

PAPER

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9582

Rearrangement of a Ge(II) aryloxide to yield a new Ge(II) oxo-cluster [Ge₆(μ₃-O)₄(μ₂-OC₆H₂-2,4,6-Cy₃)₄](NH₃)_{0.5}: main group aryloxides of Ge(II), Sn(II), and Pb(II) [M(OC₆H₂-2,4,6-Cy₃)₂]₂ (Cy = cyclohexyl)[†]

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The new Ge(II) cluster [Ge₆(μ₃-O)₄(μ₂-OC₆H₂-2,4,6-Cy₃)₄](NH₃)_{0.5} (**1**) and three divalent Group 14 aryloxide derivatives [Ge(OC₆H₂-2,4,6-Cy₃)₂]₂ (**2**), [Sn(OC₆H₂-2,4,6-Cy₃)₂]₂ (**3**), and [Pb(OC₆H₂-2,4,6-Cy₃)₂]₂ (**4**) of the new tricyclohexylphenyloxo ligand, [(OC₆H₂-2,4,6-Cy₃)₂] (Cy = cyclohexyl), were synthesized and characterized. Complexes **1–4** were obtained by reaction of the metal bisilylamides M(N(SiMe₃)₂)₂ (M = Ge, Sn, Pb) with 2,4,6-tricyclohexylphenol in hexane at room temperature. If the freshly generated reaction mixture for the synthesis of **2** is stirred in solution for 12 h at room temperature, the cluster [Ge₆(μ₃-O)₄(μ₂-OC₆H₂-2,4,6-Cy₃)₄](NH₃)_{0.5} (**1**), which features a rare Ge₆O₈ core that includes ammonia molecules in non-coordinating positions, is formed. Complexes **3** and **4** were also characterized via ¹¹⁹Sn {¹H} NMR and ²⁰⁷Pb NMR spectroscopy and feature signals at −280.3 ppm (¹¹⁹Sn{¹H}, 25 °C) and 1541.0 ppm (²⁰⁷Pb, 37 °C), respectively. The spectroscopic characterization of **3** and **4** extends known ¹¹⁹Sn parameters for dimeric Sn(II) aryloxides, but data for ²⁰⁷Pb NMR spectra for Pb(II) aryloxides are rare. We present also a rare VT-NMR study of a homoleptic 3-coordinate Pb(II) aryloxide. The crystal structures of **2**, **3**, and **4** feature interligand H⋯H contacts that are similar in number to those of related transition metal derivatives despite the larger size of the group 14 elements.

Received 25th March 2023,
Accepted 21st June 2023

DOI: 10.1039/d3dt00906h

rsc.li/dalton

Introduction

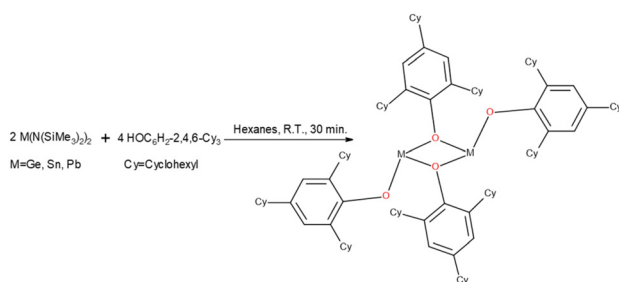
The main group bisilylamides M(N(SiMe₃)₂)₂ (M = Ge, Sn, Pb)^{1,2} are frequently employed in the synthesis of low oxidation state complexes of Ge(II), Sn(II), and Pb(II) complexes, several of which can act as precursors to nanomaterials.^{3–5} Thus, for the Ge nanomaterials, Ge(II) alkoxide and aryloxides have been synthesized as precursors for materials that could potentially replace silicon-based nanomaterials owing to the higher electron and hole mobility⁸ and smaller band gap in germanium species in contrast to those of silicon.⁹ In com-

parison to their Sn(II) analogs,^{10–19} however, low-coordinate Ge(II) and Pb(II)^{12,20–22} complexes are relatively scarce. For example, Ge(II)-oxo dimers [Ge(OR)₂]₂, monomers Ge(OR)₂, and calixarene complexes have been reported in approximately equal numbers.^{6,7,11,14–16} But, there are just three homoleptic germanium complexes of formula [Ge(OR)₂]₂ (R = −C₆H₃-2,6-Prⁱ₂, −C₆H₂-2,4,6-Me₃, −C₆H₃-2,6-Me₂).^{6,23} For lead, only one homoleptic Pb(II) aryloxide [Pb(OC₆H₃-2,6-Ph₂)₂]₂ has been characterized.²⁰ Similarly, Weinert, Guzei, Rheingold, and Sita isolated a heteroleptic Pb(II) trimethylsilanolato dimer in 1997.²¹ Extensive compilations of ¹¹⁹Sn NMR parameters for Sn(II) aryloxides can be found in reviews by Wrackmeyer,²⁴ Weinert,²⁵ and Takeuchi and Takayama.²⁶ However, ²⁰⁷Pb NMR and solution-phase ⁷³Ge NMR data for two or three-coordinate Pb(II) and Ge(II) aryloxides are very scarce.^{12,24–31} We report herein the synthesis and characterization of 3-coordinate, homoleptic aryloxide dimers of Ge(II), Sn(II), and Pb(II), with the tin and lead analogues characterized by heteronuclear NMR spectroscopy. Additionally, we detail the isolation and characterization of a rare Ge₆O₈ aryloxo cluster formed from the rearrangement of the Ge(II) aryloxo dimer.

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Results and discussion

The synthesis of the compounds in this article involves amine elimination from the divalent group 14 element amides *via* the reaction with 2,4,6-tricyclohexylphenol (Scheme 1). This produces, in the first instance, the simple divalent aryloxides $M(\text{OC}_6\text{H}_2\text{-}2,4,6\text{-Cy}_3)_2$ ($M = \text{Ge}, \text{Sn}, \text{and Pb}$), which crystallize in good yield as the dimers $[M(\text{OC}_6\text{H}_2\text{-}2,4,6\text{-Cy}_3)_2]_2$ ($M = \text{Ge}, 2; \text{Sn}, 3; \text{Pb}, 4$). If the solution of complex 2 is stirred overnight at room temperature in hexanes without isolation of the aryloxide, the solution darkens from pale yellow to orange. Removing the solvent under reduced pressure and washing the crude yellow solid with cold hexane four times (*ca.* 5 mL) until the washings become colorless, followed by recrystallization of the remaining solids from *ca.* 10 mL hot (*ca.* 100 °C) toluene, produced colorless rectangular plates of 1 (Fig. 1). Complex 1 is a Ge_6O_8 cluster composed of two 4-coordinate $\text{Ge}(\text{II})$ “caps” and four 3-coordinate $\text{Ge}(\text{II})$ atoms. This arrangement gives alternating faces composed of four Ge_2O_2 rings and four Ge_3O_3 rings (Fig. S19†). There are four ammonia molecules per unit cell nestled between the flanking cyclohexyl rings of



Scheme 1 Synthesis of compounds 2–4.

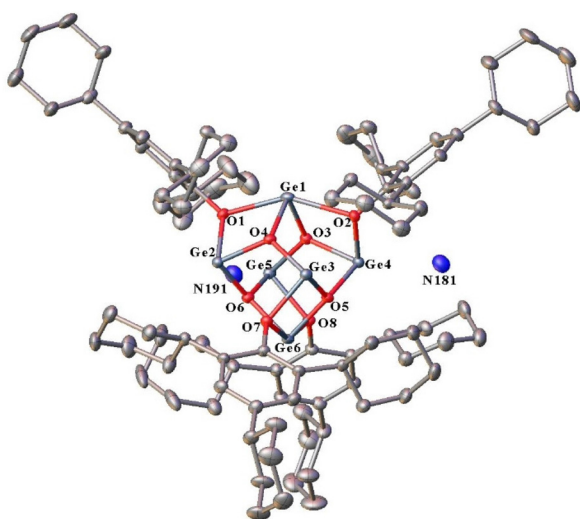


Fig. 1 Crystal structure of compound 1 featuring a Ge_6O_8 core with thermal ellipsoids shown at 30%. Co-crystallized solvent molecules (toluene) and hydrogen atoms not shown. R_1 : 0.074.

the ligand in two 25% occupancy general positions. The distance from the nitrogen atoms to the nearest $\text{Ge}(\text{II})$ atom is *ca.* 2.86 Å. This observation is the first of its kind, as ammonia has never been reported in non-coordinating positions in $\text{Ge}(\text{II})$ oxo clusters.³² There are extensive $\text{H}\cdots\text{H}$ contacts between the ammonia hydrogens and those of the flanking cyclohexyl rings. Placing crystals of cluster 1 under reduced pressure (*ca.* 0.01 torr) at ambient temperature for 30 min reveals that the ammonia molecules are tenaciously held between the cyclohexyl substituents of the aryloxo ligands, since an $\nu\text{N-H}$ absorption at 3610 cm^{-1} is observable in the IR spectrum.

Few instances of $\text{Ge}(\text{II})$ dimers rearranging to form “ Ge_xO_y ” clusters exist in the literature. The first examples, which yielded $[\text{Ge}_4(\mu\text{-O})_2(\text{OC}_6\text{H}_3\text{-}2\text{-Bu}^t\text{-}4\text{-Me})_4\text{NH}_3]_2$ and $[\text{Ge}_8(\mu_3\text{-O})_6(\text{OC}_6\text{H}_3\text{-}2\text{-Bu}^t\text{-}4\text{-Me})_4]$ were reported by the group of Weinert in 2009.³² Weinert and coworkers determined that the driving force for the rearrangement and subsequent generation of similar clusters is a result of the formation of a silyl ether and ammonia, produced from a side reaction between the substituted phenol and $\text{HN}(\text{SiMe}_3)_2$.³² To check if cluster 1 is formed from the decomposition of 2 (Fig. 2) in solution over time or *via* a similar mechanism to that reported by Weinert,³² pure 2 was placed in an NMR tube and monitored by ^1H NMR spectroscopy over 14 days. These showed that 2 is stable in deuterated toluene at room temperature when protected from air and moisture. The same sample was then exposed to the atmosphere under ambient conditions for 24 h and analysis *via* ^1H NMR spectroscopy did not indicate the formation of 1.

The synthesis of complex 1 was repeated in hexane at room temperature with a 3 : 4 $\text{Ge}(\text{II})$ to phenol ratio, since the aryloxo ligands are also the source of the $\mu_3\text{-oxo}$ ligands in the cluster,³² and stirred overnight in a hexane solution which produced crystalline 1. Notably, previously reported rearrangements occurred with ligands lacking substituents at one or both *ortho*-positions of the aryl ring.³² Thus, the formation of

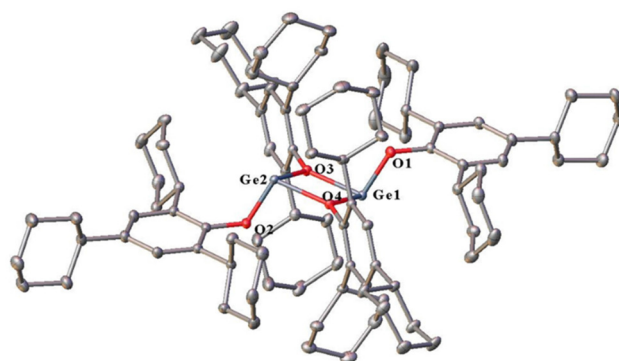


Fig. 2 Crystal structure of $[\text{Ge}(\text{OC}_6\text{H}_2\text{-}2,4,6\text{-Cy}_3)_2]_2$ (2) with thermal ellipsoids shown at 30%, hydrogen atoms are not shown. R_1 : 0.034. Selected distances (Å) and angles (°): $\text{Ge}\cdots\text{Ge}$ 3.2593(6) Å. Ge1-O1 1.8300(10) Å. Ge1-O3 2.0056(10) Å. Ge1-O4 2.0070(10) Å. Ge2-O2 1.8324(10) Å. Ge2-O3 2.0087(10) Å. Ge2-O4 2.0042(10) Å. O1-Ge1-O3 97.20(4)°. O1-Ge1-O4 99.01(4)°. O3-Ge1-O4 71.37(4)°. O2-Ge2-O3 99.43(4)°. O2-Ge2-O4 97.13(4)°. O3-Ge2-O4 71.37(4)°.

1 challenges the conclusions previously reported, which stated the formation of Ge(II) oxo clusters only occurs if one or both *ortho* positions of the ligand are lacking a substituent.³² Only one other Ge₆O₈ cluster, the [Ge₆(μ₃-O)₄(μ₂-OC₆H₄-4-Bu^t)₄] species, has been reported to date. However, it was described in a Ph.D. dissertation but has not been published apart from a CCDC report. It was synthesized from the less sterically encumbering phenol HOC₆H₄-4-Bu^t and Ge(N(SiMe₃)₂)₂.³³ Notably, there are no NH₃ molecules present which render the molecular formula and structure of cluster **1** unique. The average μ₂-O-Ge distances in complex **1** are longer than those in the closely related [Ge₆(μ₃-O)₄(μ₂-OC₆H₄-4-Bu^t)₄]³³ cluster by *ca.* 0.077 Å (Table 1) with a similar variation in the individual distances, while the average μ₃-O-Ge distances are shorter by *ca.* 0.047 Å with less variation than those observed in [Ge₆(μ₃-O)₄(μ₂-OC₆H₄-4-Bu^t)₄]. Likewise, the average C-O distances are longer and have a smaller variation in distance than those in all of the reported clusters, which vary between 1.373 Å–1.409 Å.

Complex **2** features a dimeric arrangement of two Ge(OC₆H₂-2,4,6-Cy₃)₂ units in which two bridging and two terminal aryloxy ligands adopt a *trans* configuration (Fig. 3). The *trans* arrangement of the ligands is analogous to those in known dimeric Ge(II) aryloxides (Table 2),^{6,23} although such examples remain uncommon despite interest in the application of Ge(II) alkoxy and aryloxy precursors for nanomaterials.^{6–8} The terminal Ge–O bond lengths of 1.831(2) Å (ave.) are slightly (*ca.* 0.009 Å) longer than those in [Ge(OC₆H₃-2,6-Me₂)₂]₂⁶ (av. 1.822(21) Å), while the average bridging Ge–O distance of 2.006(3) Å is slightly longer by *ca.* 0.022 Å (Table 2). The Ge...Ge separation is also longer by *ca.*

Table 2 Selected average distances (Å) and angles (°) in **2** and related [Ge(OR)₂]₂ dimers

Complex	Ge...Ge (Å)	Terminal Ge–O (Å)	Bridging μ ₂ -O–Ge (Å)
[Ge(OC ₆ H ₂ -2,4,6-Cy ₃) ₂] ₂ (2)	3.2593(6)	1.831(2)	2.006(2)
[Ge(OC ₆ H ₃ -2,6-Pr ⁱ) ₂] ₂ ²³	3.2115(4)	1.824(1)	1.997(15)
[Ge(OC ₆ H ₂ -2,4,6-Me ₃) ₂] ₂ ²³	3.2090(8)	1.825(4)	1.984(2)
[Ge(OC ₆ H ₃ -2,6-Me ₂) ₂] ₂ ⁶	3.1991(12)	1.822(21)	1.984(7)

0.06 Å, likely as a result of the increase in steric pressure on changing from methyl to cyclohexyl substituents. Similarly, the Ge...Ge distance, terminal Ge–O and bridging μ₂-O–Ge distances are all longer (Table 2) in [Ge(OC₆H₂-2,4,6-Cy₃)₂]₂ (**2**) than in [Ge(OC₆H₂-2,4,6-Me₃)₂]₂.²³ A comparison of bond lengths in complex **2** to those in [Ge(OC₆H₃-2,6-Prⁱ)₂]₂²³ is consistent with the steric similarity of isopropyl and cyclohexyl substituents.^{34,35} The Ge...Ge distance in **2** is *ca.* 0.048 Å longer than in [Ge(OC₆H₃-2,6-Prⁱ)₂]₂ while the average terminal Ge–O distances are similar (*ca.* 0.007 Å). The average bridging μ₂-O–Ge distances in **2** are slightly longer (*ca.* 0.009 Å), but this value is misleading as one of the four μ₂-O–Ge bond lengths in [Ge(OC₆H₃-2,6-Prⁱ)₂]₂ is identical (2.008(2) Å), one is longer (2.012(2) Å), and the remaining two are shorter (1.981(2) Å and 1.988(2) Å) than those in **2** (Fig. 2). The melting point of **2** is significantly lower (by *ca.* 12 °C) than those of its heavier congeners Sn and Pb, despite having a similar amount of interligand H...H close contacts between discrete molecules in the solid-state structure. Complex **2** crystallizes as colorless rectangular plates from toluene and hexane, but solutions of **2** are pale yellow in both solvents. Accordingly, the UV-Vis spectrum shows two absorbances, with one in the visible region, at 283 (7863 ε/M^{–1} cm^{–1}) and 338 nm (3200 ε/M^{–1} cm^{–1}). The ¹H NMR spectrum shows broadening of various signals in the alkyl region indicative of a dynamic system with potential exchange between terminal and bridging aryloxy ligands as well as inversion of the *trans* arrangement of the Ge₂O₂ rhomboid center.²³ A comparison of the number of interligand H...H close contacts (≤2.4 Å) in [Ge(OC₆H₃-2,6-Prⁱ)₂]₂²³ to [Ge(OC₆H₂-2,4,6-Cy₃)₂]₂ (**2**) demonstrates that despite slight increases in bond lengths, there is a substantial increase in dispersion energy donor^{36,37} interactions in the case of **2** (Fig. 3). [Ge(OC₆H₃-2,6-Prⁱ)₂]₂ features six interligand H...H close contacts, with four of the six contacts originating from a methyne hydrogen on the isopropyl substituents. In contrast, [Ge(OC₆H₂-2,4,6-Cy₃)₂]₂ (**2**) has sixteen interligand H...H close contacts, with three originating from a methyne hydrogen on the cyclohexyl groups.

The bonding in **3** (Fig. 4) and **4** (Fig. 5) is analogous to that in **2** since both complexes are dimers with a *trans* configuration of the ligands. The average terminal (2.030(8) Å) and bridging (2.186(18) Å) Sn–O bond lengths in **3** lie between values reported for monomers,^{11–15,17,38} dimers,^{18,19} and dinuclear tin(II) calixarenes.¹⁶ The terminal Sn2–O2 distance is *ca.* 0.011 Å shorter than the terminal Sn1–O1 distance, both distances are similar to the sum of the covalent radii for a

Table 1 Selected distances and angles in **1** and in other “Ge_xO_y” clusters

Complex	μ ₂ -O–Ge (Å) (average)	μ ₃ -O–Ge (Å) (average)	C–O (Å) (average)
[Ge ₆ (μ ₃ -O) ₄ (μ ₂ -OC ₆ H ₂ -2,4,6-Cy ₃) ₄](NH ₃) _{0.5} (1)	2.127(17)	1.923(3)	1.408(5)
[Ge ₆ (μ ₃ -O) ₄ (μ ₂ -OC ₆ H ₄ -4-Bu ^t) ₄] ³³	2.05(16)	1.97(14)	1.375(7)
[Ge ₄ (μ ₃ -O) ₂ (OC ₆ H ₃ -2-Bu ^t -4-Me) ₄ ·NH ₃] ₂ ³²	1.784(2)	N/A	1.384(4)
[Ge ₈ (μ ₃ -O) ₆ (OC ₆ H ₃ -2-Bu ^t -4-Me) ₄] ³²	N/A	1.920(26)	1.392(9)

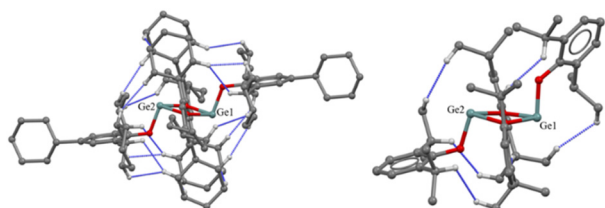


Fig. 3 Interligand H...H close (≤2.4 Å) contacts in [Ge(OC₆H₂-2,4,6-Cy₃)₂]₂ (**2**, left) and the sterically related complex [Ge(OC₆H₃-2,6-Prⁱ)₂]₂ (right).²³ Interligand H...H close contacts are shown in blue, hydrogen atoms not in close contact are not shown.

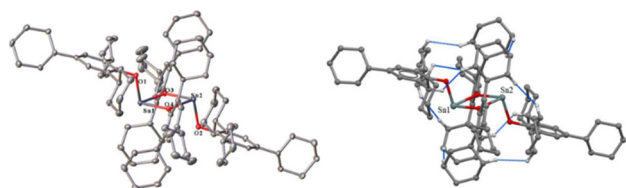


Fig. 4 Left: crystal structure of $[\text{Sn}(\text{OC}_6\text{H}_2\text{-}2,4,6\text{-Cy}_3)_2]_2$ (**3**) with thermal ellipsoids shown at 30%, hydrogen atoms and solvent molecules (toluene) not shown. R_1 : 0.044. Sn1-Sn2 3.5907(7) Å. Sn1-O1 2.035(4) Å. Sn1-O3 2.199(4) Å. Sn1-O4 2.166(4) Å. Sn2-O2 2.024(4) Å. Sn2-O3 2.174(3) Å. Sn2-O4 2.203(4) Å. O1-Sn1-O3 95.82(14)°. O1-Sn1-O4 95.74(14)°. O3-Sn1-O4 69.65(12)°. O2-Sn2-O3 96.44(14)°. O2-Sn2-O4 96.45(14)°. O3-Sn2-O4 69.42(13)°. Right: molecular model of **3** showing interligand $\text{H}\cdots\text{H}$ close contacts (≤ 2.4 Å) in blue, hydrogen atoms participating in close contacts are shown.

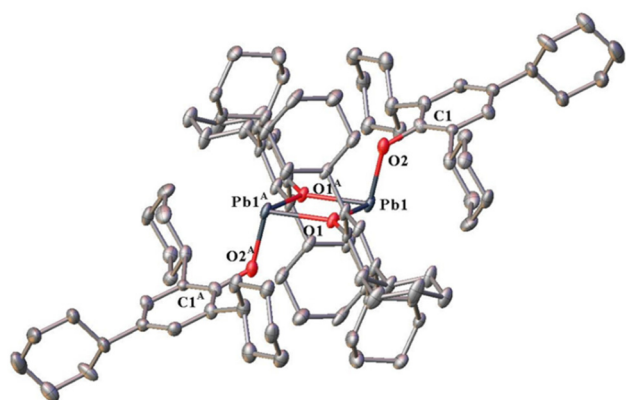


Fig. 5 Crystal structure of dimeric $[\text{Pb}(\text{OC}_6\text{H}_2\text{-}2,4,6\text{-Cy}_3)_2]_2$ (**4**) with thermal ellipsoids shown at 30%, with hydrogen atoms and co-crystallized solvent molecules (toluene) not shown. R_1 : 0.047. Selected distances (Å) and angles (°): Pb1-Pb1A 3.7725(7). Pb1-O2 2.117(6). Pb1-O1 2.284(4). Pb1-O1A 2.302(4). O1-Pb1-O2 93.87(17). O2-Pb1-O1A 98.65(17). O1-Pb1-O1A 69.34(15).

Sn-O single bond (2.03 Å).³⁹ A similar characteristic is observed in the bridging bonds of complex **3** as the Sn1-O4 and Sn2-O3 distances are shorter than the Sn1-O3 and Sn2-O4 distances by *ca.* 0.03 Å, resulting in the larger standard deviation in the average Sn-O distances for both the terminal and bridging Sn-O bonds. There are nine interligand $\text{H}\cdots\text{H}$ contacts in $[\text{Sn}(\text{OC}_6\text{H}_2\text{-}2,4,6\text{-Cy}_3)_2]_2$ (**3**) while there are sixteen in $[\text{Ge}(\text{OC}_6\text{H}_2\text{-}2,4,6\text{-Cy}_3)_2]_2$ (**2**). The decrease in the number of $\text{H}\cdots\text{H}$ close contacts is likely due to the increase in M-O ($\text{M} = \text{Ge}, \text{Sn}$) bond distances, since the radii of Ge and Sn differ by 0.19 Å.³⁹ Multiple heteroleptic Sn(II) aryloxo dimers ligated by similar ligands to 2,4,6-tricyclohexylphenol have been

reported,^{10,18,19} with the majority of the homoleptic examples existing as monomers^{10,11,18} which are stabilized by bulkier terphenyl or calixarene ligands.^{12–16,38} Reactions of the sterically unencumbering phenol $\text{HOC}_6\text{H}_4\text{-}2\text{-Me}$ with $[\text{Sn}(\text{NMe}_2)_2]_2$ produced a polymeric structure $[\text{Sn}(\mu\text{-OC}_6\text{H}_4\text{-}2\text{-Me})_2]_\infty$, while $\text{HOC}_6\text{H}_3\text{-}2,6\text{-Me}_2$ and $\text{HOC}_6\text{H}_3\text{-}2,6\text{-Pr}^i_2$ formed dimers, with the latter ligated by one NMe_2 group at one of the Sn(II) centers.¹⁸ In contrast, the reaction of $\text{HOC}_6\text{H}_3\text{-}2,6\text{-Bu}^t_2$ with $[\text{Sn}(\text{NMe}_2)_2]_2$ afforded a monomer,¹⁸ which is similar in structure to Lappert and Atwood's $\text{M}(\text{OAr})_2$ monomers ($\text{M} = \text{Ge}, \text{Sn}, \text{Pb}, \text{Ar} = \text{-C}_6\text{H}_2\text{-}2,4,6\text{-Bu}^t_3$ or $\text{-C}_6\text{H}_2\text{-}2,6\text{-Bu}^t_2\text{-}4\text{-Me}$).¹¹

Available data for both monomeric^{12,22,28} and dimeric^{20,21} homoleptic Pb(II) aryloxides are limited, with the former representing the majority by a substantial (6 : 1) margin. A comparison of reported Pb-O bond lengths to those of **4** (Fig. 5) shows that the terminal Pb-O bonds (av. 2.128(2) Å) in **4** are shorter than those in $[\text{Pb}(\text{OC}_6\text{H}_3\text{-}2,6\text{-}(\text{C}_6\text{H}_3\text{-}2,6\text{-Pr}^i_2)_2)]_2$,²² presumably as a result of the steric requirements of the terphenyl in comparison to those of the 2,4,6-tricyclohexylphenoxo ligand. The bond lengths in **4** are also similar to those in the monomeric 2- and 4-coordinate Pb(II) calixarenes $[\text{Pb}(\text{thiacalix}[4]\text{arene}^{\text{t-Bu}}(\text{O})_2(\text{OSi}^i\text{Pr}_3)_2)]$ and $[\text{Pb}(\text{thiacalix}[4]\text{arene}^{\text{t-Bu}}(\text{O})_2(\text{OBn})_2)]$ ($\text{Bn} = \text{benzyl}$), respectively.¹² The terminal (2.117(6) Å) and bridging (2.293(10) Å) Pb-O bonds in **4** are shorter than those in the dimer $[\text{Pb}(\text{OC}_6\text{H}_3\text{-}2,6\text{-Ph}_2)]_2$.²⁰ Both terminal and bridging C-O distances in $[\text{Pb}(\text{OC}_6\text{H}_3\text{-}2,6\text{-Ph}_2)]_2$ are shorter than those of complex **4** by *ca.* 0.11 Å and *ca.* 0.018 Å, respectively, despite the increase in size of the aryl ring substituents. However, the terminal and bridging Pb-O distances in $[\text{Pb}(\text{OC}_6\text{H}_3\text{-}2,6\text{-Ph}_2)]_2$ are significantly longer than those in **4** by *ca.* 0.13 Å and *ca.* 0.054 Å, respectively, while the $\text{Pb}\cdots\text{Pb}$ separation is also longer by *ca.* 0.061 Å (Table 3). There are eight interligand $\text{H}\cdots\text{H}$ close (≤ 2.4 Å) contacts in $[\text{Pb}(\text{OC}_6\text{H}_2\text{-}2,4,6\text{-Cy}_3)_2]_2$ (**4**), while there is only one present in $[\text{Pb}(\text{OC}_6\text{H}_3\text{-}2,6\text{-Ph}_2)]_2$ (Fig. 6). Due to the greater inductive effect of the phenyl residue compared to cyclohexyl, in addition to the π -donating capability of the phenyl group, the expected Pb-O and $\text{Pb}\cdots\text{Pb}$ distances should be shorter in $[\text{Pb}(\text{OC}_6\text{H}_3\text{-}2,6\text{-Ph}_2)]_2$ than in **4** as a result of greater electrostatic interaction. However, we observe shorter distances in **4**, and we propose that the increase in dispersion energy donor interactions upon exchanging the *ortho* substituents of $[\text{Pb}(\text{OC}_6\text{H}_3\text{-}2,6\text{-Ph}_2)]_2$ for the cyclohexyl groups in $[\text{Pb}(\text{OC}_6\text{H}_2\text{-}2,4,6\text{-Cy}_3)_2]_2$ is responsible for the decrease in Pb-O and $\text{Pb}\cdots\text{Pb}$ distances, counter to the steric considerations. Notably, the $[\text{Pb}(\text{OC}_6\text{H}_3\text{-}2,6\text{-Ph}_2)]_2$ ²⁰ complex is the only other 3-coordinate Pb(II) aryloxo dimer included in the Cambridge Crystallographic Structural Database.

Analysis of **3** *via* $^{119}\text{Sn}\{^1\text{H}\}$ NMR spectroscopy confirms that the structure remains associated in solution at room tempera-

Table 3 Comparison of selected average bond lengths (Å) in $[\text{Pb}(\text{OC}_6\text{H}_2\text{-}2,4,6\text{-Cy}_3)_2]_2$ (**4**) and $[\text{Pb}(\text{OC}_6\text{H}_3\text{-}2,6\text{-Ph}_2)]_2$ ²⁰

Complex	$\text{Pb}\cdots\text{Pb}$	Terminal Pb-O	Bridging Pb-O	Terminal C-O	Bridging C-O
$[\text{Pb}(\text{OC}_6\text{H}_2\text{-}2,4,6\text{-Cy}_3)_2]_2$	3.7725(7)	2.117(6)	2.293(10)	1.458(9)	1.387(7)
$[\text{Pb}(\text{OC}_6\text{H}_3\text{-}2,6\text{-Ph}_2)]_2$ ²⁰	3.833(8)	2.243(20)	2.347(26)	1.352(13)	1.369(9)

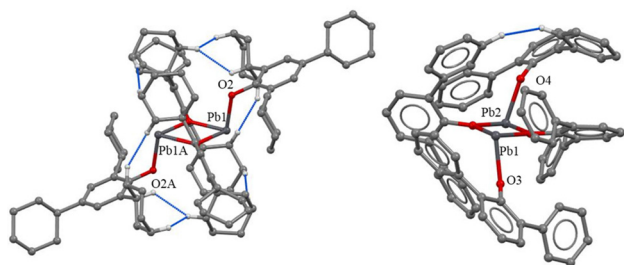


Fig. 6 Interligand H...H close (≤ 2.4 Å) contacts in $[\text{Pb}(\text{OC}_6\text{H}_2\text{-}2,4,6\text{-Cy}_3)_2]_2$ (**4**, left) and $[\text{Pb}(\text{OC}_6\text{H}_3\text{-}2,6\text{-Ph}_2)_2]_2$ (right).²⁰ Interligand H...H close contacts are shown in blue, hydrogen atoms not in close contact are not shown.

ture. Only one ^{119}Sn signal is observed at -280 ppm. From literature values,^{10,12,24} the expected shift of **3** should fall in the narrow range of $+138$ to -350 ppm observed for dimeric, 3-coordinate $\text{Sn}(\text{II})$ alkoxides and aryloxides (Table 4). A higher temperature was not required to observe the ^{119}Sn NMR resonance as the solubility of **3** in deuterated toluene was sufficient to observe a signal at room temperature. Due to the temperature sensitive nature of ^{119}Sn NMR chemical shifts, the sample was not subjected to variable temperature $^{119}\text{Sn}\{^1\text{H}\}$ NMR studies.^{10,24}

Few ^{207}Pb NMR data are available for $\text{Pb}(\text{II})$ aryloxides,^{12,22,27,28,30,31} and data for 3-coordinate $\text{Pb}(\text{II})$ aryloxide dimers were nonexistent. The majority of reported ^{207}Pb NMR chemical shifts concern lead compounds of biological relevance,²⁹ such as the calmodulin-type molecules which are bound to lead for toxicological studies. Coordination complexes of $\text{Pb}(\text{II})$ bound to EDTA have been heavily investigated.²⁸ While several complexes with structures similar to **4** have been reported (*vide supra*), no ^{207}Pb NMR parameters were given. Therefore, we estimated the shift of complex **4** (*vide infra*) based on data for 2-coordinate aryloxides of $\text{Pb}(\text{II})$ (Table 5). For 2-coordinate examples, the most relevant struc-

Table 4 ^{119}Sn NMR chemical shifts for two and three coordinate $\text{Sn}(\text{II})$ alkoxides and aryloxides 25°C unless otherwise indicated. A comprehensive list of ^{119}Sn NMR parameters for compounds with Sn -chalcogen bonds can be found in a ref. 24

Compound ^a	$\delta^{119}\text{Sn}$ NMR (ppm)
$[\text{Sn}(\text{thiacalix}[4]\text{arene}^{t\text{-Bu}}(\text{O})_2(\text{OBn})_2)]^{12}$	-647.3
$[\text{Sn}(\text{thiacalix}[4]\text{arene}^{t\text{-Bu}}(\text{O})_2(\text{OSi}^i\text{Pr}_3)_2)]^{12}$	-358.8
$[\text{Sn}(\mu\text{-OSiPh}_3)(\text{OSiPh}_3)_2]_{10}$	-338
$[(\text{DMP})\text{Sn}(\mu\text{-DMP})_2\text{-tol}]^{18}$	-293.5
$\text{Sn}(\text{OAr}^{\text{Dipp}})_2^{13}$	-289.7
$[\text{Sn}(\mu\text{-OC}_6\text{H}_2\text{-}2,4,6\text{-Cy}_3)(\text{OC}_6\text{H}_2\text{-}2,4,6\text{-Cy}_3)_2]^{10}$	-280.3
$[\text{Sn}(\mu\text{-O}^i\text{Pr})(\text{OSiPh}_3)_2]_{10}$	-246
$[\text{Sn}(\mu\text{-OSiPh}_3)(\text{Cl})_2]_{10}$	-202
$[\text{Sn}(\mu\text{-OPr}^i)(\text{OPr}^i)_2]_{10}$	-200 (60°C)
$[\text{Sn}(\mu\text{-O}^i\text{Pr})(\text{Cl})_2]_{10}$	-87
$[\text{Sn}(\text{OSiPh}_3)(\text{NMe}_2)_2]_{10}$	-38

^a DMP = dimethylpyridine; $\text{Ar}^{\text{Dipp}} = -\text{C}_6\text{H}_3\text{-}2,6\text{-(C}_6\text{H}_3\text{-}2,6\text{-Pr}^i_2)_2$; Bn = benzyl.

Table 5 Selected ^{207}Pb NMR parameters for $\text{Pb}(\text{II})$ aryloxides related species

Compound ^a	$\delta^{207}\text{Pb}$ NMR (ppm)
$[\text{Pb}(\text{EDTA})]^{2-}$ (ref. 28)	2441
$\text{Pb}(\text{EDTA-N}_2)^{28}$	2189
$[\text{Pb}(\text{OC}_6\text{H}_2\text{-Cy}_3)_2]_2$ (4)	1541.0 (37°C)
$[\text{Pb}(\text{thiacalix}[4]\text{arene}^{t\text{-Bu}}(\text{O})_2(\text{OSi}^i\text{Pr}_3)_2)]^{12}$	1210
$\text{Pb}(\text{OAr}^{\text{Dipp}})_2^{22}$	1070.3
$\text{Pb}(\text{OAr}^{\text{N}})_2^{30}$	141.5
$[\text{Pb}(\text{thiacalix}[4]\text{arene}^{t\text{-Bu}}(\text{O})_2(\text{OBn})_2)]^{12}$	111
PbL^{31}	-367

^a L = (R,R) -(-)- N,N' -bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclo-hexanedi-amine; $\text{OAr}^{\text{Dipp}} = \text{OC}_6\text{H}_3\text{-}2,6\text{-(C}_6\text{H}_3\text{-}2,6\text{-Pr}^i_2)_2$; $\text{OAr}^{\text{N}} = 2,4\text{-di-}t\text{-butyl-}6\text{-(1,4,7-trioxa-10-azacyclododec-10-ylmethyl)phenyl}$; Bn = Benzyl.

ture is $\text{Pb}(\text{OC}_6\text{H}_3\text{-}2,6\text{-(C}_6\text{H}_3\text{-}2,6\text{-Pr}^i_2)_2)$, which featured a ^{207}Pb NMR resonance at $+1070$ ppm.²² Several 4-coordinate $\text{Pb}(\text{II})$ calixarenes featured resonances in the range $+111$ ppm to $+1210$ ppm.¹²

As in the ^{119}Sn NMR spectroscopic studies, the ^{207}Pb NMR chemical shifts depend heavily upon coordination number, temperature, and electronegativity of the ligating atoms.²⁷ Given that complex **4** has 3-coordinate $\text{Pb}(\text{II})$ atoms, we expected to observe the signal between $+1210$ ppm and $+100$ ppm. However, the resonance was located further upfield than that of the two-coordinate complex $\text{Pb}(\text{OC}_6\text{H}_3\text{-}2,6\text{-(C}_6\text{H}_3\text{-}2,6\text{-Pr}^i_2)_2)$ at $+1541$ ppm. It should be noted that the signal for **4** was only observable above 37°C . Complex **4** is thermochromic, displaying a yellow color at room temperature and an orange-red color above 100°C in both the solid state and in solution. The yellow color reappears upon returning to room

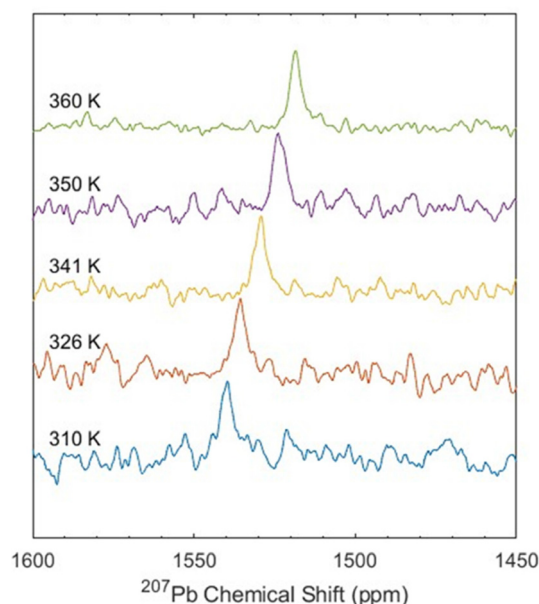


Fig. 7 ^{207}Pb Chemical shift (ppm) as a function of temperature. ^{207}Pb (500 MHz, C_7D_8) (310 K) 1541 ppm, (326 K) 1534 ppm, (341 K) 1529 ppm, (350 K) 1524 ppm, (360 K) 1519 ppm.

temperature. A ^{207}Pb VT-NMR study was carried out due to its thermochromism and difficulty in locating the signal at room temperature. We observed the signal first at +1541 ppm, which shifts further upfield in increments of approximately 6 ppm per 10 °C of temperature change (Fig. 7) as the temperature increases. Variable temperature UV-Vis studies were carried out in toluene to observe any absorption shifts or new absorptions that appeared over the temperature to range of 25 °C to 100 °C. However, no significant changes were observed aside from a decrease in the overall absorption at each data point (Fig. S17†). The observed thermochromism in compound **4** is similar to known Pb(II) aryloxo complexes, although few are known.^{20,22}

Conclusions

Three divalent group 14 aryloxo complexes were synthesized *via* protonolysis of the metal bisilylamides with 2,4,6-tricyclohexylphenol. The complexes were characterized by X-ray crystallography, $^{119}\text{Sn}\{^1\text{H}\}$ NMR, and ^{207}Pb NMR spectroscopy. A unique cluster was isolated by stirring a solution of the germanium derivative **2** in the presence of the byproduct of its formation, namely $\text{HN}(\text{SiMe}_3)_2$, for 24 h in hexanes. The new complex **1** is a rare Ge_6O_8 aryloxo cluster which is the only example of a Ge_xO_y cluster formed *via* rearrangement of a dimeric, 3-coordinate Ge(II) aryloxo featuring alkyl substituents in both *ortho* positions of the ligand aryl rings.

Experimental section

General considerations

All manipulations were carried out under anaerobic and anhydrous conditions by using standard Schlenk techniques or in a Vacuum Atmospheres OMNI-Lab drybox under an atmosphere of dry argon or nitrogen. Solvents were dried by the method of Grubbs and co-workers,⁴⁰ stored over potassium or sodium, and then degassed by the freeze-pump-thaw method. All physical measurements were made under strictly anaerobic and anhydrous conditions. Melting points of samples in flame-sealed capillaries were determined using a Meltemp II apparatus equipped with a partial immersion thermometer. IR spectra were recorded as Nujol mulls between CsI plates on a PerkinElmer 1430 spectrometer. UV-vis spectra were recorded as dilute toluene solutions in 3.5 mL quartz cuvettes using an Olis 17 modernized Cary 14 UV-Vis-near-IR spectrophotometer. Unless otherwise stated, all materials were obtained from commercial sources and used as received. The phenol 2,4,6-tricyclohexylphenol was donated to us by Toray Industries, Inc. The main group silylamides $\text{M}(\text{N}(\text{SiMe}_3)_2)_2$ ($\text{M} = \text{Ge}, \text{Sn}, \text{Pb}$) were synthesized by published procedures.^{1,2}

Synthesis

$[\text{Ge}_6(\mu_3\text{-O})_4(\mu_2\text{-OC}_6\text{H}_2\text{-2,4,6-Cy}_3)_4](\text{NH}_3)_{0.5}$ (**1**). To a 100 mL Schlenk flask were added 0.541 g (1.375 mmol) of Ge

$(\text{N}(\text{SiMe}_3)_2)_2$ and 0.6242 g (1.833 mmol) of 2,4,6-tricyclohexylphenol at room temperature in *ca.* 70 mL of hexanes. The yellow solution was stirred for a further 24 h without separation of the reaction byproducts ($\text{HN}(\text{SiMe}_3)_2$). The solvent was then removed under reduced pressure to leave a light-yellow residue which was washed with four *ca.* 5 mL portions of hexanes until the remaining solid had become colorless. The colorless solid was dissolved in *ca.* 10 mL of hot toluene and cooling in a *ca.* 5 °C refrigerator for 48 h produced microcrystalline material. The mother liquor was transferred to a separate flask *via* filter cannula and the microcrystalline solids were redissolved in *ca.* 3 mL of hot (*ca.* 100 °C) toluene. Upon cooling in a *ca.* 5 °C fridge for 48 h colorless rectangular blocks of **1** were collected to yield 0.0893 g (20.88%, calc. from Ge), mp 156–158 °C. $^1\text{H-NMR}$ (400 MHz, C_6D_6 , 25 °C) 7.19 (2H), 7.14 (1H), 7.09 (1H), 7.07 (1H), 7.05 (2H), 7.03 (1H), 3.57 (1H), 3.17–2.80 (7H), 2.56 (4H), 2.05–1.26 (120H). UV-vis λ/nm ($\epsilon/\text{M}^{-1}\text{cm}^{-1}$) 283 (10 300). IR (Nujol; $\tilde{\nu}/\text{cm}^{-1}$) 3610 m ($\nu\text{-N-H}$), 2950s, 2910s, 2840s, 1600w, 1490w, 1450s, 1370m, 1360m, 1265w, 1255s, 1230w, 1185m, 1165m, 1090s, 1010s, 945w, 890w, 950m, 930w, 800s, 720w, 690w, 650w, 550w, 455w, 380w, 310w.

$[\text{Ge}(\text{OC}_6\text{H}_2\text{-2,4,6-Cy}_3)_2]_2$ (**2**). To a 100 mL Schlenk flask were added 0.578 g (1.468 mmol) of $\text{Ge}(\text{N}(\text{SiMe}_3)_2)_2$ and 1.001 g (2.940 mmol) of 2,4,6-tricyclohexylphenol at room temperature. Hexanes (*ca.* 70 mL) were added *via* cannula and the reaction was stirred for 30 minutes. The solvent was removed under reduced pressure to leave a light-yellow residue. The flask was heated to *ca.* 40 °C for 30 minutes to remove the remaining volatile material under reduced pressure. The solid residue was dissolved in *ca.* 20 mL of hot hexane (temp. *ca.* 55 °C) and left to stand at room temperature. Colorless crystals of **2** precipitated from the room temperature solution after 12 h to yield 0.712 g (56.26%). Mp 238–239 °C. $^1\text{H-NMR}$ (400 MHz, C_7D_8 , 25 °C) 7.13–7.07 (8H), 3.49 (1H), 3.10 (6H), 2.52 (4H), 1.97–1.23 (120H). UV-vis λ/nm ($\epsilon/\text{M}^{-1}\text{cm}^{-1}$) 283 (7863), 338 (3200). IR (Nujol; $\tilde{\nu}/\text{cm}^{-1}$) 2970s, 2940s, 2870s, 1460s, 1380s, 1360m, 1350m, 1265s, 1230w, 1190m, 1170m, 1090s, 1020s, 950w, 890w, 865w, 850w, 800s, 770w, 720w, 635w, 600w, 550w, 520w, 490w, 450w, 380w, 360w, 330w, 305w, 295w, 280w.

$[\text{Sn}(\text{OC}_6\text{H}_2\text{-2,4,6-Cy}_3)_2]_2$ (**3**). Complex **3** was prepared in a similar manner to **2** from 0.654 g (1.488 mmol) of $\text{Sn}(\text{N}(\text{SiMe}_3)_2)_2$ and 1.014 g (2.976 mmol) of 2,4,6-tricyclohexylphenol at room temperature. Colorless crystals of **3** precipitated from a *ca.* 30 mL toluene extract standing at room temperature for 12 h. Yield 0.587 g (49.45%). Mp > 250 °C. $^1\text{H-NMR}$ (400 MHz, C_7D_8 , 25 °C) 7.11 (2H), 7.08–7.06 (2H), 6.96 (4H), 4.23 (1H), 4.09 (1H), 3.84 (1H), 3.40 (1H), 2.69 (4H), 2.47 (4H), 1.96–1.20 (120H). $^{119}\text{Sn}\{^1\text{H}\}$ NMR (400 MHz, C_6D_6) –280.3 ppm. UV-vis λ/nm ($\epsilon/\text{M}^{-1}\text{cm}^{-1}$) 283 (7970). IR (Nujol; $\tilde{\nu}/\text{cm}^{-1}$) 2960s, 2920s, 2850s, 1460s, 1445s, 1375s, 1360m, 1350m, 1300m, 1290m, 1270m, 1260s, 1230s, 1185s, 1140s, 1105s, 1190s, 1015s, 950w, 890w, 865m, 845m, 810s, 800s, 775m, 765m, 720w, 640w, 630w, 600w, 520w, 500w, 490w, 450w, 380w, 355w, 330w.

[Pb(OC₆H₂-2,4,6-Cy₃)₂]₂ (**4**). Complex **4** was prepared in a similar manner to **2** and **3** from 0.880 g (1.667 mmol) of Pb(N(SiMe₃)₂)₂ and 1.135 g (3.333 mmol) of 2,4,6-tricyclohexylphenol. Yellow crystals of **4** precipitated from a room temperature toluene extract (*ca.* 30 mL) after 3 h to yield 0.825 g (55.86%) of **4**. Mp > 250 °C. ¹H-NMR (400 MHz, C₇D₈, 25 °C) 7.13 (4H), 7.08 (2H), 6.97 (2H), 3.36 (1H), 2.69 (2H), 2.56 (4H), 2.12 (5H), 1.99–1.22 (120H). ²⁰⁷Pb NMR (104.61 MHz, C₇D₈) (37 °C) 1541 ppm, (53 °C) 1534 ppm, (68 °C) 1529 ppm, (77 °C) 1524 ppm, (87 °C) 1519 ppm. UV-vis λ /nm (ϵ /M⁻¹ cm⁻¹, 25 °C) 283 (15 511), 392 (2559). IR (Nujol; $\tilde{\nu}$ /cm⁻¹) 2980s, 2920s, 2850s, 2660m, 1600w, 1565w, 1490w, 1450s, 1375s, 1300s, 1290m, 1270s, 1260s, 1230s, 1190s, 1140s, 1110s, 1020s, 945w, 890w, 860s, 845m, 810s, 800s, 885m, 875m, 870m, 725m, 690w, 640w, 630w, 600w, 585w, 510w, 490w, 460w, 440w, 370w, 350w, 320w.

X-ray crystallographic studies

Crystals of **2**, **3**, and **4** suitable for X-ray crystallographic studies were obtained from saturated toluene solutions upon standing for 24 h. Crystals of **1** were collected from a saturated toluene solution after 48 h at 5 °C. The crystals were removed from the Schlenk tubes and immediately covered with a layer of hydrocarbon oil. Suitable crystals were selected, mounted on a nylon cryoloop, and then placed in the cold nitrogen stream of the diffractometer. Data for **2**, **3**, and **4** were collected at 90(2) K with Mo K α_1 radiation (λ = 0.71073 Å) using a Bruker D8 Venture dual source diffractometer in conjunction with a CCD detector while data for **1** was collected at 190(2) K with Mo K α_1 radiation (λ = 0.71073 Å). The collected reflections were corrected for Lorentz and polarization effects and for absorption by using Blessing's method as incorporated into the program SADABS.^{41,42} The structures were solved by direct methods and refined with the SHELXTL (2012, version 6.1) or SHELXTL (2013) software packages.⁴³ Refinement was by full-matrix least-squares procedures, with all carbon-bound hydrogen atoms included in calculated positions and treated as riding atoms. The thermal ellipsoid plots were drawn using OLEX2 software.⁴⁴

Spectroscopic parameters

¹H NMR spectra were collected on a Bruker Avance III spectrometer operating at 399.77 MHz (9.4 T). Using a 30° tip angle (4.62 μ s), 16 free induction decays (FIDs) were averaged for each experiment with a 4.1 s acquisition time and a repetition time of 5.1 s. Variable temperature (VT) NMR experiments were collected on a Bruker Avance Neo console operating at 300.37 MHz (7.0 T). Using a 30° tip angle (5.00 μ s), 16 free induction decays (FIDs) were averaged for each experiment with a 2.8 s acquisition time and a repetition time of 3.78 s. The sample was allowed to equilibrate at the temperature for 10 minutes before data collection was begun. Temperatures were calibrated on a sample of neat methanol. All spectra were internally referenced to the residual ¹H in the deuterated solvent (toluene). ¹¹⁹Sn{¹H} (149.07 MHz) NMR spectra were collected on a Bruker Avance III spectrometer operating at

400 MHz (9.4 T). The ¹¹⁹Sn{¹H} spectra were referenced using the IUPAC referencing recommendation⁴⁵ using the frequency ratios of the solvent residual protons and the spectra were collected using a 30° tip angle (4.152 ms) with inverse-gated decoupling (WALTZ16) applied to the ¹H spins. 24 576 FIDs were averaged with an acquisition time of 260 ms and a repetition time of 760 ms. The ²⁰⁷Pb (104.61 MHz) NMR spectra were collected on a Bruker Avance spectrometer operating at 500 MHz (11.7 T). ²⁰⁷Pb NMR spectra were collected using a 90° pulse (7.5 ms) with 494–2048 FIDs averaged, depending on the temperature of the sample. Each FID used a 327 ms acquisition time with a 250 ms recycle delay between successive acquisitions. The ²⁰⁷Pb chemical shift was referenced externally to a 1 M solution of Pb(NO₃)₂ in D₂O. For the variable temperature measurements, the sample was allowed to equilibrate at the temperature for 10 minutes before data collection began. Temperatures were calibrated on a sample of neat methanol.

Conflicts of interest

There are no conflicts of interest to declare.

Acknowledgements

We thank the U.S. National Science Foundation for funding (Grant No. CHE-2152760).

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