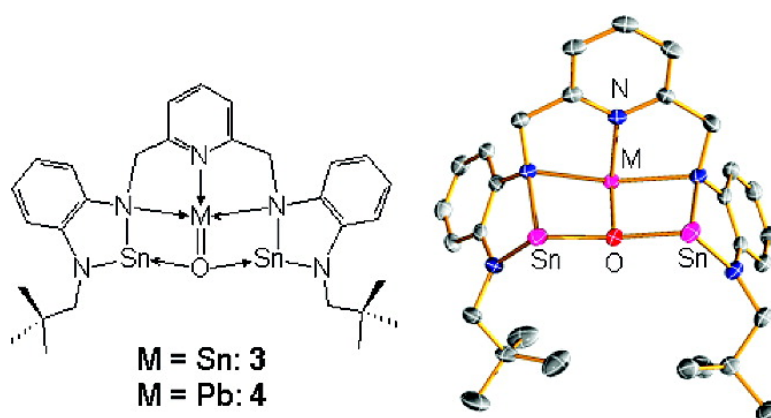


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Trapping of Tin(II) and Lead(II) Homologues of Carbon Monoxide by a Benzannulated Lutidine-Bridged Bisstannylene

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Within the resurgence of interest in stable N-heterocyclic carbenes over the last years,¹ the chemistry of their heavier analogues, silylenes,² germylenes,³ stannylenes,^{3a,4} and plumbylenes,^{3a,5} has also attracted considerable interest. Only a few bis- or polystannylene ligands are known,⁶ one of which was previously reported to act in a chelating fashion.^{6c} In analogy to benzannulated bisgermylenes,⁷ we have described benzannulated bisgermylenes which can act as chelating ligands toward transition metals.⁸ Here we describe the preparation of a benzannulated lutidine-bridged bisstannylene and its unusual coordination chemistry.

Bisstannylene **2** was prepared by a transamination reaction between the tetraamine **1** and Sn[N(SiMe₃)₂]₂⁹ (Scheme 1). The ¹¹⁹Sn NMR spectrum of **2** in toluene-*d*₈ shows a remarkable highfield shift of the tin resonance ($\delta = 132.4$ ppm) compared to *N,N'*-dialkylbenzimidazolin-2-stannylenes ($\delta = 222$ –269 ppm)^{4d} which we attribute to inter- or intramolecular Sn...N interactions similar to those observed for monodentate N-heterocyclic stannylenes.^{4d} The ¹¹⁹Sn NMR resonance of **2** is further highfield shifted in THF-*d*₈ ($\delta = 107.3$ ppm), presumably due to solvent coordination to the empty p-orbital at the tin atom.

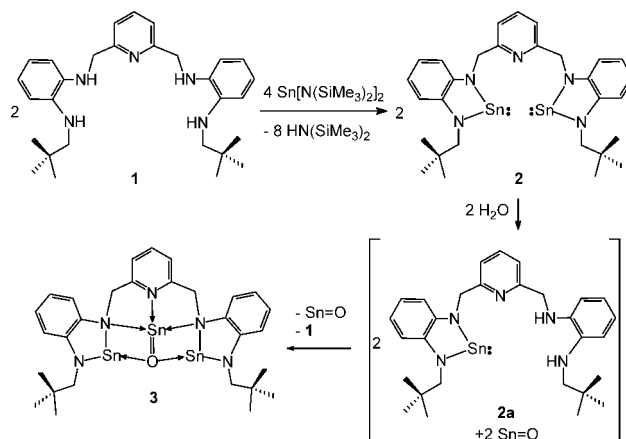
The reaction of bisstannylene **2** with 1 equiv of water gave the complex of the bisstannylene **2** with tin(II) monoxide **3** (Scheme 1). The initially obtained monostannylene **2a** is apparently not stable but disproportionates to give the bisstannylene **2** and tetraamine **1**; the latter was identified in the reaction mixture by NMR spectroscopy. Bisstannylene **2** then reacts with the generated tin(II) monoxide to give complex **3** in 28% yield. The formation of more complicated clusters, exhibiting Sn–O bonds, has been observed by Veith et al.¹⁰ upon partial hydrolysis of aminostannylenes.

Subsequently, we found that the hydrolysis of the simple diaminostannylene Sn[N(SiMe₃)₂]₂ followed by the addition of **2** yields directly complex **3** in 44% yield (Scheme 2). The related reaction with Pb[N(SiMe₃)₂]₂ gave complex **4** containing a trapped Pb=O moiety in 56% yield.

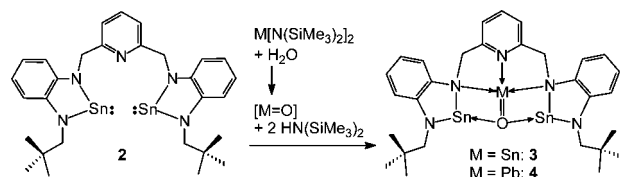
An X-ray diffraction study of an orange crystal of complex **3** shows that the lutidine moiety is coordinated in an almost perpendicular orientation (93.75(10)°) relative to the Sn=O group (Figure 1). Tin atom Sn3 gains additional electron density from the nitrogen atoms N2 and N4 of the bisstannylene moiety. The coordination geometry of the central core in **3** is best described as a tetragonal pyramid with the basal plane made up from atoms O1, N2, N3, and N4 and atom Sn3 at the apex.

The interatomic distances Sn3–N2, Sn3–N4, and Sn3–N3 (2.370(3), 2.393(3), and 2.294(3) Å) are shorter than those observed for coordinative Sn–N interactions (2.611(2)–

Scheme 1. Preparation of the Bisstannylene **2** and its Hydrolysis with Formation of Complex **3**



Scheme 2. Preparation of Complexes **3** and **4**



2.612(2),^{4d} 2.497(2)–2.541(2) Å¹¹ for benzannulated monostannylenes) but longer than covalent Sn–N bonds (2.079(2)–2.189(2),^{4d} 2.101(2)–2.202(2) Å¹¹ for benzannulated monostannylenes). The intracyclic Sn1–N2 and Sn2–N4 bond distances (2.202(3) and 2.211(3) Å) involving nitrogen atoms coordinated to the Sn=O moiety are significantly longer than the other intracyclic Sn1–N1 and Sn2–N5 bonds (2.098(3) and 2.103(3)

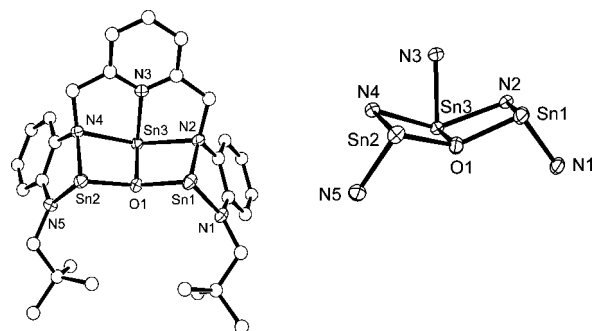


Figure 1. Molecular structure of **3** and coordination environment of the tin atoms.

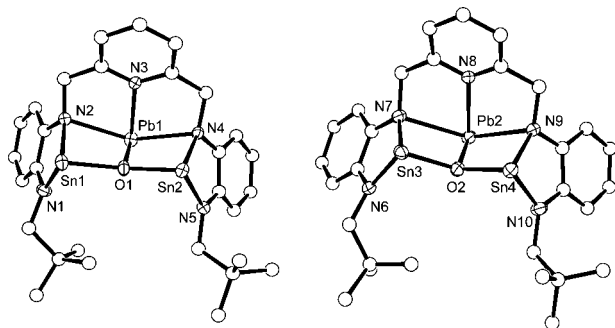


Figure 2. Molecular structures of **4a** (left) and **4b** (right).

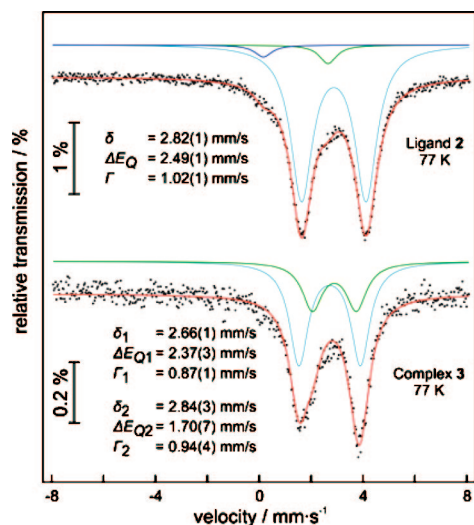


Figure 3. Measured and simulated Mössbauer spectra for the free bisstannylene ligand **2** (top) and complex **3** (bottom).

Å). The electron pairs at the atoms N2 and N4 interact not only with the vacant p-orbitals at atoms Sn1 and Sn2 within the stannylene heterocycle but also with atom Sn3, causing the reduced bond order for the Sn1–N2 and Sn2–N4 bonds. The Sn3=O1 bond (2.079(2) Å) is slightly shorter than the Sn1–O1 and Sn2–O1 bonds (2.114(2) and 2.135(2) Å). These values compare well to the Sn–O separation (2.224(8) Å) found in blue-black polymeric (SnO)_∞, which like **3** contains also a square-pyramidal coordinated Sn atom.¹²

The X-ray diffraction study of **4** shows two different molecules **4a** and **4b** to coexist in the asymmetric unit (Figure 2). They significantly differ from each other by the angles between the two stannylene moieties (**4a**: N2/Sn1/N1 and N4/Sn2/N5 42.12° vs **4b**: N7/Sn3/N6 and N9/Sn4/N10 62.25°) and by the Pb–O distances (**4a**: 2.157(5) Å; **4b**: 2.178(5) Å). These differences are caused by an intermolecular interaction of atom Pb2 with the aromatic ring of a stannylene ligand from a neighboring molecule in the solid state (see Supporting Information). Similar interactions between a vacant p-orbital at a lead(II) atom and the π -system of the benzene ring of an adjacent molecule were recently observed for monodentate benzannulated plumblylenes.⁵ The bisstannylene ligand **2** in **4a,b** coordinates

to the lead(II) monoxide moiety in a fashion similar to its coordination to Sn=O in complex **3**.

The valence states of the tin atoms in the complexes **3** and **4** were estimated by Mössbauer spectroscopy (Figure 3). The ¹¹⁹Sn Mössbauer spectrum clearly shows the presence of nonequivalent tin atoms for **3** and can be simulated as addition of two signals with relative intensities of 2:1. For both tin atoms in **3**, the values of the isomer shifts are typical for divalent tin (δ = 2.66(1) and 2.84(3) mm/s). The Mössbauer spectrum nicely reflects the changes in electron density upon complex formation. Only one signal (δ = 2.63(1) mm/s, subject to quadrupole splitting) was observed for complex **4**.

We have prepared a lutidine-linked bisstannylene ligand **2** with pincer topology. The bisstannylene ligand is capable of binding and stabilizing Sn=O or Pb=O moieties in complexes **3** and **4**, respectively. ¹¹⁹Sn Mössbauer spectroscopy shows the tin atoms in **3** and **4** retain their stannylene character. Further studies are directed toward the binding and stabilization of Ge=O and Si=O with ligands of type **2**.

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Supporting Information Available: Experimental details for the synthesis of **2**, **3**, and **4** and X-ray crystallographic files for compounds **3** and **4** in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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