A new type of heteroleptic complex of divalent lead and synthesis of the *P*-plumbyleniophosphasilene, $R_2Si{=}P{-}Pb(L)$: (L = β-diketiminate)†

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The synthesis and structures of the first heteroleptic β-diketiminato complexes of lead(II) with terminal phenolato, bis(trimethylsilyl)amido, bis(trimethylsilyl)phosphanido and silylidenephosphanido ligands are reported; ^{207}Pb NMR spectroscopic data indicate that lead(II) can serve as a σ-donor or acceptor centre, depending on the electronegativity of the terminal ligand.

The β-diketiminate ligand is a particularly versatile ligand for the stabilisation of single-site metal centres in unusual low valence states.[1] Their coordination feature resembles those of related *N*-heterocyclic ligands which were used for the synthesis of unusual low-coordinate metal complexes. The low-valent (or low-coordinate) metal centres in such complexes benefit from intramolecular N→M donor–acceptor bonds and the presence of sterically demanding substituents at the nitrogen atoms. Diketiminato metal complexes were employed as pre-catalysts for polymerisation and C–X coupling processes in homogeneous catalysis.[2] In line with that, main-group metal complexes can be employed for a better understanding and a rational design of particular molecular catalysts.

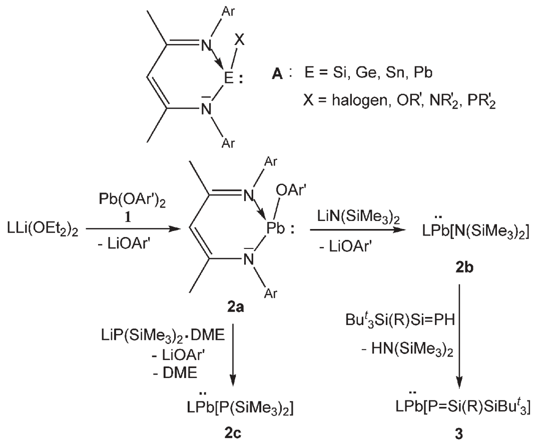
Recently, it was shown that appropriate tin(II) complexes can serve as single-site initiators for the polymerisation of lactides.[3] We are particularly interested in the structure–reactivity relationship of *N*-heterocyclic divalent group 14 element complexes L(X)E: **A** (L = β-diketiminate; X = alkoxide, amide, halide, phosphanide; E = Si, Ge, Sn, Pb) (Scheme 1). These complexes can serve as Lewis-acid catalysts for ring-opening polymerisations and represent new ligands for the synthesis of isolable carbene-analogue transition metal complexes (E = M) capable of olefin metathesis reactions. However, while a series of appropriate tin(II)[4] and germanium(II) complexes **A**[5] were already reported, the respective isolable divalent silicon and lead complexes of type **A** are still rare or currently unknown. Recently, we reported the synthesis of the first *N*-heterocyclic silylene of type **A**.[6] Here we describe the synthesis and structural features of the novel isolable heteroleptic lead(II) complexes of type **A**, compounds **2a**–**c**, including the first plumbyleno-substituted phosphasilene $R_2Si{=}P{-}PbL$, compound **3**.

In contrast to the procedure for the synthesis of the *N*-heterocyclic chloro complexes L(Cl)E: **A** (E = Ge, Sn), the analogous reaction of $[LLi(OEt_2)]$[7] with $PbCl_2$ in ethereal solvents leads exclusively to redox reactions, with formation of elemental lead. In order to circumvent redox processes, the reactions were performed in hydrocarbons as solvents, using the sterically encumbered Pb(II) diphenolate **1**[8] instead of $PbCl_2$. Thus, the latter conversion yielded the desired plumbylene **2a** in the form of yellow crystals in 83% yield (Scheme 1). According to an X-ray diffraction analysis, the asymmetric unit contains two independent molecules of **2a**.†

The molecules of **2a** consist of slightly puckered six-membered C_3N_2Pb rings in which the lead atoms adopt a trigonal pyramidal geometry with angles of 83.6–97.9° between the nitrogen donor and phenoxy-oxygen atoms (Fig. 1). The folding angle between the planes defined by the N1, N2, C2, C3, C4 atoms (plane 1) and the N1, Pb1, N2 atoms (plane 2) is 14.6° (14.9° in molecule 2).

The sum of bond angles at lead (274.8 and 286.9°) illustrates the high 6p-character of the lead σ-orbitals in the Pb–X (X = N, O) bonds due to a relativistic contraction of the lead 6s orbital which prevents mixing (hybridisation) of the lead-based valence orbitals.[9]

In other words, the lone pair of electrons at lead possess high s-character. The Pb–N and Pb–O distances are similar to values observed in related divalent Pb–N(amido)[10] and Pb–O(phenolato) complexes.[11] The electronic situation of the Pb(II) atom in **2a** is also reflected in its ^{207}Pb NMR spectrum which reveals a singlet at δ 1040 ppm. This value is close to that observed for a related donor-supported bis(β-diketiminato)plumbylene (δ 1060 ppm).[12] Since the phenolato ligand is a good nucleophilic leaving group, the reaction of **2a** with $LiN(SiMe_3)_2$ in a 1 : 1 molar stoichiometry



Scheme 1 Group 14 metal β-diketiminato complexes of type **A** and synthesis of **2a**–**2c** and **3** (Ar = $C_6H_3Pr^i_2$-2,6; R = $C_6H_2Pr^i_3$-2,4,6; Ar′ = $C_6H_3Bu^t_2$-2,6).

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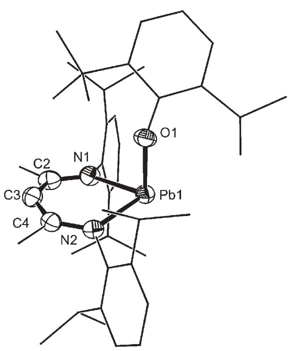

Fig. 1 Molecular structure of **2a** with thermal ellipsoids for C2–C4, N1, N2, Pb1, O1 drawn at the 50% probability level (one of the two molecules in the asymmetric unit; hydrogen atoms are not shown). Selected distances (pm) and angles (°): Pb1–O1 221.6(5), Pb1–N1 230.3(6), Pb1–N2 228.9(6); N1–Pb1–N2 83.6(2), O1–Pb1–N1 97.9(2), O1–Pb1–N2 93.3(2).

furnishes solely the desired amido complex **2b** which was isolated in 88% yield in the form of pale yellow crystals. Its composition is proven by multinuclear NMR spectroscopy and elemental analysis. Single crystal X-ray data were obtained for **2b** which revealed similar geometric parameters of the almost planar six-membered C_3N_2Pb ring with those in **2a** (Fig. 2).† The sum of bond angles around lead is 289°. The N1 atom of the terminal $N(SiMe_3)_2$ group is almost trigonal planar coordinated (sum of bond angles 358.4°) due to the intrinsically low inversion barrier of nitrogen in silyl-substituted amines.[13] Owing to the stronger σ-acceptor character of the N atom in the $N(SiMe_3)_2$ group, the exocyclic Pb–N distance (227.1(8) pm) is smaller than those of the endocyclic ones (Pb1–N3 231.5(8) and Pb1–N2 233.4(8) pm).

Interestingly, replacement of the phenolato ligand in **2a** by the $N(SiMe_3)_2$ group in **2b** causes a significant deshielding of the ^{207}Pb nucleus of $\Delta\delta$ 784 ppm in the ^{207}Pb NMR spectrum (δ 1824 ppm); this suggests that the $N(SiMe_3)_2$ group is a stronger Pb(II)→X (X = O, N) σ-acceptor than the phenolato ligand. Furthermore, we investigated the electronic changes at Pb by using the more electropositive phosphanido ligand $P(SiMe_3)_2$. The synthesis of the analogous phosphanido complex **2c** is as simple and straightforward as the access to **2b**. Thus, conversion of **2a** with $LiP(SiMe_3)_2$ affords the desired compound **2c** in the form of orange crystals in 79% yield (Scheme 1). Compound **2c** is the second isolated monomeric phosphanyl-substituted plumbylene.[14] It is remarkably stable in non-protic organic solvents and remains unchanged even in boiling toluene for 12 h. Cryoscopic measurements prove that **2c** remains monomeric in hydrocarbon solutions. The structure of **2c**, determined from X-ray diffraction analysis,† shows that the phosphanido group at lead causes a drastic geometrical change in the ring conformation to give a boat-shaped six-membered C_3N_2Pb ring (Fig. 3). The folding angle between the planes defined by the N1, C2, C3, C4, N2 atoms and the N1, Pb1, N2 atoms is 43.9° and thus much larger than those in **2a** (14.6°) and **2b** (11°). However, this does not influence the degree of pyramidalisation of the Pb(II) atom (sum of bond angles at Pb 281.7°) which is only slightly different from that in **2a** and **2b**. The same is true for the endocyclic Pb–N distances which are practically unchanged. The P atom is pyramidally coordinated, with a sum of bond angles of 305.7° owing to the pronounced σ-donor character of the silyl groups to phosphorus. As expected, the Pb–P distance of 271.5(2) pm is similar to those in the dimeric plumbylene $\{Pb[P(SiMe_3)_2]_2\}_2$ with a puckered Pb_2P_2 and three coordinate Pb(II) atoms (terminal Pb–P 269.6(7) pm)[15] but longer than that in a homoleptic diphosphanyl-substituted plumbylene with dicoordinate lead (265.4(4) pm).[14]

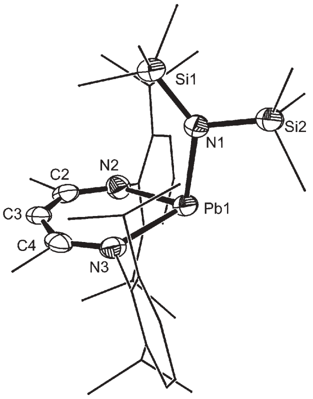

Fig. 2 Molecular structure of **2b** with thermal ellipsoids for C2–C4, N1–N3, Pb1, Si1, Si2 drawn at the 50% probability level (hydrogen atoms are not shown). Selected distances (pm) and angles (°): Pb1–N1 227.1(8), Pb1–N2 233.4(8), Pb1–N3 231.5(8), Si1–N1 171.5(8), Si2–N1 174.6(8); N1–Pb1–N3 99.2(3), N1–Pb1–N2 106.6(3), N3–Pb1–N2 83.2(3).

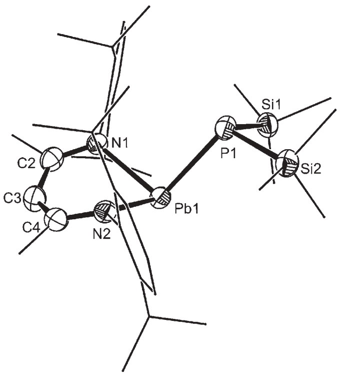

Fig. 3 Molecular structure of **2c** with thermal ellipsoids for C2–C4, N1, N2, Pb1, P1, Si1, Si2 drawn at the 50% probability level (hydrogen atoms are not shown). Selected distances (pm) and angles (°): Pb1–P1 271.5(2), Pb1–N1 235.9(6), Pb1–N2 232.5(6), Si1–P1 226.0(3), Si2–P1 224.8(3); N1–Pb1–N2 81.2(2), P1–Pb1–N1 97.3(2), P1–Pb1–N2 103.2(2).

What factors are responsible for the drastic change in the C_3N_2Pb ring conformation? Doubtless, the σ-donor ability of phosphorus (intrinsic $P^{\delta+}$–$Pb^{\delta-}$ bond polarity) plays a major role, whereas a Pb=P π-bond can be excluded because of the unfavourable P and Pb configurations and the inert pair effect of the 6s-electrons at Pb. The proposed $P^{\delta+}$–$Pb^{\delta-}$ bond polarity is in accordance with the ^{31}P and ^{207}Pb NMR spectra of **2c**: the ^{31}P nucleus of the $P(SiMe_3)_2$ ligand resonates at much lower field (δ −116.6 ppm) than that of the terminal $P(SiMe_3)_2$ group in the related dimer $\{Pb[P(SiMe_3)_2]_2\}_2$ (δ −217.3 ppm). Correspondingly, the ^{207}Pb nucleus in **2c** shows in the ^{207}Pb NMR spectrum (δ −1737 ppm) a remarkably strong shielding of $\Delta\delta$ −3561 ppm in comparison to **2b**. Also intriguing is the unprecedentedly large magnitude of the $^{1}J(^{31}P, ^{207}Pb)$ coupling constant of 2852 Hz, which is much larger than that of $\{Pb[P(SiMe_3)_2]_2\}_2$ (1264 and 1183 Hz) and even exceeds the value observed for related

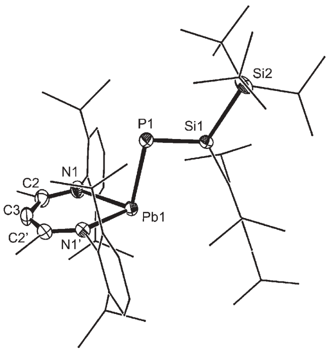

Fig. 4 Molecular structure of **3** with thermal ellipsoids for C2, C3, C2′, N1, N1′, Pb1, P1, Si1, Si2 drawn at the 50% probability level (hydrogen atoms are not shown). The molecule lies about a mirror plane. The atom labels with the additional prime character (′) indicate that these atoms are at equivalent positions (*x*, 1/2 − *y*, *z*). Selected distances (pm) and angles (°): Pb1–P1 267.1(1), Pb1–N1 236.8(3), Pb1–N1′ 236.8(3), P1–Si1 208.5(2), Si1–Si2 241.4(2); N1–Pb1–N1′ 82.0(1), N1–Pb1–P1 97.2(3), Si1–P1–Pb1 97.10(5), P1–Si1–Si2 117.05(7).

monomeric homoleptic diphosphanyl plumbylenes (1995 and 1979 Hz) with di-coordinate Pb(II) atoms.[14] The large magnitude of the $^{1}J(^{31}\mathrm{P}, {}^{207}\mathrm{Pb})$ coupling constant in **2c** clearly suggests a higher 3s-contribution of phosphorus in the Pb–P σ-bond. Reducing the donor ability of the P atom in the silylphosphane moiety should result in a re-planarisation of the six-membered C_3N_2Pb ring and, in turn, deshielding of the ^{207}Pb nucleus in the ^{207}Pb NMR spectrum as observed in **2b**. This was confirmed through replacement of the $P(SiMe_3)_2$ group at lead by the more electronegative P=SiR$_2$ group, bearing an sp^2-hybridised P atom. Thus, the relatively inert silylidenephosphanyl moiety (“*P*-phosphasilene” group), $\mathrm{Bu}^t{}_3\mathrm{Si(R)Si{=}P}$– (R = $\mathrm{C_6H_2Pr}^i{}_3$-2,4,6), was chosen in order to examine the outcome of the reduced donor ability of phosphorus towards lead. The compound $\mathrm{Bu}^t{}_3\mathrm{Si(R)Si{=}PH}$,[16] generated *in situ* from the corresponding lithium fluorosilylphosphane through LiF elimination, was allowed to react with **2b**, affording the desired *P*-plumbylenio-phosphasilene **3** in the form of red-brown crystals in 65% yield (Scheme 1). Compound **3** is the first isolable phosphasilene derivative with a divalent Group 14 metal bonded to low-valent phosphorus. Its composition is proven by elemental analysis and mass spectrometry. According to the multinuclear NMR spectra, only one stereoisomer (the *E*-form; see Fig. 4) was formed, doubtless for steric reasons. The $\delta\ ^{31}$P and $\delta\ ^{29}$Si values are similar to those observed for a related *P*-zincio derivative,[16] and the ^{207}Pb NMR spectrum of **3** reveals a broad singlet at δ 1068 ppm. The low-field ^{207}Pb chemical shift indicates that the P atom serves as a σ-acceptor in the Pb–P bond ($\mathrm{Pb}^{\delta+}$–$\mathrm{P}^{\delta-}$), in contrast to the electronic situation in **2c** and analogous to that in **2b**. In turn, the negative partial charge at phosphorus in **3** favours n(P)→σ*(Si–Si) hyperconjugation as shown for a *P*-zinciophosphasilene.[16] Accordingly, the electronic difference in the P atom in **3** *vs.* **2c** causes also a drastic change in the C_3N_2Pb ring conformation.

The folding angle between the planes defined by the N1, N1′, C2, C3, C2′ atoms (plane 1) and the N1, Pb1, N1′ atoms (plane 2) is 7.7°. The single-crystal X-ray diffraction analysis† of **3** (Fig. 4) revealed an almost planar C_3N_2Pb ring in which the lead atom adopts a trigonal pyramidal geometry similar to that in **2a** and **2b**.

The Pb–P distance of 267.1(1) pm is *ca.* 4 pm shorter than that in **2c** owing to the lower coordination number of phosphorus.

As expected, the low-valent silicon atom is trigonal planar coordinated and the Si=P and Si–Si distances are marginally longer than those in the related *P*-zinciophosphasilene.[16]

The novel plumbylene complexes **2a–c** and **3** are surprisingly robust under anaerobic conditions in non-protic organic solvents even at elevated temperatures (<110 °C). Thus, they represent valuable building blocks for the synthesis of other heteroleptic plumbylene complexes with Pb–X bonds (X = non-metal, metal atom) and tunable electrophilic or nucleophilic properties. Preliminary results show that the new compounds are very active initiators for the synthesis of polylactides and its copolymers.

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