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## Lead(II) siloxides

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In celebration of the 100<sup>th</sup> anniversary of the foundation of the Romanian University in Cluj-Napoca

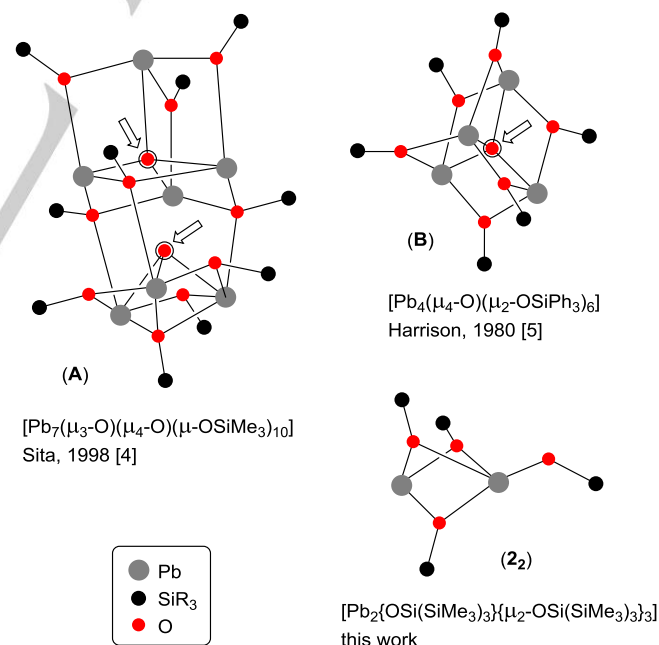
**Abstract:** While Pb<sup>II</sup>-siloxides have until now been known to decompose to oxoclusters, we present here  $[\{RO^F\}PbOSi(SiMe_3)_3]$  ( $RO^F$  = fluoroalkoxide) and, most importantly,  $[Pb_2\{OSi(SiMe_3)_3\}(\mu_2-OSi(SiMe_3)_3)_3]$ . The unusual bonding pattern in this thermally stable dinuclear complex is investigated by crystallographic and computational methods. Its stability is much greater than that of the simple, yet elusive  $[Pb(OSiPh_3)_2]$ , for which decomposition pathways towards  $[Pb_4(\mu_4-O)(\mu_2-OSiPh_3)_6]$  have been clearly established.

Lead(II) dialkoxides  $[Pb(OR)_2]_n$  have long been used as volatile precursors to produce lead-based binary metal oxide materials, e.g. lead ferroelectrics  $PbMO_3$  ( $M = Ti, Zr$ ), through chemical vapour deposition of thin films.<sup>[1]</sup> Yet, their nuclearity in solution and overall stability have often been debated, and they easily generate oxoclusters such as  $[Pb_4(\mu_4-O)(\mu_2-OR)_6]$  and  $[Pb_6(\mu_3-O)_4(\mu_3-OR)_4]$  ( $R = Et, nPr, tBu$ , etc.) in the presence of impurities (e.g. water, other protic sources or bases) or upon heating.<sup>[2]</sup>

Metal triorganosiloxides can also be used as molecular precursors to  $MSiO_x$  metal silica-based materials.<sup>[3]</sup> However compared to alkoxides,  $[Pb^II]-OSiR_3$  siloxides remain very scarce, as Pb-O-Si patterns are notoriously difficult to stabilise in discrete molecular complexes. The first authenticated molecular Pb<sup>II</sup>-siloxide, the heteroleptic  $[Pb\{N(SiMe_3)_2\}(\mu_2-OSiMe_3)]_2$ , was a dimer prepared by Sita through heterocumulene metathesis of  $[Pb\{N(SiMe_3)_2\}_2]$ .<sup>[4]</sup> Attempts at isolating the homoleptic congener  $[Pb(OSiMe_3)_2]_n$  met no success, although it was thought to be an intermediate in the observed formation of the cluster  $[Pb_7(\mu_3-O)(\mu_4-O)(\mu-OSiMe_3)_{10}]$  (Fig. 1, A). Prior to this, the synthesis of the homoleptic  $[Pb(OSiPh_3)_2]_n$  had also been sought, but returned instead the tetranuclear  $[Pb_4(\mu_4-O)(\mu_2-OSiPh_3)_6]$  (Fig. 1, B) which was thought to further evolve towards the octanuclear  $[Pb_8O_5(OSiPh_3)_6]$ .<sup>[5]</sup> Decomposition pathways for  $[Pb(OSiMe_3)_2]_n$  and  $[Pb(OSiPh_3)_2]_n$  were not ascertained; they were said to proceed through release of siloxanes,  $(R_3Si)_2O$ , but the non-metallic products of decomposition remain poorly, if at all, characterised. Taken collectively, these data highlighted the propensity of Pb<sup>II</sup>-O motifs to generate oxoclusters through uncontrolled decomposition pathways. This scenario contrasts

with that in related tin(II) chemistry, where  $[Sn(OSiPh_3)(\mu_2-OSiPh_3)]_2$  and heteroleptic Sn<sup>II</sup>-siloxides are stable.<sup>[6]</sup> Hence, unsupported homoleptic lead(II) triorganosiloxides remain elusive. The solvate  $[Pb\{OSi(OtBu)_3\}_2 \cdot tBuOH \cdot MeCN]$  was reported, but it was not structurally characterised; only its plumbate analogue  $[NaPb\{OSi(OtBu)_3\}_3]$  was authenticated by XRD analysis.<sup>[7]</sup>

We are seeking to improve our understanding of the nature and reactivity of Pb<sup>II</sup>-O bonds,<sup>[8]</sup> and have recently reported that bulky borinic acids afford low-coordinate Pb<sup>II</sup>-boryloxides that display good thermal stability.<sup>[8c-d]</sup> Yet, without the Lewis bases found in  $[Pb\{OCH(CF_3)_2\}(\mu_2-OCH(CF_3)_2 \cdot dmap)]_2$  ( $dmap = 4$ -dimethylamino-pyridine),<sup>[9]</sup> hexafluoroisopropoxide, a smaller ligand, was unable to prevent the uncontrolled formation of the oxocluster  $[Pb_4(\mu_4-O)(\mu_2-OCH(CF_3)_2)_5(\mu_3-OCH(CF_3)_2)]$ .<sup>[8c]</sup> We document here the syntheses and structural characterisation of the first homoleptic Pb<sup>II</sup>-siloxides, notably  $[Pb_2\{OSi(SiMe_3)_3\}(\mu_2-OSi(SiMe_3)_3)_3]$  (Fig. 1, 2<sub>2</sub>). The stability of this complex is compared to that of the easily degraded  $[Pb(OSiPh_3)_2]$  and its unusual structure is discussed in the light of DFT computations.



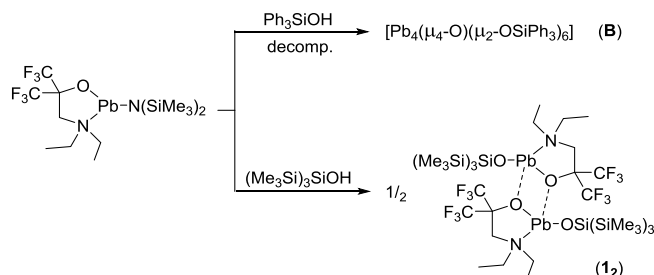
**Figure 1.** Representation of structurally authenticated lead(II)-siloxides oxoclusters (Sita, Harrison)<sup>[4,5]</sup> and disiloxides (this work). The arrows indicate bridging  $\mu_3$ - and  $\mu_4$ -oxides in the oxoclusters.

The synthesis of the heteroleptic Pb<sup>II</sup>-triphenylsiloxide  $[\{RO^F\}PbOSiPh_3]$  was first attempted, using the bidentate 2-((diethylamino)methyl)-hexafluoropropan-2-oxide ( $\{RO^F\}^-$ ) to stabilise the targeted complex (Scheme 1). This ancillary ligand

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Supporting information for this article is given via a link at the end of the document.

has recently been utilised to produce a stable  $\text{Pb}^{\text{II}}$ -boryloxide.<sup>[8d]</sup> However, regardless of the choice of experimental conditions, the reaction of the known  $[(\text{RO}^{\text{F}})\text{PbN}(\text{SiMe}_3)_2]$ <sup>[8d]</sup> with an equimolar amount of  $\text{Ph}_3\text{SiOH}$  only returned the tetranuclear oxocluster **B** as large crops of colourless crystals. We therefore turned our attention to the bulkier silanol  $(\text{Me}_3\text{Si})_3\text{SiOH}$ , used previously to prepare a variety of transition metal siloxides,<sup>[3b]</sup> and, very recently, two barium siloxides.<sup>[10,11]</sup>

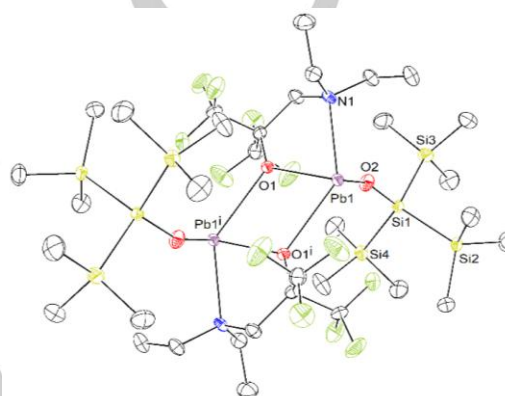


**Scheme 1.** Synthesis of  $\text{Pb}^{\text{II}}$ -siloxides from the heteroleptic amido precursor  $[(\text{RO}^{\text{F}})\text{PbN}(\text{SiMe}_3)_2]$ .  $(\text{RO}^{\text{F}})\text{H} = 2-((\text{diethylamino})\text{methyl})\text{-hexafluoropropan-2-ol}$ . All attempts to obtain  $[(\text{RO}^{\text{F}})\text{PbOSiPh}_3]$  (top reaction) were unsuccessful.

The siloxide  $[(\text{RO}^{\text{F}})\text{PbOSi}(\text{SiMe}_3)_3]$  (**1**) is available in 70–75% yields upon reaction of  $[(\text{RO}^{\text{F}})\text{PbN}(\text{SiMe}_3)_2]$  with one equivalent of  $(\text{Me}_3\text{Si})_3\text{SiOH}$  in petroleum ether. This colourless complex crystallised as a loosely associated O-bridged dimer **12** (*vide infra*), but  $^1\text{H}$  DOSY NMR data recorded in benzene- $d_6$  suggest the presence of a single, mononuclear species in solution in this solvent. The complex is characterised by a single resonance at  $\delta_{207\text{Pb}}$  2130 ppm by  $^{207}\text{Pb}$  NMR spectroscopy, i.e. shielded by 700 ppm compared to the boryloxide  $[(\text{RO}^{\text{F}})\text{PbOB}(\text{CH}(\text{SiMe}_3)_2)_2]$ .<sup>[8d]</sup> Chemical shifts in  $^{207}\text{Pb}$  NMR do not simply reflect the electron withdrawing/donating properties of the metal-bound ligands. The absolute isotropic shielding is instead the overall expression of three distinct components: the diamagnetic ( $\sigma_{\text{D}}$ ), paramagnetic ( $\sigma_{\text{P}}$ ) and spin-orbit ( $\sigma_{\text{SO}}$ ) shieldings.<sup>[12]</sup> Without accurate deconstruction of these different contributions by DFT methods, the interpretation of  $^{207}\text{Pb}$  chemical shifts is rather unsound, hence we are refraining here from doing so. The  $^{29}\text{Si}$ -INEPT NMR spectrum of **1** features the two expected resonances, a main one at  $\delta_{29\text{Si}}$  −16.80 ppm and a minor one at −18.22 ppm. The  $^{19}\text{F}$  NMR spectrum exhibits a resonance (sharp singlet) at  $\delta_{19\text{F}}$  −76.4 ppm, and shows the presence of a small amount of  $[(\text{RO}^{\text{F}})_2\text{Pb}]_2$  (broad resonance at −77.0 ppm<sup>[8d]</sup>) presumably formed through Schlenk equilibrium.  $^1\text{H}$ - $^{19}\text{F}$  HOESY NMR data show the existence of intramolecular through-space  $\text{H}\cdots\text{F}$  interactions between  $\text{CF}_3$  atoms on the one hand and  $\text{NCH}_2\text{C}(\text{CF}_3)_2$  and  $\text{NCH}_2\text{CH}_3$  hydrogens on the other. Note that the complex is thermally stable in the solid state under inert atmosphere; it melts and decomposes irreversibly at 111 °C.

The molecular solid state structure of **1** as depicted in Figure 2 forms a centro-symmetric O-bridged dinuclear complex. Each lead atom is four-coordinate, with a hemi-coordinated,<sup>[13]</sup> distorted trigonal pyramidal environment ( $\tau_4 = 0.77$ ).<sup>[14]</sup> The

interatomic distances to the bridging O atoms show a very large variation ( $\text{Pb1-O1} = 2.256(2)$  Å vs.  $\text{Pb1-O1}^i = 2.725(2)$  Å) indicating weak association of the dinuclear edifice. A similarly asymmetric bridging mode was found in Hoffman's four-coordinate  $[\text{Pb}\{\text{OCH}(\text{CF}_3)_2\}\{\mu_2\text{-OCH}(\text{CF}_3)_2\}\cdot\text{dmap}]_2$  ( $\text{Pb-O}_{\text{bridging}} = 2.247(6)$  and  $2.716(6)$  Å).<sup>[9]</sup> The interatomic distance to the terminal O atom in **12** ( $\text{Pb1-O2} = 2.128(2)$  Å) is substantially shorter than those to the bridging ones, and also than the corresponding  $\text{Pb-O}_{\text{terminal}}$  bond length in Hoffman's fluoroalkoxide ( $2.260(6)$  Å).<sup>[9]</sup> The arrangement about the bridging O atoms in **12** approaches perfect trigonal planar geometry ( $\Sigma_{\text{e}}(\text{O1}) = 358.4^\circ$ ).

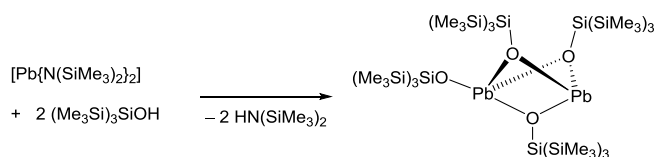


**Figure 2.** ORTEP representation of the molecular solid state structure of  $[(\text{RO}^{\text{F}})\text{PbOSi}(\text{SiMe}_3)_3]_2$  (**12**). H atoms omitted for clarity. Selected interatomic distances (Å) and angles ( $^\circ$ ):  $\text{Pb1-O1} = 2.2562(18)$ ,  $\text{Pb1-O1}^i = 2.7253(19)$ ,  $\text{Pb1-O2} = 2.128(2)$ ,  $\text{Pb1-N1} = 2.536(2)$ ;  $\text{O2-Pb1-O1} = 95.75(7)$ ,  $\text{O2-Pb1-N1} = 83.29(8)$ ,  $\text{O1-Pb1-N1} = 70.60(7)$ ,  $\text{O2-Pb1-O1}^i = 112.83(7)$ ,  $\text{O1-Pb1-O1}^i = 70.18(7)$ ,  $\text{N1-Pb1-O1}^i = 138.75(6)$ . Colour code: purple, Pb; red, O; blue, N; yellow, Si; green, F; black, C. Symmetry operation "i":  $-x, -y, -z$ .

DFT calculations reveal that the energy of optimised structure **12** is 29.8 kcal mol $^{-1}$  lower than the energy of two hypothetical monomers (**1**; see ESI, Figure S37). The free Gibbs energy of the reaction corresponding to the transformation of **12** into two **1** in gas phase at 298.15 K is also small (10.83 kcal mol $^{-1}$ ). Analysis of natural bond orbitals (NBO) carried out on the optimised structure of **12** shows that the lone pair of Pb features mainly s character (97.4% s, 2.6% p), slightly larger than in the monomer **1** (94.3% s, 5.7% p). In **1**, in the Pb-O bonding, the largest contributions to the NBOs correspond to the two oxygen atoms (93.9 and 94.0%). Second order perturbation theory analysis of Fock matrix in NBO basis indicates that donation of N atom electrons into the empty non-bonding Pb atom orbital in **1** corresponds to a stabilisation energy of 19.65 kcal mol $^{-1}$ . NBO analysis of an alternative Lewis structure **1'** (Figures S41–S44) which includes the Pb-N bond shows that the contributions to intramolecular interaction are 95.4% N and 4.6% Pb; besides, the contributions of the oxygen atoms to the P-O NBO slightly increase (94.0% and 94.2%) with respect to **1**.

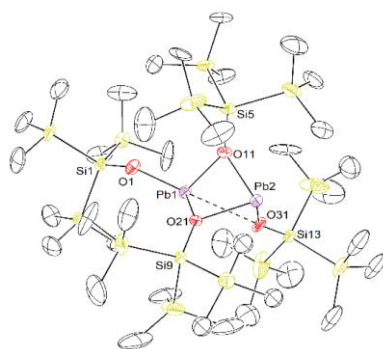
Quantum theory of atoms in molecules (QTAIM) analysis was next performed on **12**. The values of electron density and its Laplacian corresponding to the Pb-O bond critical points (BCP)

indicate that the bonds have ionic character, results which are consistent to the NBO analysis (Table S34).



**Scheme 2.** Synthesis of homoleptic  $[\text{Pb}_2\{\text{OSi}(\text{SiMe}_3)_3\}\{\mu_2\text{-OSi}(\text{SiMe}_3)_3\}_3]$  (**2**).

The dinuclear  $[\text{Pb}_2\{\text{OSi}(\text{SiMe}_3)_3\}\{\mu_2\text{-OSi}(\text{SiMe}_3)_3\}_3]$  (**2**), the first example of a stable homoleptic  $\text{Pb}^{\text{II}}$ -siloxide, was isolated in 58% yield upon treatment of  $[\text{Pb}\{\text{N}(\text{SiMe}_3)_2\}_2]$  with two equivalents of  $(\text{Me}_3\text{Si})_3\text{SiOH}$  (Scheme 2).<sup>[15]</sup> The green **2** is characterised by a broad singlet at  $\delta_{\text{H}}$  0.38 ppm and a resonance at  $\delta_{\text{C}}^{\text{1H}}$  2.37 ppm in the  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra, respectively, recorded in benzene- $d_6$ . The  $^{207}\text{Pb}$  NMR spectrum contains a single, broad resonance centred on  $\delta_{207\text{Pb}}$  1349 ppm. The molecular structure of **2** established by XRD analysis shows the complex to exist as a structurally very unusual  $C_s$ -symmetric dimer (Figure 3). It contains a single siloxide in terminal position (corresponding to O1, with  $\text{Pb1-O1} = 2.137(8)$  Å) and two other siloxides in bridging positions for O11 and O21 with comparatively long interatomic distances to the metals ( $\text{Pb1-O11} = 2.345(8)$ ,  $\text{Pb1-O21} = 2.383(8)$ ,  $\text{Pb2-O11} = 2.289(8)$  and  $\text{Pb2-O21} = 2.256(7)$  Å). The last siloxide, corresponding to O31 bound to Pb2, is in a very unusual position. Instead of pointing away from Pb1 as expected for a terminal ligand, it is actually bent towards Pb1, with a very narrow  $\text{Pb1-Pb2-O31}$  angle compared to  $\text{Pb2-Pb1-O1}$  involving the regular terminal siloxide moiety at O1 (resp.  $61.6(2)$  and  $132.8(2)^\circ$ ).



**Figure 3.** ORTEP representation of the molecular solid state structure of  $[\text{Pb}_2\{\text{OSi}(\text{SiMe}_3)_3\}\{\mu_2\text{-OSi}(\text{SiMe}_3)_3\}_3]$  (**2**). H atoms omitted for clarity. Only one component in each disordered  $\text{SiMe}_3$  groups is depicted. Selected interatomic distances (Å) and angles ( $^\circ$ ):  $\text{Pb1-O1} = 2.137(8)$ ,  $\text{Pb1-O11} = 2.345(8)$ ,  $\text{Pb1-O21} = 2.383(8)$ ,  $\text{Pb1-O31} = 2.997(9)$ ,  $\text{Pb2-O31} = 2.152(9)$ ,  $\text{Pb2-O21} = 2.256(7)$ ,  $\text{Pb2-O11} = 2.289(8)$ ;  $\text{O1-Pb1-O11} = 104.80(3)$ ,  $\text{O1-Pb1-O21} = 105.70(3)$ ,  $\text{O11-Pb1-O21} = 73.40(3)$ ,  $\text{O1-Pb1-O31} = 171.90(28)$ ,  $\text{O11-Pb1-O31} = 69.77(28)$ ,  $\text{O21-Pb1-O31} = 67.28(25)$ ,  $\text{O31-Pb2-O21} = 86.50(3)$ ,  $\text{O31-Pb2-O11} = 88.50(3)$ ,  $\text{O21-Pb2-O11} = 76.80(3)$ ,  $\text{Pb1-Pb2-O31} = 61.6(2)$ ,  $\text{Pb2-Pb1-O1} = 132.8(2)$ .

The  $\text{Pb2-O31}$  interatomic distance ( $2.152(9)$  Å) is only mildly longer than the  $\text{Pb1-O1}$  one. Although much longer than the other Pb-O bond lengths in **2**, the  $\text{Pb1-O31}$  interatomic distance ( $2.997(9)$  Å) is much below the sum of Van der Waals radii for lead and oxygen ( $2.02$  and  $1.52$  Å), suggesting a strong interaction between the two atoms. It is therefore tempting to consider that Pb1 is formally four-coordinate, while Pb2 is three-coordinate with a degree of pyramidalisation (DoP) of 120%, where  $\text{DoP} = [360 - \sum_{i=1}^3 \theta(i)]/0.9$  and where  $\theta(i)$  are the angles around Pb2.<sup>[16]</sup> This high DoP reflects the values of angles around Pb2 ( $86.50(3)$ ,  $88.50(3)$  and  $76.80(3)^\circ$ ), one of which is much lower than the theoretical  $90^\circ$ .

The nature of the bonding in **2** was further probed by DFT computations. The metric parameters in the optimised structure matched well those determined by XRD (Table S32) except that corresponding to the  $\text{Pb1}\cdots\text{O31}$  interaction which is slightly longer. In order to understand the energy gain by the system in the unusual arrangement, a molecular structure (**2a**) with the torsion angles  $\text{O1-Pb1}\cdots\text{Pb2-O31}$  constrained to  $180^\circ$  was optimised (Figure S39). The energy of **2a** is  $16.3 \text{ kcal mol}^{-1}$  higher than that found for the optimised geometry of **2**. Optimisation of a second structure (**2b**) in which two torsion angles were constrained (Figure S40), i.e.  $\text{O1-Pb1}\cdots\text{Pb2-O31} = 180^\circ$  and the four membered ring  $\text{Pb}_2\text{O}_2$  is planar, is also  $16.3 \text{ kcal mol}^{-1}$  higher in energy. This suggests that the intramolecular interaction  $\text{Pb1}\cdots\text{O31}$  leads also to the non-planarity of the  $\text{Pb}_2\text{O}_2$  ring. Besides, dimerisation from a putative monomer **2** to **2** results in a huge energy gain,  $42.7 \text{ kcal mol}^{-1}$ .

The NBO analysis carried out on optimised geometry for **2** reveals a similar situation as in **1**. The lone pair on Pb atoms have mainly *s* character (Pb1: 97.5% *s*, 2.5% *p*; Pb2: 98.2% *s*, 1.8% *p*), and are slightly larger than in the monomeric structure **2** (94.9% *s*, 5.1% *p*) (Figure S38). The NBOs in the alternative Lewis structure **2'** with Pb-O bonds are localised mainly on the oxygen atom (94.2 and 94.5%), suggesting a significant ionic character (Figures S45-S47). Second order perturbation theory analysis of Fock matrix in NBO basis indicates that among the largest contributions to the stabilisation of **2** is the electron donation from an electron pair of oxygen atom (O31) into a *p* orbital on Pb2 ( $10.53 \text{ kcal mol}^{-1}$ ).

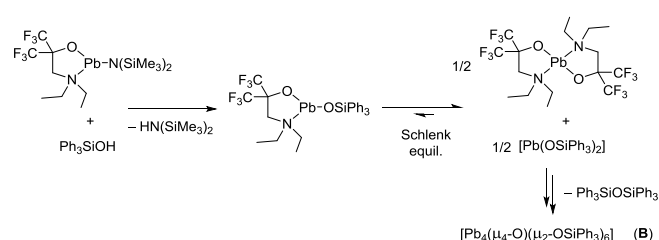
The bonding at the lead atoms in the optimised **2** was also probed by QTAIM analysis. The values corresponding to electron density and its Laplacian of Pb-O bonds and  $\text{Pb}\cdots\text{O}$  interaction have small, positive values indicating an ionic or very polar character of these bonds (Table S36).

The nucleophilicity of the siloxide in **2** was assessed by reacting the complex with different electrophiles. In the presence of  $\text{CO}_2$  (1 bar), **2** reacted to generate unidentified species. NMR data indicated that the siloxide moiety had been displaced, but no compound could be isolated or authenticated. By contrast, the  $\beta$ -diketiminato/alkoxide  $[\{\text{BDI}^{\text{DIPP2}}\}\text{PbO}^+\text{Pr}]$  ( $\text{BDI}^{\text{DIPP2}} = [\text{N}(2,6\text{-iPr}_2\text{C}_6\text{H}_3)\text{C}(\text{Me})_2\text{CH}]$ ) cleanly formed the carbonate derivative  $[\{\text{BDI}^{\text{DIPP2}}\}\text{PbOC}(\text{=O})\text{O}^+\text{Pr}]$ .<sup>[17]</sup> Similarly, **2** did not react with the carbodiimine  $\text{Cy-N}=\text{C}=\text{N-Cy}$ . Yet, upon treatment with two equivalents of the isocyanate  $1\text{-Ad-N}=\text{C}=\text{O}$  (Ad = adamantyl), it returned  $[\text{Pb}\{\text{N}(\text{Ad})\text{C}(\text{=O})\text{OSi}(\text{SiMe}_3)_3\}_2]$  (**3**), a structurally identified mononuclear complex featuring a four-coordinate lead atom (see the ESI). On the whole, **2** appears to be much less reactive towards electrophiles than regular  $[\text{Pb}^{\text{II}}]\text{-alkoxides}$ .<sup>[16,17]</sup>



In addition, unlike lighter tetrelenes,<sup>[8a]</sup> it is inert towards PhSeSePh.

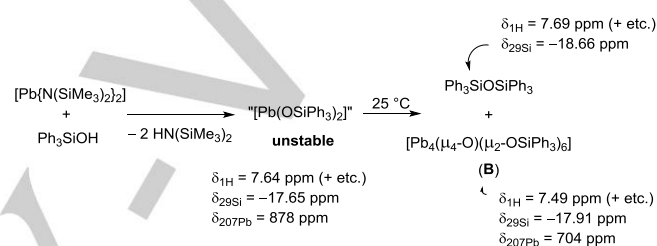
The decomposition of Pb<sup>II</sup>-siloxides and concomitant production of oxoclusters, such as encountered in our attempted synthesis of [(RO<sup>F</sup>)PbOSiPh<sub>3</sub>] (see above), has been reported on several occasions.<sup>[4,5,18]</sup> We thus sought to understand our failure to synthesise this heteroleptic complex. It is proposed that the sole isolable product from these trials, [Pb<sub>4</sub>(μ<sub>4</sub>-O)(μ<sub>2</sub>-OSiPh<sub>3</sub>)<sub>6</sub>] (**B**), forms through decomposition of [Pb(OSiPh<sub>3</sub>)<sub>2</sub>] and release of Ph<sub>3</sub>SiOSiPh<sub>3</sub> as a by-product. [Pb(OSiPh<sub>3</sub>)<sub>2</sub>] must itself be generated as one of the two homoleptic products following ligand redistribution (aka Schlenk equilibrium) in the attempted synthesis of [(RO<sup>F</sup>)PbOSiPh<sub>3</sub>] (Scheme 3). Consistent with this assumption, near-quantitative formation of [(RO<sup>F</sup>)<sub>2</sub>Pb]<sup>[8d]</sup> was detected spectroscopically for reactions performed in J-Young NMR tubes.



**Scheme 3.** Proposed pathway for the formation of [Pb<sub>4</sub>(μ<sub>4</sub>-O)(μ<sub>2</sub>-OSiPh<sub>3</sub>)<sub>6</sub>] (**B**) during the attempted synthesis of [(RO<sup>F</sup>)PbOSiPh<sub>3</sub>].

To further probe this scenario, the synthesis of the bis-siloxide [Pb(OSiPh<sub>3</sub>)<sub>2</sub>] and its degradation into **B** were investigated. The Schlenk-scale reaction of [Pb(N(SiMe<sub>3</sub>)<sub>2</sub>)<sub>2</sub>] and 2 equivalents of Ph<sub>3</sub>SiOH in Et<sub>2</sub>O only returned large crops of single crystals of **B** after work-up and crystallisation from Et<sub>2</sub>O.<sup>[19]</sup> The same reaction was then performed in a J-Young NMR tube in C<sub>6</sub>D<sub>6</sub> and was monitored by NMR spectroscopy (see data sets in the ESI). Within the first point of analysis, the <sup>1</sup>H NMR spectrum confirmed full conversion of the starting materials and quantitative release of HN(SiMe<sub>3</sub>)<sub>2</sub>. It also indicated the formation of a main species characterised in particular by a major doublet at δ<sub>1H</sub> 7.64 ppm and assigned to the targeted [Pb(OSiPh<sub>3</sub>)<sub>2</sub>], together with minor doublets at 7.49 ppm (assigned to the oxocluster **B**) and 7.69 ppm (belonging to Ph<sub>3</sub>SiOSiPh<sub>3</sub>). These latter assignments were unambiguously made on the basis on the NMR data for independently isolated single crystals of **B** and Ph<sub>3</sub>SiOSiPh<sub>3</sub> (a poorly soluble, colourless compound).<sup>[20]</sup> Detailed monitoring of the reaction by <sup>1</sup>H, <sup>29</sup>Si INEPT and <sup>207</sup>Pb NMR spectroscopies confirmed that the initially formed [Pb(OSiPh<sub>3</sub>)<sub>2</sub>] (δ<sub>207Pb</sub> = 878 ppm; δ<sub>29Si</sub> = -17.65 ppm) decomposed gradually over the course of 24 h to yield Ph<sub>3</sub>SiOSiPh<sub>3</sub> (δ<sub>29Si</sub> = -18.66 ppm) and **B** (δ<sub>207Pb</sub> = 704 ppm; <sup>29</sup>Si NMR, δ<sub>29Si</sub> = -17.90 ppm),<sup>[21]</sup> together with a small amount of other unidentifiable species, presumably some higher lead(II) oxo-bridged aggregates.<sup>[4,5]</sup> The mechanism for the formation of **B** upon decomposition of transient [Pb(OSiPh<sub>3</sub>)<sub>2</sub>] is summarised in Scheme 4. It is worth noting that our numerous attempts to build [Pb(OSiPh<sub>3</sub>)<sub>2</sub>] starting from [Pb(N(SiMe<sub>3</sub>)<sub>2</sub>)<sub>2</sub>] were

unsuccessful. It may well be that the evolution of [Pb(OSiPh<sub>3</sub>)<sub>2</sub>] into **B** is actually facilitated by the by-product from this reaction, HN(SiMe<sub>3</sub>)<sub>2</sub>, as shown for the decomposition of [Pb<sub>3</sub>(μ-O<sup>t</sup>Bu)<sub>6</sub>].<sup>[22,23]</sup> Yet, we found the reaction of Lappert's [Pb{CH(SiMe<sub>3</sub>)<sub>2</sub>}<sub>2</sub>]<sup>[24]</sup> with Ph<sub>3</sub>SiOH also returned **B**, although the by-product of this reaction, CH<sub>2</sub>(SiMe<sub>3</sub>)<sub>2</sub>, is both a very weak acid and essentially chemically inert. Finally, we also tried to obtain **B** upon salt metathesis between PbCl<sub>2</sub> and freshly prepared [LiOSiPh<sub>3</sub>], but this reaction again only afforded the isolation of another (hybrid) oxocluster of overall composition [Pb<sub>8</sub>(μ<sub>4</sub>-O)<sub>2</sub>(μ<sub>2</sub>-Cl)(μ<sub>3</sub>-Cl)(μ<sub>4</sub>-Cl)(μ<sub>2</sub>-OSiPh<sub>3</sub>)<sub>8</sub>], as authenticated by XRD analysis (Figure S28). On the whole, the elusive [Pb(OSiPh<sub>3</sub>)<sub>2</sub>] thus appears to be thermodynamically unstable. Its easy decomposition actually highlight favourably the relative thermal and chemical stability displayed by the new siloxide **2**.



**Scheme 4.** Decomposition of [Pb(OSiPh<sub>3</sub>)<sub>2</sub>] into [Pb<sub>4</sub>(μ<sub>4</sub>-O)(μ<sub>2</sub>-OSiPh<sub>3</sub>)<sub>6</sub>] (**B**).

In conclusion, stability and potential decomposition pathways in lead(II) siloxides have been probed, enabling us to overcome a notorious stalemate in lead(II) chemistry. [Pb<sub>2</sub>{OSi(SiMe<sub>3</sub>)<sub>3</sub>}<sub>2</sub>], the first stable, homoleptic Pb<sup>II</sup>-siloxide, has been obtained through the use of a very bulky siloxide. Unlike all previous congeners, it does not evolve towards oxoclusters. Decomposition pathways for the seminal and yet, still elusive, [Pb(OSiPh<sub>3</sub>)<sub>2</sub>], have been delineated, and they do not apply to **2**. Beyond the sheer bulk of the siloxides, the behaviour of this dinuclear complex can perhaps be also linked to its uncommon structural features, which have been probed by a combination of XRD and DFT methods. Besides, it is reactive towards strong electrophiles but, not surprisingly, less so than regular alkoxides. These results shed new light on a famous chapter of lead(II) chemistry and further improve our understanding of the reactivity of Pb<sup>II</sup>-O bonds.

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**Keywords:** lead(II) siloxides • bulky siloxide • triphenyl siloxide • lead(II) oxocluster • decomposition pathway

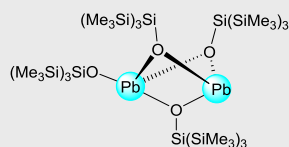
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- [19] Note that a large amount of precipitate consisting of a ca. 15:85 mixture of **B** and the expected  $[\text{Pb}(\text{OSiOPh}_3)_2]$  formed within the first 5 min of the reaction; this initial ratio increased rapidly in favour of **B** upon standing in solution in  $\text{C}_6\text{D}_6$ . Besides, in an attempt to stabilise  $[\text{Pb}(\text{OSiPh}_3)_2]$ , addition of 1 equivalent of 4-dimethylaminopyridine (see ref. [9]) to the reaction mixture only delayed the formation of the precipitate by another 15-20 min, and did not change the eventual outcome of the reaction, i.e. formation of **B** as the main lead-containing product.
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- [22]  $[\text{Pb}_3(\mu\text{-O}^t\text{Bu})_6]$  was shown to yield the oxocluster  $[\text{Pb}_4(\mu\text{-O})(\mu\text{-O}^t\text{Bu})_6]$  upon release of  $^t\text{BuOH}$  and  $\text{Me}_2\text{C}=\text{CH}_2$  upon reflux in toluene for 36 h in the presence of 30%  $\text{HN}(\text{SiMe}_3)_2$ , see ref. [5].
- [23] Note that complex **2**<sub>2</sub> is perfectly stable in pentane in the presence of  $\text{HN}(\text{SiMe}_3)_2$  (10 equiv).
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## COMMUNICATION

Stable lead(II) siloxides that do not decompose towards oxocluster have been prepared. This includes the first homoleptic Pb<sup>II</sup>-siloxide, which also exhibits unique structural features.

**1980** "[Pb(OSiPh<sub>3</sub>)<sub>2</sub>]"  $\rightleftharpoons$  [Pb<sub>4</sub>(O)(OSiPh<sub>3</sub>)<sub>7</sub>]

**2019** **Stable, homoleptic Pb(II)-siloxide !**



**No decomposition to oxoclusters !**

*Adrian-Alexandru Someșan, Erwann Le Coz, Ciprian Raț, Vincent Dorcet, Thierry Roisnel, Cristian Silvestru\* and Yann Sarazin\**

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**Lead(II) siloxides**