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Lead(II) siloxides

Adrian-Alexandru Someșan,^[a] Erwann Le Coz,^[b] Ciprian Ionuț Raț,^[a] Vincent Dorcet,^[b] Thierry Roisnel,^[b] Cristian Silvestru^{*[a]} and Yann Sarazin^{*[b]}

In celebration of the 100th anniversary of the foundation of the Romanian University in Cluj-Napoca

Abstract: While Pb^{II}-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.^[1] 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 $[Pb_6(\mu_3-O)_4(\mu_3-OR)_4]$ ($R = Et, iPr, tBu$, etc.) in the presence of impurities (e.g. water, other protic sources or bases) or upon heating.^[2]

Metal triorganosiloxides can also be used as molecular precursors to $MSiO_x$ metal silica-based materials.^[3] 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^{II}-siloxide, the heteroleptic $[Pb\{N(SiMe_3)_2\}(\mu_2-OSiMe_3)]_2$, was a dimer prepared by Sita through heterocumulene metathesis of $[Pb\{N(SiMe_3)_2\}_2]$.^[4] 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 $[Pb_8O_5(OSiPh_3)_6]$.^[5] 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^{II}-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^{II}-siloxides are stable.^[6] 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.^[7]

We are seeking to improve our understanding of the nature and reactivity of Pb^{II}-O bonds,^[8] and have recently reported that bulky borinic acids afford low-coordinate Pb^{II}-boryloxides that display good thermal stability.^[8c-d] 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),^[9] hexafluoroisopropoxide, a smaller ligand, was unable to prevent the uncontrolled formation of the oxocluster $[Pb_4(\mu_4-O)(\mu_2-OCH(CF_3)_2)_5(\mu_3-OCH(CF_3)_2)]$.^[8c] We document here the syntheses and structural characterisation of the first homoleptic Pb^{II}-siloxides, notably $[Pb_2\{OSi(SiMe_3)_3\}(\mu_2-OSi(SiMe_3)_3)_3]$ (Fig. 1, 2). 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)^[4,5] and disiloxides (this work). The arrows indicate bridging μ_3 - and μ_4 -oxides in the oxoclusters.

The synthesis of the heteroleptic Pb^{II}-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

[a] A.-A. Someșan, Dr. C. I. Raț, Prof. Dr. C. Silvestru
Supramolecular Organic and Organometallic Chemistry Centre
Chemistry Department, Faculty of Chemistry and Chemical
Engineering, Babeș-Bolyai University
Cluj-Napoca RO-400028 (Romania)
E-mail: cristian.silvestru@ubbcluj.ro; Tel: +40 264-593833
[b] E. Le Coz, Dr. V. Dorcet, Dr. T. Roisnel, Dr. Y. Sarazin
Univ Rennes, CNRS
ISCR (Institut des Sciences Chimiques de Rennes)-UMR 6226
35000 Rennes (France)
E-mail: yann.sarazin@univ-rennes1.fr

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has recently been utilised to produce a stable Pb^{II} -boryloxide.^[8d] However, regardless of the choice of experimental conditions, the reaction of the known $[(\text{RO}^{\text{F}})\text{PbN}(\text{SiMe}_3)_2]$ ^[8d] with an equimolar amount of Ph_3SiOH 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,^[3b] and, very recently, two barium siloxides.^[10,11]

Scheme 1. Synthesis of Pb^{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 ^1H 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}Pb NMR spectroscopy, i.e. shielded by 700 ppm compared to the boryloxide $[(\text{RO}^{\text{F}})\text{PbOB}(\text{CH}(\text{SiMe}_3)_2)_2]$.^[8d] Chemical shifts in ^{207}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 (σ_{D}), paramagnetic (σ_{P}) and spin-orbit (σ_{SO}) shieldings.^[12] Without accurate deconstruction of these different contributions by DFT methods, the interpretation of ^{207}Pb chemical shifts is rather unsound, hence we are refraining here from doing so. The ^{29}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}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^[8d]) presumably formed through Schlenk equilibrium. ^1H - ^{19}F HOESY NMR data show the existence of intramolecular through-space $\text{H}\cdots\text{F}$ interactions between CF_3 atoms on the one hand and $\text{NCH}_2\text{C}(\text{CF}_3)_2$ and NCH_2CH_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,^[13] distorted trigonal pyramidal environment ($\tau_4 = 0.77$).^[14] 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).^[9] 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).^[9] The arrangement about the bridging O atoms in **12** approaches perfect trigonal planar geometry ($\Sigma_e(\text{O1}) = 358.4^\circ$).

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 Pb^{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).^[15] The green **2** is characterised by a broad singlet at δ_{H} 0.38 ppm and a resonance at $\delta_{\text{C}}^{\text{H}}$ 2.37 ppm in the ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra, respectively, recorded in benzene- d_6 . The ^{207}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 Pb1-Pb2-O31 angle compared to 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 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 Pb2-O31 interatomic distance ($2.152(9)$ Å) is only mildly longer than the Pb1-O1 one. Although much longer than the other Pb-O bond lengths in **2**, the 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.^[16] 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° .

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° 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 Pb_2O_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 Pb_2O_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 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 β -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 $[\{\text{BDI}^{\text{DIPP2}}\}\text{PbOC}(\text{=O})\text{O}^+\text{Pr}]$.^[17] 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 $1\text{-Ad-N}=\text{C}=\text{O}$ ($\text{Ad} = \text{adamantyl}$), 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 $[\text{Pb}^{\text{II}}]\text{-alkoxides}$.^[16,17]

In addition, unlike lighter tetrelenes,^[8a] it is inert towards PhSeSePh.

The decomposition of Pb^{II}-siloxides and concomitant production of oxoclusters, such as encountered in our attempted synthesis of [(RO^F)PbOSiPh₃] (see above), has been reported on several occasions.^[4,5,18] We thus sought to understand our failure to synthesise this heteroleptic complex. It is proposed that the sole isolable product from these trials, [Pb₄(μ₄-O)(μ₂-OSiPh₃)₆] (**B**), forms through decomposition of [Pb(OSiPh₃)₂] and release of Ph₃SiOSiPh₃ as a by-product. [Pb(OSiPh₃)₂] must itself be generated as one of the two homoleptic products following ligand redistribution (aka Schlenk equilibrium) in the attempted synthesis of [(RO^F)PbOSiPh₃] (Scheme 3). Consistent with this assumption, near-quantitative formation of [(RO^F)₂Pb]^[8d] was detected spectroscopically for reactions performed in J-Young NMR tubes.

Scheme 3. Proposed pathway for the formation of [Pb₄(μ₄-O)(μ₂-OSiPh₃)₆] (**B**) during the attempted synthesis of [(RO^F)PbOSiPh₃].

To further probe this scenario, the synthesis of the bis-siloxide [Pb(OSiPh₃)₂] and its degradation into **B** were investigated. The Schlenk-scale reaction of [Pb(N(SiMe₃)₂)₂] and 2 equivalents of Ph₃SiOH in Et₂O only returned large crops of single crystals of **B** after work-up and crystallisation from Et₂O.^[19] The same reaction was then performed in a J-Young NMR tube in C₆D₆ and was monitored by NMR spectroscopy (see data sets in the ESI). Within the first point of analysis, the ¹H NMR spectrum confirmed full conversion of the starting materials and quantitative release of HN(SiMe₃)₂. It also indicated the formation of a main species characterised in particular by a major doublet at δ_{1H} 7.64 ppm and assigned to the targeted [Pb(OSiPh₃)₂], together with minor doublets at 7.49 ppm (assigned to the oxocluster **B**) and 7.69 ppm (belonging to Ph₃SiOSiPh₃). These latter assignments were unambiguously made on the basis on the NMR data for independently isolated single crystals of **B** and Ph₃SiOSiPh₃ (a poorly soluble, colourless compound).^[20] Detailed monitoring of the reaction by ¹H, ²⁹Si INEPT and ²⁰⁷Pb NMR spectroscopies confirmed that the initially formed [Pb(OSiPh₃)₂] (δ_{207Pb} = 878 ppm; δ_{29Si} = -17.65 ppm) decomposed gradually over the course of 24 h to yield Ph₃SiOSiPh₃ (δ_{29Si} = -18.66 ppm) and **B** (δ_{207Pb} = 704 ppm; ²⁹Si NMR, δ_{29Si} = -17.90 ppm),^[21] together with a small amount of other unidentifiable species, presumably some higher lead(II) oxo-bridged aggregates.^[4,5] The mechanism for the formation of **B** upon decomposition of transient [Pb(OSiPh₃)₂] is summarised in Scheme 4. It is worth noting that our numerous attempts to build [Pb(OSiPh₃)₂] starting from [Pb(N(SiMe₃)₂)₂] were

unsuccessful. It may well be that the evolution of [Pb(OSiPh₃)₂] into **B** is actually facilitated by the by-product from this reaction, HN(SiMe₃)₂, as shown for the decomposition of [Pb₃(μ-O^tBu)₆].^[22,23] Yet, we found the reaction of Lappert's [Pb{CH(SiMe₃)₂}₂]^[24] with Ph₃SiOH also returned **B**, although the by-product of this reaction, CH₂(SiMe₃)₂, is both a very weak acid and essentially chemically inert. Finally, we also tried to obtain **B** upon salt metathesis between PbCl₂ and freshly prepared [LiOSiPh₃], but this reaction again only afforded the isolation of another (hybrid) oxocluster of overall composition [Pb₈(μ₄-O)₂(μ₂-Cl)₂(μ₃-Cl)(μ₄-Cl)(μ₂-OSiPh₃)₈], as authenticated by XRD analysis (Figure S28). On the whole, the elusive [Pb(OSiPh₃)₂] 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(OSiPh₃)₂] into [Pb₄(μ₄-O)(μ₂-OSiPh₃)₆] (**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. [Pb₂{OSi(SiMe₃)₃}₂], the first stable, homoleptic Pb^{II}-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(OSiPh₃)₂], 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^{II}-O bonds.

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- [15] Note that the heteroleptic $[\text{Pb}\{\text{N}(\text{SiMe}_3)_2\}\{\text{OSi}(\text{SiMe}_3)_3\}]_n$ can be obtained by reaction of $[\text{Pb}\{\text{N}(\text{SiMe}_3)_2\}]$ with one equivalent of $(\text{Me}_3\text{Si})_3\text{SiOH}$. NMR evidence was conclusive as to the formation of this heteroleptic complex, but the colourless microcrystals we obtained were of insufficient quality to establish the molecular structure of this complex, see SI.
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- [18] The oxocluster **B** was also the sole isolated product in our attempted synthesis of $[(\text{C}^*\text{N})\text{Pb}\{\text{OSiPh}_3\}]$ starting from $[(\text{C}^*\text{N})\text{PbN}(\text{SiMe}_3)_2]$ and Ph_3SiOH , where $\{\text{C}^*\text{N}\}^-$ is the bidentate $\{2\text{-Me}_2\text{NCH}_2\text{C}_6\text{H}_4\}^-$.
- [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 C_6D_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].
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COMMUNICATION

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

1980 "[Pb(OSiPh₃)₂]" $\rightleftharpoons$ [Pb₄(O)(OSiPh₃)₇]

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