub>GeN<sub>2</sub>OPS<sub>3</sub>Si<sub>4</sub> (M<sup>+</sup>), *m/z* 597.0826; found 597.0825.

**3b**: NMR (C<sub>6</sub>D<sub>6</sub>): <sup>31</sup>P{<sup>1</sup>H} δ 56.5, satellites due to coupling with <sup>119</sup>Sn observed (75 Hz); <sup>119</sup>Sn{<sup>1</sup>H} δ –240 (d, <sup>2</sup>J<sub>PSn</sub> 76 Hz); <sup>1</sup>H δ 8.17–8.26 (m, 2 H, aryl), 7.02–7.06 (m, 2 H, aryl), 3.91 (s, 3 H, OCH<sub>3</sub>), 0.49 [s, 18 H, Si(CH<sub>3</sub>)<sub>3</sub>], 0.31 [s, 18 H, Si(CH<sub>3</sub>)<sub>3</sub>]; <sup>13</sup>C δ 161.6 (s, *p*-C<sub>aryl</sub>), 137.0 (d, <sup>1</sup>J<sub>PC</sub> 94 Hz, *ipso*-C<sub>aryl</sub>), 132.2 (d, <sup>3</sup>J<sub>PC</sub> 15 Hz, *m*-C<sub>aryl</sub>), 113.7 (d, <sup>2</sup>J<sub>PC</sub> 17 Hz, *o*-C<sub>aryl</sub>), 54.9 (s, OCH<sub>3</sub>), 6.2 (s, SiCH<sub>3</sub>), 5.7 (s, SiCH<sub>3</sub>). HRMS (CI<sup>+</sup>): calc. for C<sub>19</sub>H<sub>43</sub>N<sub>2</sub>OPS<sub>3</sub>Si<sub>4</sub>Sn (M<sup>+</sup>), *m/z* 674.0374; found 674.0361.

**10**: NMR (C<sub>6</sub>D<sub>6</sub>): <sup>31</sup>P{<sup>1</sup>H} δ 45.6; <sup>1</sup>H δ 7.47–7.50 (m, 2 H, aryl), 6.92–6.95 (m, 2 H, aryl), 3.79 (s, 3 H, OCH<sub>3</sub>), 0.49 [s, 18 H, Si(CH<sub>3</sub>)<sub>3</sub>], 0.31 [s, 18 H, Si(CH<sub>3</sub>)<sub>3</sub>]; <sup>13</sup>C δ 161.6 (s, *p*-C<sub>aryl</sub>), 133.4 (d, <sup>3</sup>J<sub>PC</sub> 15 Hz, *m*-C<sub>aryl</sub>), 114.6 (d, <sup>2</sup>J<sub>PC</sub> 17 Hz, *o*-C<sub>aryl</sub>), 54.0 (s, OCH<sub>3</sub>), *ipso*-C<sub>aryl</sub> not observed.

§ *Crystal data*: **3b**: C<sub>19</sub>H<sub>43</sub>N<sub>2</sub>OPS<sub>3</sub>Si<sub>4</sub>Sn, *M* = 673.75, monoclinic, space group *I2/a*, *a* = 27.250(2), *b* = 11.542(1), *c* = 20.522(1) Å, β = 98.200(4)°, *U* = 6388.6(8) Å<sup>3</sup>, *Z* = 8, *D*<sub>c</sub> = 1.401 g cm<sup>–3</sup>, *F*(000) = 2784, *T* = 183(2) K. 7313 independent reflections were collected on a Siemens P4 diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å, 2.01° < θ < 27.50°, μ = 4.35 cm<sup>–1</sup>); an absorption correction was applied: *wR*<sub>2</sub> = 0.0578, *R* = 0.0261 for reflections with *I* > 2σ(*I*).

**10**: C<sub>28</sub>H<sub>28</sub>GeO<sub>4</sub>P<sub>4</sub>S<sub>4</sub>, *M* = 753.21, monoclinic, space group *C2/c*, *a* = 24.248(6), *b* = 7.931(1), *c* = 20.152(5) Å, β = 122.34(1)°, *U* = 3274.5(1) Å<sup>3</sup>, *Z* = 4, *D*<sub>c</sub> = 1.528 g cm<sup>–3</sup>, *F*(000) = 1536, *T* = 293(2) K. 3721 independent reflections were collected on an Enraf Nonius CAD4 diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å, 2.39° < θ < 27.50°, μ = 14.19 cm<sup>–1</sup>); an absorption correction was applied: *wR*<sub>2</sub> = 0.1243, *R* = 0.0499 for reflections with *I* > 2σ(*I*). CCDC 182/691.

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