Aminofluoroalkoxide amido and boryloxo lead(ii) complexes
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We report here on the utilisation of a readily available bidentate aminofluoroalkoxide in lead(II) chemistry. Stable heteroleptic three-coordinate complexes can be produced in high yields, including a convenient amido synthetic precursor and a rare case of Pb\(^{\text{II}}\)-boryloxide.

Known for 6000 years, lead is a versatile metal that has been used in water pipes by Romans owing to its malleability and resistance against corrosion and, closer to us, as an anti-knock agent in petrol and as a paint additive. However, it is a highly toxic element, and its use for industrial purposes is now essentially prohibited. In spite of its historical significance, the organometallic chemistry of lead, and in particular that of divalent lead, has been rather overlooked. Investigations on organometallic chemistry of lead, and in particular that of Pb\(^{\text{II}}\), including a convenient amido synthetic precursor and a rare case of Pb\(^{\text{II}}\)-boryloxide.

We report here on the utilisation of a readily available bidentate aminofluoroalkoxide in lead(II) chemistry. Stable heteroleptic three-coordinate complexes can be produced in high yields, including a convenient amido synthetic precursor and a rare case of Pb\(^{\text{II}}\)-boryloxide.

The aminofluoroalcohol 2-EtNCH\(_2\)C\((\text{CF}_3)\)OH (aka \((\text{RO})\text{H}\)) was prepared in 90% yield upon stoichiometric reaction of HNEt\(_2\) with 2,2-bis(trifluoromethyl)oxirane in Et\(_2\)O (Scheme 1). The proligand was isolated as a colourless, volatile liquid. The formulation was confirmed by NMR spectroscopy in benzene-\(d_6\) and HR-MS spectrometry, and bulk purity was further confirmed by combustion analysis. Notably, the \(^{19}\text{F}\) NMR spectrum exhibits a sharp singlet at \(\delta_{\text{19F}} = -77.8\) ppm, while the \(^{13}\text{C}\)\(^{(1)}\text{H}\) spectrum features a quartet centred on \(\delta_{\text{13C}} = 124.4\) ppm (\(J_{\text{CF}} = 287\) Hz) and a septet at \(\delta_{\text{13C}} = 71.8\) ppm (\(J_{\text{CF}} = 29\) Hz). All resonances are sharp and well resolved in the \(^{1\text{H}}\) NMR spectrum.

The reaction of \([\text{Pb}(\text{N}(\text{SiMe})_3)_2]\) with one equivalent of \((\text{RO})\text{H}\) afforded the heteroleptic, mononuclear amido complex \([(\text{RO})\text{PbN}(\text{SiMe})_3)] (1) in good yields, ca. 75-80%, and with excellent reproducibility. Complex 1 was isolated as a pale yellow crystalline solid that displays good solubility in all common organic solvents, including aliphatic hydrocarbons. It is a rare occurrence of heteroleptic alkoxide/amide lead(II) species.

Single crystals of 1 suitable for X-ray diffraction

\[\text{HNEt}_2 + \text{CF}_3\text{C} = \text{O} \rightarrow \text{Et}_2\text{O} \quad 90\%\]

\[\text{Pb} + \text{CF}_3\text{C} = \text{O} \rightarrow \text{CF}_3\text{C} = \text{O} \quad \text{Pb} \text{N}(\text{SiMe})_3 \quad \text{78}\%\]

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**Scheme 1.** Synthesis of 2-EtNCH\(_2\)C\((\text{CF}_3)\)OH (\((\text{RO})\text{H}\)) and [(\(\text{RO}\))\text{PbN}(\text{SiMe})_3] (1).
analysis were grown from a concentrated solution in Et₂O stored at −43 °C. The identity and purity of the complex were supported by NMR data recorded in benzene-

pyramidalisation (DoP) in 1,³³ where DoP = [360 − Σθ(i)/i] / 0.9 and where θ(i) are the angles around the metal (sum of angles = 264°). This value is in particular much greater than that in the β-diketiminate complex [{BDI²⁺}PbN(SiMe₃)₂] (DiPP = 2,6-Pr₂-C₆H₄), that is, 78%.³² It matches those in [{BDI²⁺}PbCl] (110°)¹⁰ and in the iminoanilide lead(II) chloride [{N=N}PbCl] (111°).³⁴ The solid-state structure of 1 features four short H⋯F interatomic distances involving the H atoms on C4. They are in the range 2.460(8)-2.518(8) Å, i.e. below the sum of Van der Waals radii for H and F (1.09 and 1.47 Å); these measurements indicate mild interactions and are consistent with the results of ¹⁹F HOSY NMR analysis in solution.

As mentioned, complex 1 decomposes in solution to return the homoleptic 2 and [Pb(N(SiMe₃)₂)₂] (Kstab = 4.0 × 10⁻² at 25 °C in benzene-d₆). The colourless 2 was otherwise prepared in 97% yield by reacting [Pb(N(SiMe₃)₂)] with two equivalents of (RO)²H. It is characterised by resonances at δ307ppm 1187 ppm and δ19F = −71.7 ppm (broad singlet at 25 °C, showing the equivalence of all CF₃ substituents on the NMR timescale) by ²⁰⁷Pb and ¹⁹F NMR spectroscopies in benzene-d₆. The molecular structure of complex was established by XRD methods (Figure 2). It shows a four-coordinate metal in a hemi-directed tetrahedral geometry.³⁵ The Pb-O and Pb-N interatomic distances in 2 are similar to those in 1.

Scheme 2. Synthesis of [{(RO)²PbO}(CH(SiMe₃)₂)] (3)
128 °C and decomposes irreversibly at 150 °C, is a rare example of stable lead(II) boryloxide.\(^{17}\) It exhibits good solubility in most common organic solvents, including hydrocarbons. Colourless single crystals suitable for X-ray diffraction analysis were grown from a concentrated petroleum ether solution stored at –43 °C. Two sets of analogous site occupancies were found, with one (82% site occupancy) is depicted. H atoms omitted for clarity. Representative bond lengths (Å) and angles (°): Pb1-O1 = 2.128(2), Pb1-O28 = 2.181(4), Pb1-N21B = 2.448(4); O1-Pb1-O28 = 87.25(19), O1-Pb1-N21B = 94.65(12), O28-Pb1-N21B = 71.60(2), O1-B2-C2 = 118.20(3), O1-B2-C10 = 123.40(3), C3-B2-C10 = 118.40(3), B2-O1-Pb1 = 132.90(2), Torsion angle (°): N21B-C26A-C27-O28 = –9.50(6).

The lead atom in 3 is planar (ΣB2(μ3-B) = 360.0°) and the two-coordinate Pb-N backbone (torsion angle N21B-C26A-C27-O28 = 132.90(2)°) suggests only a small p-contribution to the O1 bond length (2.128 Å), which is comparable to that in PbOB(2,4,6-iPr3-C6H3)\(_2\) (2.194 Å). The complex is stable in the solid state and shows minor formation of homoleptic species upon ligand scrambling in solution (see above). Its stability is seen as the expression of the chelating bidentate ligand (RO)\(_2\)F, but also of the steric protection, and hence the kinetic stability, imparted by the very bulky boryloxide [(Me3Si)CH2]2BO.\(^{17}\) For instance, our attempts to use a different borinic acid, (2,4,6-iPr3-C6H3)\(_2\)BOH, to produce related well-defined, mononuclear Pb\(_{\text{II}}\)-boryloxide species, were unsuccessful. They instead returned crops of the centrosymmetric oxocluster of composition [Pb\(_2\)(μ3-O)\(_2\)(μ3-OB(2,4,6-iPr3-C6H3))\(_2\)] (4), as authenticated by XRD analysis (Figure 4). No other compound could be identified from the crude of these reactions, which were not probed further. The uncontrolled formation of this aggregate is reminiscent of that observed for Pb\(_{\text{II}}\)-siloxides, e.g. [Pb\(_2\)(μ3-O)(μ3-O3SiPh\(_3\))] or [Pb\(_2\)(μ3-O)(μ3-O)(μ3-O3SiMe\(_3\))]\(_{10}\).\(^{37,38}\) The molecular structure of 4 shows two distinct lead(II) environments. Both are in a three-coordinate distorted trigonal pyramidal geometry, with DoP = 113% and 118% for Pb1 and Pb2, together with uneven Pb-O interatomic distances. The geometry about the boron atom is trigonal planar (ζB(8) = 360.0° and 359.7° for B1 and B41).

Figure 4. ORTEP representation of the molecular solid-state structure of [Pb\(_2\)(μ3-O)\(_2\)(μ3-OB(2,4,6-iPr3-C6H3))\(_2\)] (4). Ellipsoids at the 50% probability level. H atoms and iPr groups not represented for clarity. Representative bond lengths (Å) and angles (°): Pb1-O1 = 2.201(5), Pb1-O2 = 2.231(5), Pb1-O3 = 2.675(6), Pb2-O2 = 2.206(5), Pb2-O2’ = 2.231(5), Pb2-O3 = 2.473(5), O2-Pb1-O1 = 81.08(18), O2-Pb1-O2’ = 76.85(17), O1-Pb1-O3’ = 100.50(17), O2-Pb2-O2 = 77.70(2), O2-Pb2-O3 = 102.02(17), O2-Pb2-O3’ = 74.52(17). Symmetry transformations used to generate equivalent atoms: -x, y, -z.

The \(^{19}F\) NMR spectrum of crystalline 3 in benzene-\(d_6\) exhibits a singlet at \(\delta_{19F} = 77.1\) ppm, and satellites owing to coupling with the metal (\(^{125}Pb, J_{PB} = 125\) Hz); the presence of traces of 2 and an unknown impurity (singlet at \(\delta_{19F} = 73.2\) ppm, with satellites presenting a coupling constant of 252 Hz to a nucleus whose natural abundancy, ca. 30-40%, does not match that of \(^{207}Pb\), 22.6%; this impurity was also at times detected in variable quantities in the \(^{19}F\) NMR data for 1 and 2) is also visible. Compound 3 gives rises to a multiplet at \(\delta_{19F} = 1425\) ppm (\(^{207}Pb\) ≈ 125 Hz matching that determined in the \(^{19}F\) NMR spectrum) in the \(^{207}Pb\) NMR spectrum. The \(^{13}B\) NMR spectrum contains a single, broad resonance at \(\delta_{13B} = 49.5\) ppm diagnostic of this boryloxide, while a sharp singlet is seen at \(\delta_{29Si} = 3.49\) ppm in the \(^{29}Si\) NMR spectrum.

On the whole, complex 3 is an unusual example of three-coordinate lead(II) compounds, and is one of the three cases of known Pb-boryloxide.\(^{17}\) The complex is stable in the solid state and shows minor formation of homoleptic species upon ligand scrambling in solution (see above). Its stability is seen as the expression of the chelating bidentate ligand (RO)\(_2\)F, but also of the steric protection, and hence the kinetic stability, imparted by the very bulky boryloxide [(Me3Si)CH2]2BO.\(^{17}\) For instance, our attempts to use a different borinic acid, (2,4,6-iPr3-C6H3)\(_2\)BOH, to produce related well-defined, mononuclear Pb\(_{\text{II}}\)-boryloxide species, were unsuccessful. They instead returned crops of the centrosymmetric oxocluster of composition [Pb\(_2\)(μ3-O)\(_2\)(μ3-OB(2,4,6-iPr3-C6H3))\(_2\)] (4), as authenticated by XRD analysis (Figure 4). No other compound could be identified from the crude of these reactions, which were not probed further. The uncontrolled formation of this aggregate is reminiscent of that observed for Pb\(_{\text{II}}\)-siloxides, e.g. [Pb\(_2\)(μ3-O)(μ3-O3SiPh\(_3\))] or [Pb\(_2\)(μ3-O)(μ3-O)(μ3-O3SiMe\(_3\))]\(_{10}\).\(^{37,38}\) The molecular structure of 4 shows two distinct lead(II) environments. Both are in a three-coordinate distorted trigonal pyramidal geometry, with DoP = 113% and 118% for Pb1 and Pb2, together with uneven Pb-O interatomic distances. The geometry about the boron atom is trigonal planar (ζB(8) = 360.0° and 359.7° for B1 and B41).

Figure 3. ORTEP representation of the molecular solid-state structure of [(RO)\(_2\)PbOB(2,4,6-iPr3-C6H3)]\(_2\) (3). Ellipsoids at the 50% probability level. Only the main component (82% site occupancy) is depicted. H atoms omitted for clarity. Representative bond lengths (Å) and angles (°): Pb1-O1 = 2.128(2), Pb1-O28 = 2.181(4), Pb1-N21B = 2.448(4); O1-Pb1-O28 = 87.25(19), O1-Pb1-N21B = 94.65(12), O28-Pb1-N21B = 71.60(2), O1-B2-C2 = 118.20(3), O1-B2-C10 = 123.40(3), C3-B2-C10 = 118.40(3), B2-O1-Pb1 = 132.90(2), Torsion angle (°): N21B-C26A-C27-O28 = –9.50(6).
Conclusions

In summary, the readily available fluoroalkoxide (RO$_1$F) enables the high-yield syntheses of three-coordinate heteroleptic lead(II) alkoxides. The amido complex 1 is a convenient entry point into further organometallic and inorganic chemistry of these species, as illustrated by the preparation of the boryloxide 3, a new addition to the limited set of discrete Pb$_3$-alkoxide currently available. Not all boryloxide are suited to lead(II) chemistry, as exemplified by the uncontrolled formation of the oxocluster 4. We are currently further exploring the potential offered by the ligand core (RO$_1$F) in this chemistry and will communicate on these results in a forthcoming report.

Conflicts of interest

There are no conflicts to declare.

Notes and references

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