Stable lead(II) boroxides

Adrian-Alexandru Somesan, Erwann Le Coz, Thierry Roisnel, Cristian Silvestru, Yann Sarazin

ChemCommun

COMMUNICATION

Stable lead(II) boroxides†

Adrian-Alexandru Someşan,[a] Erwann Le Coz,[b] Thierry Roisnel,[b] Cristian Silvestru*[a] and Yann Sarazin*[b]

The first examples of lead(II) boroxides, [Pb(OB{CH(SiMe$_3$)$_2$}$_2$)$_2$] (1) and [{N^C}PbOB{CH(SiMe$_3$)$_2$}$_2$] (5; N^C = 2-Me$_2$NCH$_2$C$_6$H$_4$), were prepared via simple protocols. These structurally characterised compounds are stable and, unlike lead(II) alkoxides and siloxides, do not trigger uncontrolled formation of lead(II) oxoclusters.

Lead(II) alkoxides [Pb(OR)$_2$]$_n$ are excellent precursors to lead-containing metal oxide materials such as glasses,[1] but they are infamously tedious to prepare. They are often poorly soluble, and show tremendous propensity to form oxoclusters such as [Pb$_4$(μ^4-O)(μ^2-OR)$_6$] and [Pb$_6$(μ^3-O)$_4$(μ^3-OR)$_4$]. This has been said to result from the release of dialkyl ethers R$_2$O upon heating,[2] from decomposition in the presence of moisture or other impurities,[3] or from release of isobutene and ROH upon action of HN(SiMe$_3$)$_2$ or metal amides.[4] Structurally authenticated lead(II) alkoxides have for long been limited to the trinuclear [Pb$_3$(μ^2-O^{t}Bu)$_6$] and to polymeric [Pb(μ^2-O^{i}Pr)$_2$]$_∞$ and [Pb(η^1,μ^2-OCH$_2$CH$_2$OMe)$_2$]$_∞$.[3,5] Of late, dinuclear mixed alkoxo/amido [Pb(N(SiMe$_3$)$_2$)(μ^2-O^{i}Pr)]$_2$ and [Pb(N(SiMe$_3$)$_2$)(η^1,μ^2-O^Se^N)]$_2$ have been reported,[5,6] while a handful of heteroleptic, mononuclear complexes [{BDI}Pb(OR)] supported by bulky β-diketiminato ligands have also been disclosed.[7]

This paucity is even more pronounced for lead(II) siloxides. The attempted formation of [Pb(OSiPh$_3$)$_2$]$_n$ either from [Cp$_2$Pb] or [Pb(N(SiMe$_3$)$_2$)$_2$] has been repeatedly shown to return the oxocluster [Pb$_4$(μ^4-O)(μ^2-OSiPh$_3$)$_6$].[8] Thus, [Pb(OSiR$_3$)$_2$]$_n$ species remain unauthenticated to this day,[9] even though the heteroleptic [Pb(N(SiMe$_3$)$_2$)(μ^2-OSiMe$_3$)]$_2$ was obtained by reaction of [Pb(N(SiMe$_3$)$_2$)$_2$] with ^{t}BuNCO;[10] the attempted synthesis of [Pb(OSiMe$_3$)$_2$]$_n$ following the same method only yielded the oxocluster [Pb$_7$(μ^3-O)(μ^4-O)(μ^2-OSiMe$_3$)$_{10}$] upon elimination of Me$_3$SiOSiMe$_3$.

Our attention was recently drawn to the fact that borinic acids R$_2$BOH have never been implemented in lead chemistry,[11] although boroxides exist for a variety of other main group metals, e.g. lithium,[12] magnesium,[12d] zinc,[12d,13] cadmium,[13a] and aluminium.[14] Boroxides R$_2$BO$^-$ can be seen as electron poor versions of alkoxides, due to delocalisation of the O-atom lone pairs in the empty p_z orbital at boron. We reasoned that this consideration, combined with its considerable steric demands, should render the boroxide (Me$_3$Si)$_2$BO$^-$ a suitable candidate to alleviate the tendency of regular alkoxides to form lead(II) clusters, and therefore could fill the existing loophole in lead(II) chemistry. We report here on the first lead(II) boroxides (and a tin(II) congener), which show superior stability with respect to other alkoxides.

[a.] Supramolecular Organic and Organometallic Chemistry Centre, Chemistry Department, Faculty of Chemistry and Chemical Engineering, Babes-Bolyai University, RO-400028 Cluj-Napoca, Romania.
E-mail: cristian.silvestru@ubbcluj.ro; Tel: (+40) 264-593833.
Univ Rennes, CNRS, ISCR (Institut des Sciences Chimiques de Rennes) – UMR 6226, F-35000 Rennes, France.
E-mail: yann.sarazin@univ-rennes1.fr; Tel: (+33) 2 23 23 30 19.
† Electronic Supplementary Information (ESI) available: Synthetic details; NMR and crystallographic data. See DOI: 10.1039/x0xx00000x
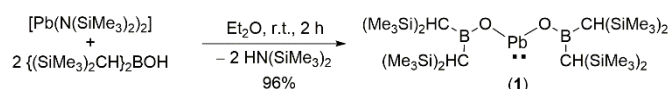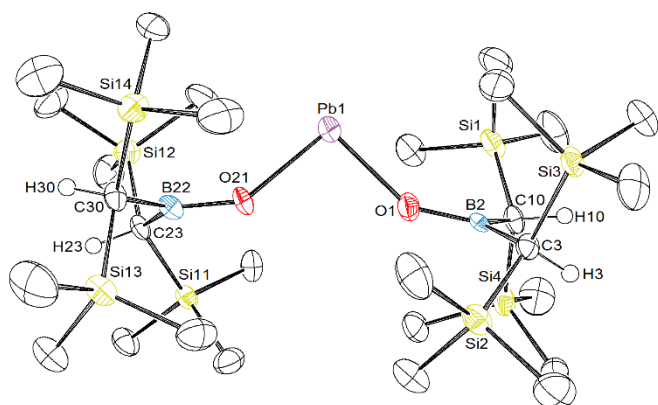
Scheme 1 Synthesis of [Pb(OB{CH(SiMe$_3$)$_2$}$_2$)$_2$] (1)

Fig. 1 ORTEP representation of the solid state structure of [Pb(OB{CH(SiMe$_3$)$_2$}$_2$)$_2$] (**1**). Ellipsoids drawn at the 50% probability level. All methyl H atoms omitted for clarity. Selected interatomic distances (Å): Pb1–O1 = 2.067(6), Pb1–O21 = 2.089(5), O1–B2 = 1.356(10), B2–C3 = 1.573(12), B2–C10 = 1.584(13), O21–B22 = 1.353(10), B22–C23 = 1.590(11), B22–C30 = 1.591(12). Selected angles (°): O1–Pb1–O21 = 95.60(2), B2–O1–Pb1 = 147.90(5), B22–O21–Pb1 = 145.10(5).

We met in the past little difficulty in preparing and handling the known alkoxides [Pb(μ^2-O^{i}Pr)$_2$]$_\infty$ and [Pb$_3$(μ^2-O^{t}Bu)}$_6$].[5] Yet, all attempts at synthesising the related siloxide [Pb(OSiPh$_3$)$_2$]$_n$ only yielded the known oxocluster [Pb$_4$(μ^4-O)(μ^2-OSiPh$_3$)$_6$]. We anticipated that the bulky borinic acid {(Me$_3$Si)$_2$CH}$_2$BOH[15] should provide steric protection to the metal centre (and yield soluble complexes), despite a greater distance between the cumbersome alkyl groups and the metal centre with respect to conventional alkoxides. Treatment in Et$_2$O of freshly distilled [Pb(N(SiMe$_3$)$_2$)$_2$][16] with 2 equivalents of {(Me$_3$Si)$_2$CH}$_2$BOH at room temperature for 2 h afforded the bis-boroxide complex [Pb(OB{CH(SiMe$_3$)$_2$}$_2$)$_2$] (**1**) upon clean elimination of HN(SiMe$_3$)$_2$ (Scheme 1). It was isolated in near-quantitative yield as a very pale yellow, air-sensitive solid upon removal of the volatiles. Its composition was formulated on the basis of spectroscopic and crystallographic data. It is very soluble in common organic solvents, including aromatic and aliphatic hydrocarbons. Complex **1** is the first occurrence of a lead(II) boroxide.[11]

The molecular structure of **1** was established by X-ray diffraction analysis of single crystals grown from pentane at −40 °C. The complex exists as a monometallic species in the solid state, with a two-coordinate metal centre (Fig. 1). The Pb1–O1 and Pb1–O21 interatomic distances of 2.067(6) and 2.089(5) Å are remarkably short. They are for instance substantially larger in the bis-alkoxo complexes [Pb(μ^2-O^{i}Pr)$_2$]$_\infty$ (2.210(3)-2.522(2) Å)[5] and in [Pb$_3$(μ^2-O^{t}Bu)}$_6$] (2.17(1)-2.55(1) Å),[3] in the amido-alkoxide [Pb(N(SiMe$_3$)$_2$)(μ^2-O^{i}Pr)]$_2$ (2.289(9) Å)[5] and in the amido-siloxide [Pb(N(SiMe$_3$)$_2$)(μ^2-OSiMe$_3$)]$_2$ (2.276(8)-2.291(8) Å).[10] The O1–Pb1–O21 angle of 95.60(2)° is close to the ideal value of 90° expected for lead(II), testifying to a mostly 6s^2 lone pair of electrons with a minimal contribution of the empty 6p_z orbital to the formation of an hybrid orbital. The geometry about the boron atoms is trigonal planar (Σ_θ(B2) = 360.0° and Σ_θ(B22) = 359.9°). The B2–O1–Pb1 and B22–O21–Pb1 angles of 147.90(5) and 145.10(5)° suggest only small π-contributions to the O1–Pb1 and O21–Pb1 bonds. The O1–B2 and O21–B22 distances (1.356(10) and 1.353(10) Å)

are only slightly shortened compared to that in the parent borinic acid (1.3805(17) Å).

The NMR spectroscopic data for **1** were recorded in C$_6$D$_6$.
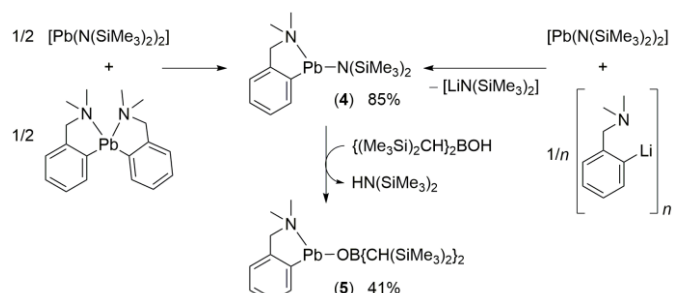
The ^{1}H, ^{13}C{^{1}H} and ^{29}Si spectra are unremarkable (see the Electronic Supporting Information). In the ^{11}B NMR spectrum, a single, well-defined resonance is detected at 53.5 ppm, i.e. very close to the resonance seen for {(Me$_3$Si)$_2$CH}$_2$BOH in the same solvent (δ_{11B} = 53.3 ppm). In its ^{207}Pb NMR spectrum, **1** gives rise to a very sharp resonance at 1805 ppm. It is located at much higher field than that for the two-coordinate precursor [Pb(N(SiMe$_3$)$_2$)$_2$] (δ_{207Pb} = 4916 ppm), and it is also shielded compared to [Pb(N(SiMe$_3$)$_2$)(μ^2-OSiMe$_3$)]$_2$ (δ_{207Pb} = 2443 ppm)[10] and [Pb(N(SiMe$_3$)$_2$)(μ^2-O^{i}Pr)]$_2$ (δ_{207Pb} = 2531 ppm);[5] the ^{207}Pb NMR data for [Pb(μ^2-O^{i}Pr)$_2$]$_\infty$ and [Pb$_3$(μ^2-O^{t}Bu)}$_6$] were not reported in Buhro's seminal papers.[3,5] Chemical shifts in ^{207}Pb NMR do not necessarily vary in line with the electron withdrawing/donating abilities of the substituents on the metal. Instead, the overall isotropic shielding it is a composite of the diamagnetic shielding (σ_D), the paramagnetic shielding (σ_p) and the spin-orbit shielding (σ_{so}). Without deconvolution of these contributions by DFT methods,[17] and in view of the different coordination environments in the above compounds, we are refraining from unsound interpretation of ^{207}Pb chemical shifts.

The congeneric tin(II) complex [Sn(OB{CH(SiMe$_3$)$_2$}$_2$)$_2$] (**2**) was obtained in similar fashion in 82% yield upon stoichiometric reaction of [Sn(N(SiMe$_3$)$_2$)$_2$] and {(Me$_3$Si)$_2$CH}$_2$BOH. It also crystallised as colourless plates, and its molecular structure is isomorphous with that of **1** (ESI).

The preparation of a stable, monometallic, bisalkoxide-like lead(II) complex [Pb(OR)$_2$] is for now restricted to the above example with utilisation of the cumbersome boroxide {(Me$_3$Si)$_2$CH}$_2$BO$^-$. We also attempted to prepare a base-free [Pb(OCH(CF$_3$)$_2$)$_2$] bearing two electron-poor fluoroalkoxides by action of (CF$_3$)$_2$CHOH onto [Pb(N(SiMe$_3$)$_2$)$_2$], but it only returned the oxocluster [Pb$_4$(μ^4-O)(μ^2-OCH(CF$_3$)$_2$)$_5$(μ^3-OCH(CF$_3$)$_2$)] (**3**). Prior to this, the dimethylaminopyridine adduct [Pb(μ^2-OCH(CF$_3$)$_2$)(OCH(CF$_3$)$_2$)(DMAP)]$_2$ and the salt [Me$_2$NH$_2$]$_2$[Pb$_2$(μ^2-OCH(CF$_3$)$_2$)$_2$(OCH(CF$_3$)$_2$)$_4$],[18] as well as the complex [Li$_2$Pb$_2$(μ^2-OCH(CF$_3$)$_2$)$_4$(μ^3-OCH(CF$_3$)$_2$)$_2$],[19] were reported. Although it compares to the adamantane-like [Pb$_4$(μ^4-O)(μ^2-OSiPh$_3$)$_6$][8] and [Pb$_4$(μ^4-O)(μ^2-O^{t}Bu)$_6$],[2,20] the molecular solid state structure of **3** differ from those of these compounds; its Pb$_4$O$_7$ core features C$_s$ symmetry (ESI). Crystals of **3** were characterised by multinuclear NMR spectroscopy.

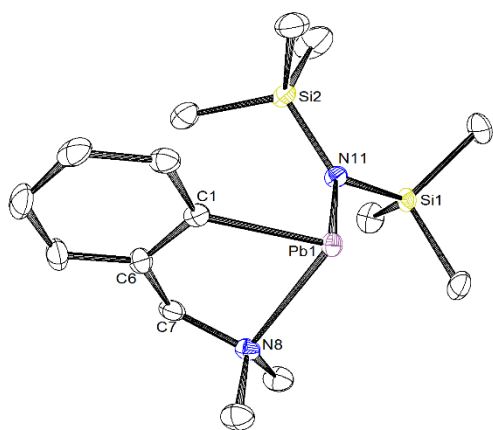Notably, a resonance at 693 ppm is detected in its ^{207}Pb NMR

Fig. 2 ORTEP representation of the solid state structure of [{N^C}PbN(SiMe$_3$)$_2$] (**4**). Ellipsoids drawn at the 50% probability level. H atoms omitted for clarity. Selected interatomic distances (Å): Pb1–N11 = 2.249(3), Pb1–C1 = 2.308(4), Pb1–N8 = 2.490(3). Selected angles (°): N11–Pb1–C1 = 99.02(12), N11–Pb1–N8 = 94.18(11), C1–Pb1–N8 = 73.25(12).

Scheme 2 Synt [{N^C}PbOB{CH

spectrum.

The synthesis of lead(II)-boroxides can be extended to the production of heteroleptic complexes. The bidentate, monoanionic ligand 2-Me$_2$NCH$_2$C$_6$H$_4^-$ (aka {N^C}$^-$) sharing 3 electrons lends itself well to the organometallic chemistry of lead(II), owing to the propensity of the ion Pb^{2+} to form 3-coordinate, 18-electron complexes. The amido precursor [{N^C}PbN(SiMe$_3$)$_2$] (**4**) was obtained in 85% isolated yield by mixing equimolar quantities of [Pb(N(SiMe$_3$)$_2$)$_2$] and [{N^C}$_2$Pb].[21] It can also be prepared by reaction between [Pb(N(SiMe$_3$)$_2$)$_2$] and 1/n equivalent of [(N^C)Li]$_n$ following elimination of [LiN(SiMe$_3$)$_2$] (Scheme 2), although in this case separation from this by-product can be tedious. Complex **4** is a very rare case of low coordinate organolead(II) amide,[22] and the sole mononuclear one. It was isolated as a pale yellow solid. The N(SiMe$_3$)$_2^-$ amido moiety very typically imparts both kinetic stability and good solubility to the complex (it dissolves readily in organic solvents, including hydrocarbons). It is also sufficiently basic to open access to further organometallic derivatives (*vide infra*). A resonance at δ_{207Pb} 2595 ppm is seen in the ^{207}Pb NMR spectrum of **4**. Its molecular solid state structure was determined by single-crystal X-ray diffraction (Fig. 2). The metal is 3-coordinate with a distorted pyramidal geometry; the angles around the lead atom vary much, between 73.25(12) and 99.02(12)°. The Pb1–N8 interaction of the N_{amine} in the pendant arm is stronger in **4** (2.490(3) Å) than in the 4-coordinate [{N^C}$_2$Pb] (2.616(3)-2.727(3) Å),[21] but the Pb–C interatomic distances in the two complexes are commensurate. The Pb–C distance in **4** also compares well with those in four-coordinate Pb(II) complexes bearing a O^C^O pincer ligand.[23] The Pb1–N11 interatomic distance

(2.249(3) Å) is characteristic for such 3-coordinate lead(II) complexes.[6]

The reaction of **4** with equimolar {(Me$_3$Si)$_2$CH}$_2$BOH does not release {N^C}H. Instead, it proceeds to generate the very moisture- and air-sensitive, colourless heteroleptic boroxide [{N^C}PbOB{CH(SiMe$_3$)$_2$}$_2$] (**5**) through selective release of HN(SiMe$_3$)$_2$. The observed reactivity was unexpected on account of the respective basicity of the substituents on the metal (pK_a: HN(SiMe$_3$)$_2$/N(SiMe$_3$)$_2^-$, 25.8; C$_6$H$_6$/C$_6$H$_5^-$ = 43.0). Instead, it presumably reflects the greater covalent character of the Pb(II)–C bond compared to the Pb(II)–N one. The colourless **5** was isolated in a non-optimised 41% yield by recrystallisation from pentane. The complex exhibits a resonance at δ_{11B} 48.1 ppm in ^{11}B NMR spectroscopy, i.e. it is shielded by ca. 5 ppm compared to **1**. This is assumed to reflect the greater electronic density at the metal centre in the 3-coordinate **5**. In the ^{207}Pb NMR spectrum, a sole resonance is visible at δ_{207Pb} 3095 ppm. The composition and structure of **5** were corroborated by XRD analysis. The environment about the 3-coordinate metal is trigonal pyramidal (Fig. 3). The Pb1–N8 and Pb1–C1 interatomic distances match those in **4**. On the other hand, the Pb1–O11 contact (2.1874(19) Å) to $O_{boroxide}$ is longer than in **1**. The angles around Pb1 in **5** are also substantially different from those in **4**, i.e. they are narrower except for the matching O–Pb–C angles. The B12–O11–Pb1 angle in **5** (136.46(18)°) is also narrower than the pertaining B2–O1–Pb1 and B22–O21–Pb1 angles in **1** (147.90(5) and 145.10(5)°). Taken collectively, these data point at a lower participation of the π lone pairs at O11 to the formation of the Pb–O$_{boroxide}$ bond in **5** than seen in **1**. The geometry around the boron atom is perfectly trigonal planar (Σ_θ(B12) = 360.0°). Note that **5** can also be prepared cleanly by mixing the homoleptic precursors [{N^C}$_2$Pb] and **1** in equimolar amounts at room temperature.

The reactivity observed between **4** and {(Me$_3$Si)$_2$CH}$_2$BOH and the stability of the resulting complex **5** both appear to be exceptional. Hence, all our attempts at preparing a congeneric alkoxide or siloxide of the type [{N^C}PbOR] met with failure. The reactions of [{N^C}$_2$Pb] with [Pb(μ^2-O^{i}Pr)$_2$]$_\infty$ or [Pb$_3$(μ^2-O^{t}Bu)}$_6$] returned pure, unreacted starting materials. Moreover, no reaction took place between [(N^C)Li]$_n$ and the well soluble [Pb$_3$(μ^2-O^{t}Bu)}$_6$]. Finally, [{N^C}$_2$Pb] was the sole isolable product generated by treatment of **4** with ^{t}BuOH or (CF$_3$)$_2$CHOH. The stability of **5** hence appears to stem from the combination of the bidentate {N^C}$^-$ ligand and the bulky, "electron poor" boroxide.

In conclusion, the utilisation of the bulky ligand {(Me$_3$Si)$_2$CH}$_2$BO$^-$ enables the facile syntheses of the first lead(II) boroxides, the homoleptic 2-coordinate [Pb(OB{CH(SiMe$_3$)$_2$}$_2$)$_2$] (**1**) and the 3-coordinate, heteroleptic organolead(II) [{N^C}PbOB{CH(SiMe$_3$)$_2$}$_2$] (**5**). These compounds fill a loophole that hitherto existed in the coordination chemistry of lead and, more generally, group 14 metals. Although air-sensitive, **1** and **5** are stable in solution and in the solid state (a clean melting temperature of 141 °C was even determined for **5**, although **1** decomposed between 110-130 °C to generate a dark red unidentified solid), and do
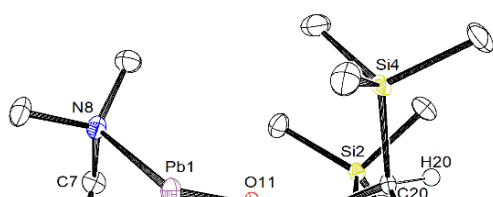

Fig. 3 ORTEP representation of the solid state structure of [{N^C}PbOB{CH(SiMe$_3$)$_2$}$_2$] (**5**). Ellipsoids drawn at the 50% probability level. Most H atoms omitted for clarity. Selected interatomic distances (Å): Pb1–O11 = 2.1874(19), Pb1–C1 = 2.286(3), Pb1–N8 = 2.467(2), O11–B12 = 1.340(4), B12–C13 = 1.607(4), B12–C20 = 1.609(4). Selected angles (°): O11–Pb1–C1 = 89.01(9), O11–Pb1–N8 = 86.24(8), C1–Pb1–N8 = 73.37(9), B12–O11–Pb1 = 136.46(18), O11–B12–C13 = 117.50(2), O11–B12–C20 = 125.30(2), C13–B12–C20 = 117.20(2).

not seem to generate the oxoclusters that have so often plagued the chemistry of more traditional lead(II) alkoxides and siloxides. We are now pursuing our efforts to understand the specificity of lead(II) boroxides, and we are also hoping to use these compounds to probe unchartered areas of organolead(II) chemistry.

Conflicts of interest

There are no conflicts to declare.

Notes and references

1   (*a*) W. H. Dumbaugh and J. C. Lapp, *J. Am. Ceram. Soc.*, 1992, **75**, 2315; (*b*) S. Kohara, H. Ohno, M. Takata, T. Usuki, H. Morita, K. Suzuya, J. Akola and L. Pusztai, *Phys. Rev. B,* 2010, **82**, 134209; (*c*) R. G. Fernandes, J. Ren, A. S. S. de Camargo, A. C. Hernandes and H. Eckert , *J. Phys. Chem. C*, 2012, **116**, 6434.

2   (*a*) R. Papiernik, L. G. Hubert-Pfalzgraf and M. C. Massiani, *Inorg. Chim. Acta*, 1989, **165**, 1; (*b*) R. Papiernik, L. G. Hubert-Pfalzgraf and M. C. Massiani, *Polyhedron*, 1991, **10**, 1657.

3   S. C. Goel, M. Y. Chiang and W. E. Buhro, *Inorg. Chem.*, 1990, **29**, 4640.

4   D. J. Teff, J. C. Huffman and K. G. Caulton, *J. Am. Chem. Soc.*, 1996, **118**, 4030.

5   L. Wang, S. Fadlallah, C. Bellini, C. Orione, V. Dorcet, J.-F. Carpentier and Y. Sarazin, *Organometallics*, 2015, **34**, 1321.

6   A. Pop, L. Wang, V. Dorcet, T. Roisnel, J.-F. Carpentier, A. Silvestru and Y. Sarazin, *Dalton Trans.*, 2014, **43**, 16459.

7   (*a*) E. C. Y. Tam, N. C. Johnstone, L. Ferro, P. B. Hitchcock and J. R. Fulton, *Inorg. Chem.*, 2009, **48**, 8971; (*b*) E. C. Y. Tam, M. P. Coles, J. D. Smith and J. R. Fulton, *Polyhedron*, 2015, **85**, 284.

8   C. Gaffney, P. G. Harrison and T. J. King, *J. Chem. Soc., Chem. Commun.*, 1980, 1251.

9   W. Patnode and F. C. Schmidt, *J. Am. Chem. Soc.*, 1945, **67**, 2272.

10 C. S. Weinert, I. A. Guzei, A. L. Rheingold and L. R. Sita, *Organometallics*, 1998, **17**, 498.

11 M. P. Coles, *Coord. Chem. Rev.*, 2016, **323**, 52.

12 (*a*) K. J. Weese, R. A. Bartlett, B. D. Murray, M. M. Olmstead and P. P. Power, *Inorg. Chem.*, 1987, **26**, 2409; (*b*) G. Beck, P. B. Hitchcock, M. F. Lappert and l. A. MacKinnon, *J. Chem. Soc., Chem. Commun.*, I989, 1312; (*c*) V. C. Gibson, C. Redshaw, W. Clegg and M. R. J. Elsegood, *Polyhedron*, 1997, **16**, 2637; (*d*) S. C. Cole, M. P. Coles and P. B. Hitchcock, *Organometallics*, 2004, **23**, 5159.

13 (*a*) S. Luliński, I. Madura, J. Serwatowski and J. Zachara, *Inorg. Chem.*, 1999, **38**, 4937; (*b*) R. Anulewicz-Ostrowska, S. Luliński, E. Pindelska and J. Serwatowski, *Inorg. Chem.*, **2002**, 41, 2525; (*c*) S. J. Birch, S. R. Boss, S. C. Cole, M. P. Coles, R. Haigh, P. B. Hitchcock and A. E. H. Wheatley, *Dalton Trans.*, 2004, 3568.

14 (*a*) L. Synoradzki, M. Bolesławski and J. Lewínski, *J. Organomet. Chem.*, 1985, **284**, 1; (*b*) R. Köster, Y.-H. Tsay, C. Krüger and J. Serwatowski, *Chem. Ber.*, 1986, **119**, 1174; (*c*) R. Anulewicz-Ostrowska, S. Luliński, J. Serwatowski and K. Suwińska, *Inorg. Chem.*, 2000, **39**, 5763; (*d*) V. C. Gibson, S. Mastroianni, A. J. P. White and D. J. Williams, *Inorg. Chem.*, 2001, **40**, 826.

15 S. Al-Hashimi and J. D. Smith, *J. Organomet. Chem.*, 1978, **153**, 253.

16 T. Heidemann and S. Mathur, *Eur. J. Inorg. Chem.*, 2014, 506.

17 M. J. Taylor, E. J. Coakley, M. P. Coles, H. Cox and J. R. Fulton, *Organometallics*, 2015, **34**, 2515.

18 S. Suh and D. M. Hoffman, *Inorg. Chem.*, 1996, **35**, 6164

19 D. J. Teff, J. C. Huffman and K. G. Caulton, *Inorg. Chem.*, 1997, **36**, 4372.

20 The structure of the hexanuclear $[Pb_6(\mu^3\text{-}O)_4(\mu^3\text{-}O^iPr)_4]$ is known, see: A. I. Yanovskii, N. Y. Turova, E. P. Turevskaya and Y. T. Struchkov, *Koord. Khim.*, 1982, **8**, 153. For the structure of the tetranuclear $[Pb_4(\mu^4\text{-}O)(\mu^2\text{-}OSiPh_3)_6]$, see ref. 8.

21 J. Bareš, V. Šourek, Z. Padělková, P. Meunier, N. Pirio, I. Císařová, A. Růžička and J. Holeček, *Collect. Czech. Chem. Commun.*, 2010, **75**, 121.

22 A. C. Filippou, N. Weidemann and G. Schnakenburg, *Angew. Chem. Int. Ed.*, 2008, **47**, 5799.

23 K. Jurkschat, K. Peveling and M. Schürmann, *Eur. J. Inorg. Chem.*, 2003, 3563.