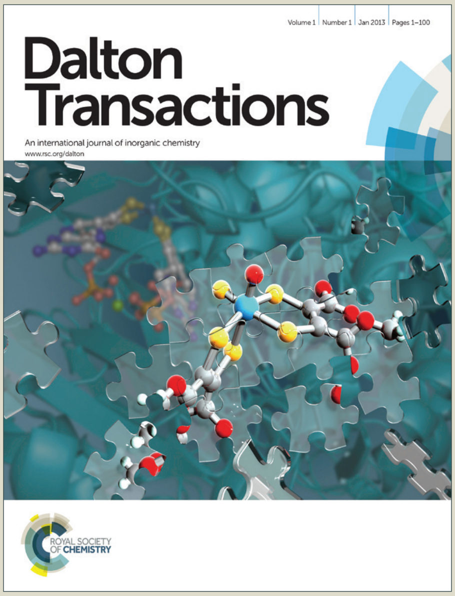
Dalton Transactions



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On the coordination chemistry of organochalcogenolates R^{NMe2}^E^- and R^{NMe2}^E^O^- (E = S, Se) onto lead(II) and lighter divalent tetrel elements[‡]

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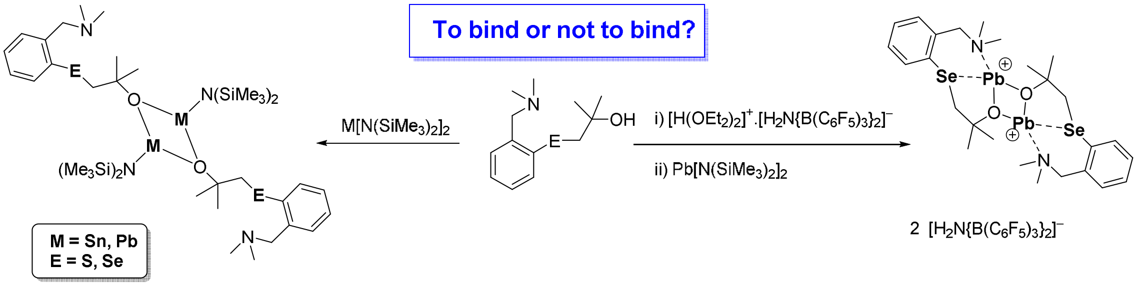

The coordination chemistry of potentially multidentate organochalcogenolato ligands containing both hard (N, O) and soft (S, Se) atoms onto divalent group 14 metals (Ge, Sn, Pb) in tetrelene complexes is explored.

On the coordination chemistry of organochalcogenolates R^{NMe2}^E^- and R^{NMe2}^E^O^- (E = S, Se) onto lead(II) and lighter divalent tetrel elements[‡]

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Abstract

Several families of heteroleptic tetrelenes of general formulae $M(E^\wedge R^{NMe2})[N(SiMe_3)_2]$ and $M(O^\wedge E^\wedge R^{NMe2})[N(SiMe_3)_2]$ (where E = S, Se; M = Ge, Sn, Pb; R^{NMe2} = $2\text{-}(Me_2NCH_2)C_6H_4$] supported by organochalcogenolato ligands have been prepared and fully characterised. The coordination chemistry of these ligands containing both hard (N, O) and soft (S, Se) atoms onto metals of varying size, polarisability, electropositivity and electrostatic surface potential has been explored. In the molecular solid-state, the complexes $M(E^\wedge R^{NMe2})[N(SiMe_3)_2]$ are monomeric, although an occurrence of weak Pb···Se intermolecular interactions yielding a bimolecular species has been identified in the case of the plumbylene $Pb[SeC_6H_4(CH_2NMe_2)\text{-}2][N(SiMe_3)_2]$. On the other hand, all complexes $M(O^\wedge E^\wedge R^{NMe2})[N(SiMe_3)_2]$ form centro-symmetric bimetallic dimers with *O*-bridging atoms. Multinuclear (^{29}Si, ^{77}Se, ^{119}Sn, ^{207}Pb) NMR spectroscopy and crystallographic studies reveal that the metal preferably remains 3-coordinated in all these heteroleptic complexes with absence of coordination of N and S/Se atoms, unless severe depletion of electronic density onto the metal is enforced. Coordination of these heteroelements can thus be achieved either through replacement of α-CH_3 substituents (as in the ligand $2\text{-}(Me_2NCH_2)C_6H_4SeCH_2C(Me)_2O^-$) by electron-withdrawing α-CF_3 moieties (as in the ligand $2\text{-}(Me_2NCH_2)C_6H_4SeCH_2C(CF_3)_2O^-$), or else with recourse to the use of a cationizing agent leading to the formation of the ion pair $[\{2\text{-}(Me_2NCH_2)C_6H_4SeCH_2C(Me)_2O\}Pb]^+\cdot[H_2N\{B(C_6F_5)_3\}_2]^-$ where the cationic metal complex is associated to a weakly-coordinating anion. The data collated herein provide compelling evidence that the coordination chemistry of divalent tetrel elements with ligands featuring both hard and soft donors cannot be reliably anticipated by sole use of general concepts such as the HSAB theory. The related metal complexes containing the rigid 8-(NMe_2)naphthalen-1-yl group are also discussed.

Introduction

Metal chalcogenolato complexes have attracted interest in the past decades owing to their rich structural chemistry and for their potential as single-source precursors for M/E materials (E = S, Se, Te) through chemical vapour deposition (CVD) processes.[1] Because they enable a satisfactory degree of synthetic control over size and morphology, the combination of chalcogenolates with main-group metals has proved worthy for the production of semiconducting materials. Notably, germanium and the earth-abundant tin and lead give narrow-gap semiconductor nanocrystals that find widespread applications in photovoltaics.[2] The nuclearity, molecular stability and volatility of divalent tetrel complexes is key in defining their usefulness as CVD precursors. Several stable divalent tin(II) and lead(II) chalcogenolates (which are also attracting increasing attention as heavier analogues of carbenes) of low nuclearity have been prepared using bulky ligands, *e.g.* $Sn[2,4,6\text{-}(t\text{Bu})_3\text{-}C_6H_2S]_2$,[3] $[Sn\{ESi(SiMe_3)_2\}_2]_2$ (E = S, Se, Te),[4] $[M(2,6\text{-}(i\text{Pr})_2\text{-}C_6H_3S)_2]_3$ (M = Sn, Pb)[3] or $[Pb(3\text{-}SiMe_3\text{-}2\text{-}SeNC_5H_4)_2]_3$.[1d]

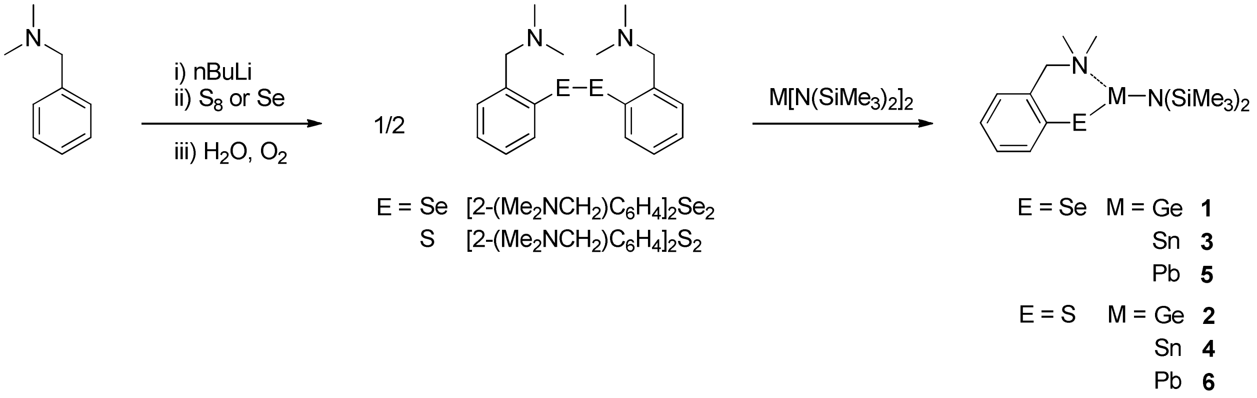
The presence of a side-arm containing one or more heteroatoms is known to help stabilise monomeric selenolate complexes of main-group metals.[5] We have employed hypervalent organoselenium species that contain a pendant amino or phosphino tether for the preparation of group 12 complexes,[6] and we have also taken an interest in the implementation of divalent tetrel complexes in catalysis.[7] Aminoether phenolate ligands $\{LO\}^-$ have enabled the synthesis of the kinetically inert monomeric, singlet tetrelenes $M\{OL\}[N(SiMe_3)_2]$ (M = Ge, Sn and Pb),[8] yet the range of available supporting ligands yielding heteroleptic complexes for these three elements remains rather limited. As part of our ongoing investigations, we report here on heteroleptic complexes $M(E\text{^}R^{NMe2})[N(SiMe_3)_2]$ and $M(O\text{^}E\text{^}R^{NMe2})[N(SiMe_3)_2]$ [E = S, Se; M = Ge, Sn, Pb; R^{NMe2} = $2\text{-}(Me_2NCH_2)C_6H_4$] supported by the organochalcogenolato ligands $R^{NMe2}\text{^}E^-$ and

R^{NMe2}^E^O^{-} , in which the variety of potential binding modes resulting from the presence of both hard (O, N) and soft (S, Se) donors with increasingly large and polarisable elements is illustrated. For comparison, the related metal complexes containing the rigid 8-(NMe_2)naphthalen-1-yl group are also discussed.

Results and Discussion

Synthesis and characterisation of organo-thiolato and -selenolato complexes

The ligand precursor $[2\text{-}(Me_2NCH_2)C_6H_4]_2S_2$ was isolated as a yellow oil following an ortho-lithiation procedure analogous to that reported for the preparation of its selenium congener,[9] $[2\text{-}(Me_2NCH_2)C_6H_4]_2Se_2$. The reactions of these precursors with two equivalents of $Ge[N(SiMe_3)_2]_2$, $Sn[N(SiMe_3)_2]_2$ or $Pb[N(SiMe_3)_2]_2$ in diethyl ether afforded the analytically pure heteroleptic divalent complexes $Ge[SeC_6H_4(CH_2NMe_2)\text{-}2][N(SiMe_3)_2]$ (**1**), $Ge[SC_6H_4(CH_2NMe_2)\text{-}2][N(SiMe_3)_2]$ (**2**), $Sn[SeC_6H_4(CH_2NMe_2)\text{-}2][N(SiMe_3)_2]$ (**3**), $Sn[SC_6H_4(CH_2NMe_2)\text{-}2][N(SiMe_3)_2]$ (**4**), $Pb[SeC_6H_4(CH_2NMe_2)\text{-}2][N(SiMe_3)_2]$ (**5**) and $Pb[SC_6H_4(CH_2NMe_2)\text{-}2][N(SiMe_3)_2]$ (**6**) in yields generally well over 70% (Scheme 1). The formulation proposed for **1**–**6** is established on the basis of ^1H and $^{13}C\{^1H\}$ NMR spectroscopy and combustion analysis; it is confirmed by X-ray diffraction crystallography in the case of the lead(II) complexes **5** and **6**. The germanium complexes **1** and **2** are pale yellow oils, while the heavier congeners **3–4** are yellow solids. All are fully soluble and stable in common organic solvents, and are increasingly sensitive to air and moisture on descending in the column according to Ge < Sn < Pb.



Scheme 1. Synthesis of $M[SeC_6H_4(CH_2NMe_2)\text{-}2][N(SiMe_3)_2]$ complexes **1–6**.

The multinuclear NMR data for complexes **1–6** are collated in Table 1. The $^{29}Si\{^1H\}$ NMR resonances for the lead(II) complexes are shifted towards high field in comparison with their tin(II) analogue, which reflects the increasing ionicity of the M–N(SiMe$_3$)$_2$ bond in these complexes. Broad resonances are observed in the $^{207}Pb\{^1H\}$ NMR spectra of **5** and **6** at δ_{207Pb} = +3230 and +2927 ppm, respectively, *i.e.* in the region characteristic of 3-coordinated lead(II)-amide complexes.[8] The ^{119}Sn and ^{207}Pb resonances for complexes containing the organothiolato ligand are significantly shielded compared with their derivatives incorporating the organoselenolato group. Note that the ^{119}Sn resonance was located at δ_{119Sn} = −63 ppm for $Sn[OC_6H_2\text{-}2\text{-}CH_2NEt_2\text{-}4,6\text{-}t\text{Bu}_2][N(SiMe_3)_2]$, a stannylene structurally related to **3** and **4** (δ_{119Sn} = +196 and −78 ppm, respectively),[7a] and therefore we cannot rationalise simply the role of the chalcogen on ^{119}Sn NMR data in these complexes.[10] The $^{77}Se\{^1H\}$ NMR spectra display a single broad signal at δ_{77Se} = +264 ppm for **5** and sharp resonances at +258 and +188 ppm for **1** and **3**, *i.e.* at much higher field than seen for the ligand precursor (+427 ppm). These chemical shifts appear in the range reported for alkali arylselenolates,[11] but at lower field by *ca.* 200–400 ppm than in related homoleptic zinc and cadmium bis(organoselenolate) complexes.[6f,12,13] In the $^{77}Se\{^1H\}$ spectrum of the tin(II) complex **3**, satellites due to the coupling with ^{117}Sn and ^{119}Sn atoms can be seen ($^1J_{\text{Se-119Sn}}$ = 865 Hz and $^1J_{\text{Se-117Sn}}$ = 815 Hz), while the corresponding selenium satellites were observed in the ^{119}Sn{^{1}H} NMR spectrum of this complex. Both the chemical shifts and coupling constants observed in the tin(II) complex **3** differ considerably from those seen in the tin(IV) complex $Mes_2C_6H_3SeSnMe_3$ (mes = mesityl): δ_{119Sn} = +49 and δ_{77Se} = −44 ppm, $^1J_{\text{Se-119Sn}}$ = 1190 Hz;[14] the corresponding NMR data are not available for the 3-coordinated tin(II) complex with RSe^- ligands structurally characterized in the CCDC database, *e.g.* Sn(2-$SeNC_5H_4)_2$ or $[Yb(THF)_6][Sn(SeC_6H_5)_3]_2$.[1d,15]

Table 1. Multinuclear NMR data for the ligand precursors and complexes **1–6**.[a]

		δ_{77Se} [b] [ppm]	δ_{119Sn} [c] [ppm]	δ_{207Pb} [d] [ppm]	δ_{29Si} [e] [ppm]
$[2\text{-}(Me_2NCH_2)C_6H_4]_2Se_2$		+427	-	-	-
$Ge[SeC_6H_4(CH_2NMe_2)\text{-}2][N(SiMe_3)_2]$	**1**	+258	-	-	+5.7
$Ge[SC_6H_4(CH_2NMe_2)\text{-}2][N(SiMe_3)_2]$	**2**	-	-	-	-
$Sn[SeC_6H_4(CH_2NMe_2)\text{-}2][N(SiMe_3)_2]$	**3**	+188	+196	-	+6.5
$Sn[SC_6H_4(CH_2NMe_2)\text{-}2][N(SiMe_3)_2]$	**4**	-	−78	-	+5.2
$Pb[SeC_6H_4(CH_2NMe_2)\text{-}2][N(SiMe_3)_2]$[f]	**5**	+264	-	+3230	−1.8
$Pb[SC_6H_4(CH_2NMe_2)\text{-}2][N(SiMe_3)_2]$	**6**	-	-	+2927	−1.7

[a] Data for {^{1}H} heterodecoupled NMR in benzene-d_6 at 298 K unless otherwise specified. [b] 76.32 MHz. [c] 149.21 MHz. [d] 83.71 MHz. [e] 79.49 MHz. [f] Recorded in toluene-d_8.

The ^{1}H NMR spectrum of the plumbylene **5** recorded in toluene-d_8 at 298 K features broad resonances for the methyl and methylene hydrogen atoms of the $CH_2N(CH_3)_2$ tether. The corresponding fluxional processes could be frozen at low temperatures. The broad resonance detected at *ca.* δ_{1H} = 1.84 ppm at 298 K and assigned to $N(CH_3)_2$ gives rise to two sharp singlets on lowering the temperature, *e.g.* at δ_{1H} 1.58 and 2.28 ppm at 183 K; the coalescence temperature T_c = 263 K was determined, with a free energy of activation of $\Delta G^\ddagger$ = 11.9 kcal·mol^{-1} for the associated dynamic process. The broad resonance corresponding to the $CH_2N(CH_3)_2$ methylene hydrogens (δ_{1H} = 3.54 ppm at 298 K) gives rise to an AB spin system at lower temperature (δ_{1H} = 4.21 and 2.84 ppm , $^2J_{H-H}$ = 11.4 Hz at 205 K); the free energy of activation calculated at the coalescence (T_c = 273 K, $\Delta G^{\ddagger}$ = 12.2 kcal·mol^{-1}) matched well that established above. Note that a similar behaviour was observed for the plumbylene **6**, but not for the congeneric complexes **1–4** based on the smaller germanium and tin.

The molecular solid-state structures of the plumbylenes **5** and **6** were established by XRD analysis on single crystals. The metal atom is 3-coordinated in **5** (Figure 1), with strong coordination of the $N_{side\text{-}arm}$ atom [Pb(1)–N(11) = 2.673(4) Å, Σr_{vdw}(Pb,N) = 3.55 Å]. The angles around lead are in the range 82–99°, which indicates limited hybridisation of *s* and p_z orbitals, and therefore the lone pair of electrons is mostly *s* character, as expected for the large divalent group 14 elements. The coordination of the $N_{side\text{-}arm}$ to lead results in the formation of a six-membered Pb(1)-N(11)-C(14)-C(15)-C(20)-Se(2) ring folded about the Se(1)···C(14) axis. This induces planar chirality (with the phenyl ring as chiral plane) and, as a consequence, **5** crystallises as a racemic mixture of *R* and *S* isomers.[16] The Pb–Se and Pb–$N_{side\text{-}arm}$ bond distances in this complex are however closely comparable to those measured in $Pb(SeCH_2CH_2NMe_2)_2$ (*ca.* 2.725–2.750 Å and 2.620–2.642 Å, respectively), the only example of a 4-coordinated $Pb(Se\text{^}N)_2$ complex in the CCDC database.[17] The molecules in the crystals of **5** are further associated into dimers through weak secondary interactions, compare Pb(1)···Se(1') = 3.4021(5) Å with Σr_{cov}(Pb,Se) = 2.63 Å and Σr_{vdw}(Pb,Se) = 3.92 Å. In this way, typical T-shaped coordination geometry is obtained about the selenium atoms. NMR spectroscopy ($^{207}Pb\{^1H\}$ and $^{77}Se\{^1H\}$ NMR) provided no indication that these weak interactions are preserved in solution. The molecular solid-state structure of the thiolate complex **6** is similar to that of **5**, and is available in the electronic supporting information (ESI).

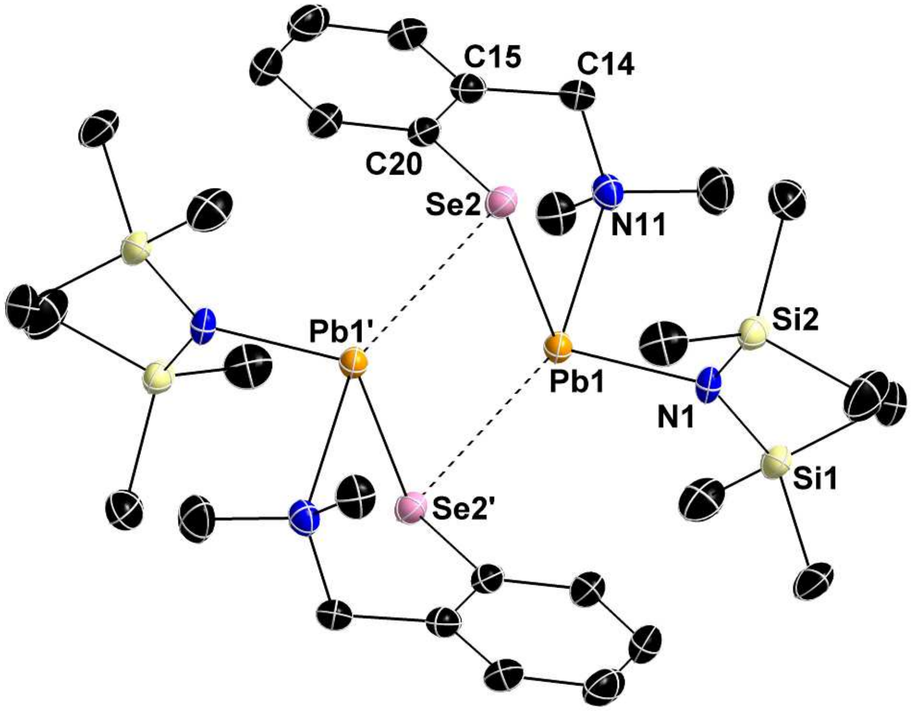
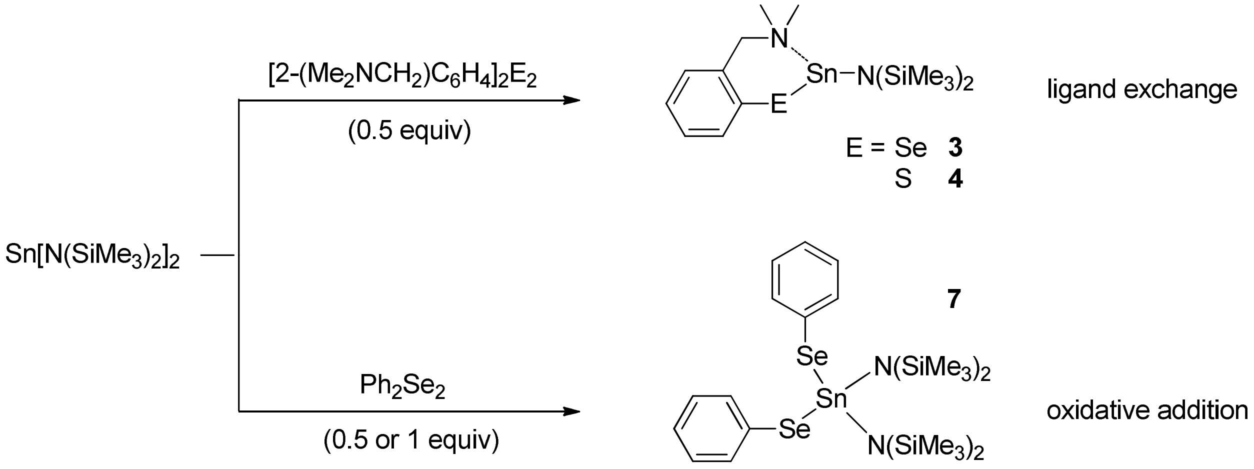


Figure 1. ORTEP representation of the molecular solid-state structure of Pb[$SeC_6H_4(CH_2NMe_2)$-2][$N(SiMe_3)_2$] (**5**), with thermal ellipsoids set at 50% probability. Hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Pb(1)–N(1) = 2.251(4), Pb(1)–N(11) = 2.673(4), Pb(1)–Se(2) = 2.7589(5), Se(2)–C(20) = 1.931(5), Pb(1)···Se(2') = 3.4021(5); N(1)–Pb(1)–N(11) = 98.66(14), N(1)–Pb(1)–Se(2) = 100.60(10), N(11)–Pb(1)–Se(2) = 82.59(9), C(20)–Se(2)–Pb(1) = 93.89(14), C(20)–Se(2)–Pb(1') = 109.604(16), Pb(1)–Se(2)–Pb(1') = 91.563(15).

On the reaction of R_2Se_2 precursors with $M[N(SiMe_3)_2]_2$

By contrast with the reaction leading to the formation of the tin(II) heteroleptic complexes **3** and **4**, the treatment of Ph_2Se_2 with one or two equivalents of $Sn[N(SiMe_3)_2]_2$ affords in near-quantitative yields the oxidised product $Sn(SePh)_2[N(SiMe_3)_2]_2$ (**7**) following oxidative addition onto the tin(II) bis(amido) precursor (Scheme 2).



Scheme 2. Ligand exchange *vs.* oxidative addition for diorganodiselenides and tin(II) precursors.

The identity of the tin(IV) complex **7** was authenticated by NMR spectroscopy (Figure 2) and XRD analysis performed on single crystals grown from pentane (Figure 3), and its purity was corroborated by elemental analysis. The ^{77}Se{^{1}H} NMR spectrum exhibits a narrow singlet at δ_{77Se} = +206 ppm ($\Delta\nu_{1/2}$ = 5.5 Hz), with clearly distinguishable ^{117}Sn ($^{1}J_{Se-117Sn}$ = 1614 Hz) and ^{119}Sn ($^{1}J_{Se-119Sn}$ = 1688 Hz) satellites. The complex is manifested as a sharp singlet in its ^{119}Sn{^{1}H} NMR spectrum (δ_{119Sn} = −183 ppm, $\Delta\nu_{1/2}$ = 13 Hz, $^{1}J_{119Sn-Se}$ = 1688 Hz), and is also characterized by a singlet at δ_{29Si} = 6.15 ppm by ^{29}Si{^{1}H} NMR ($\Delta\nu_{1/2}$ = 1.35 Hz, $^{1}J_{Si-C}$ = 55.7 Hz, $^{2}J_{Si-119Sn}$ = 12.3 Hz).

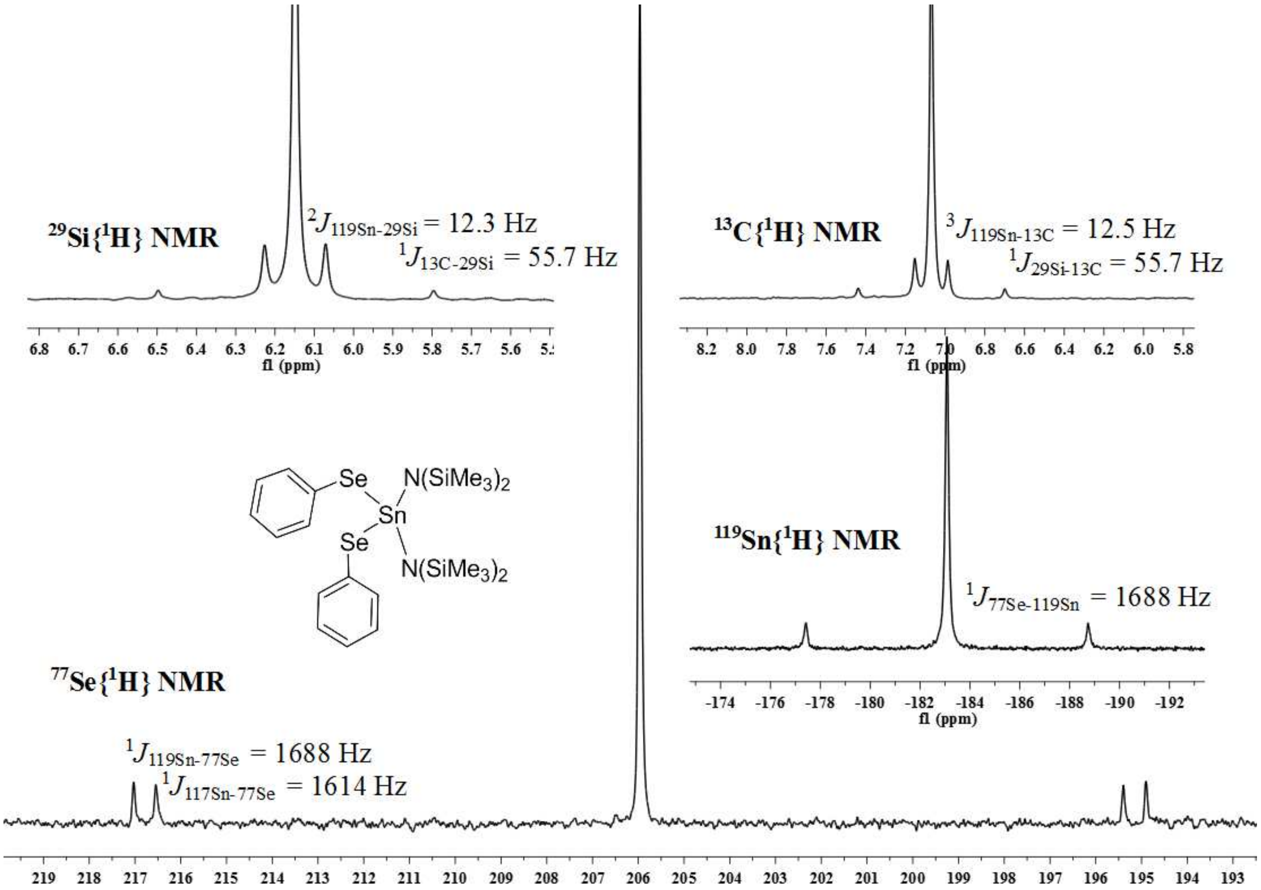


Figure 2. NMR data for $Sn(SePh)_2[N(SiMe_3)_2]_2$ (**7**) recorded in benzene-d_6 at 298 K.

The molecular structure of **7** shows the metal atom to exist in a tetrahedral environment (Figure 3). The Sn(1)–Se(2) [2.5523(4) Å] bond distance in **7** matches that in $Sn(SePh)_4$ (2.513 Å),[18] while the Sn(1)–N(1) length [2.052(2) Å] compares well with those in $Sn^{II}[N(SiMe_3)_2]_2$ (2.09 Å)[19] or $Sn^{IV}[N(SiMe_3)_2](Cl)(CH_2Cl)$ (2.03 Å);[20] they are also similar to those in Lappert's $[Sn^{IV}(N\{SiMe_3)_2\}_2(\mu\text{-}Se)]_2$ (Sn–N = 2.05 Å, Sn–Se = 2.54 Å).[21] Oxidative addition also occurs between $Sn[N(SiMe_3)_2]_2$ and the ditelluride Ph_2Te_2 to give $Sn(TePh)_2[N(SiMe_3)_2]_2$. This compound has been fully characterised, and is isostructural to **7** (ESI). Oxidative addition also takes place between $Ge[N(SiMe_3)_2]_2$ and Ph_2Se_2 or Ph_2Te_2 to give $Ge(SePh)_2[N(SiMe_3)_2]_2$ and $Ge(TePh)_2[N(SiMe_3)_2]_2$, respectively (ESI). This contrasts with known reports based on bis(amidinate) Ge^{II} complexes of the type Ge[CyNC(R)NCy]$_2$: the reaction of Ph_2Se_2 affords Ge(SePh)$_2$[CyNC(R)NCy]$_2$, but under identical conditions no reaction takes place with Ph_2Te_2.[22]

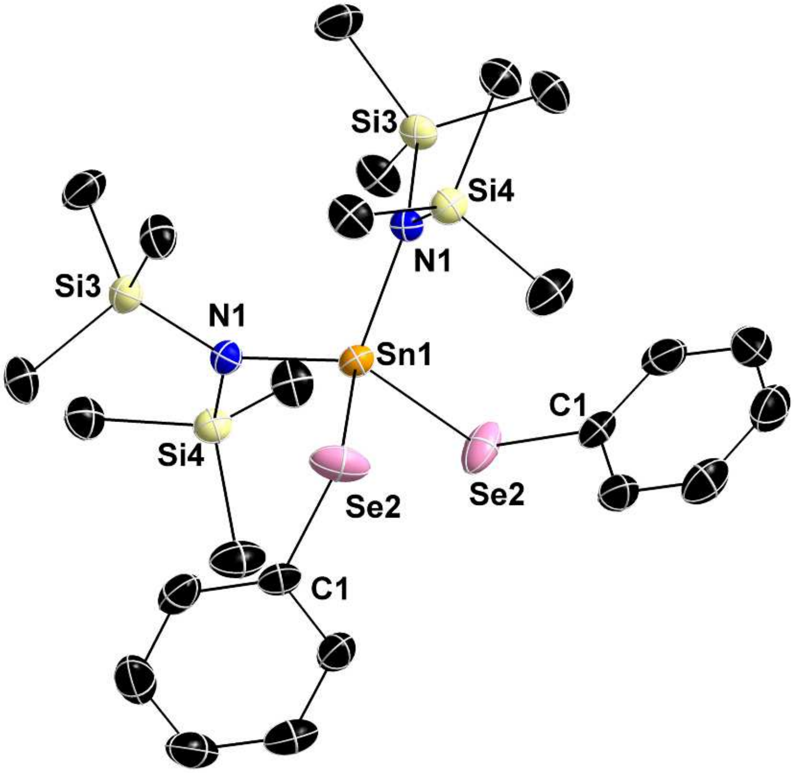
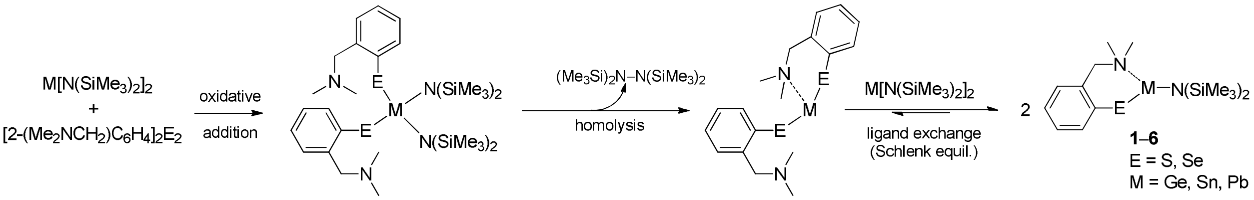


Figure 3. ORTEP representation of the molecular structure of Sn(SePh)$_2$[N(SiMe$_3$)$_2$]$_2$ (**7**), with thermal ellipsoids set at 50% probability. Hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Sn(1)–N(1) = 2.052(2), Sn(1)–Se(2) = 2.5523(4), Se(2)–C(1) = 1.923(3), N(1)-Sn(1)-N(1)$^{\#1}$ = 114.21(12), N(1)–Sn(1)–Se(2) = 110.90(7), N(1)$^{\#1}$–Sn(1)–Se(2) = 106.65(6), N(1)–Sn(1)–Se(2)$^{\#1}$ = 106.65(6), N(1)$^{\#1}$–Sn(1)–Se(2)$^{\#1}$ = 110.90(7), Se(2)–Sn(1)–Se(2)$^{\#1}$ = 107.36(2), C(1)–Se(2)–Sn(1) = 98.96(9).

In view of these observations, the question of the mechanism leading to the formation of **1–6** remains. Compared to Ph_2Se_2, the presence of an amino side-arm in [2-(Me$_2$NCH$_2$)C$_6$H$_4$]$_2$Se$_2$ plays obviously a key role towards the production of thermodynamically stable and/or kinetically inert heteroleptic divalent tetrelenes. Several mechanistic pathways can be envisaged, but we are not able to provide experimental evidence to substantiate any of them. The homolysis of Ln–N bonds (Ln = Yb, Eu) in *trivalent* rare-earth complexes bearing methoxyethyl-functionalised indenyl ligands has been reported to eventually yield the reduced *divalent* Yb^{II} and Eu^{II} complexes *via* concomitant loss of the hydrazine $(Me_3Si)_2N–N(SiMe_3)_2$.[23] Knowing this, and bearing in mind the propensity of heteroleptic divalent tin(II) and lead(II) complexes to participate in ligand-redistribution (Schlenk-type) reactions in solution (*vide infra*), one can speculate that **3–6** form through (*i*) oxidative addition giving $M[SeC_6H_4(CH_2NMe_2)\text{-}2]_2[N(SiMe_3)_2]_2$, followed by (*ii*) ligand-assisted homolysis, generating $M[SeC_6H_4(CH_2NMe_2)\text{-}2]_2$ and $(Me_3Si)_2N–N(SiMe_3)_2$ (attempts to identify the presence of this by-product have failed), and (*iii*) ligand redistribution between $M[SeC_6H_4(CH_2NMe_2)\text{-}2]_2$ and yet unreacted $M[N(SiMe_3)_2]_2$.[24] That said, this suggestion (Scheme 3) can hardly be envisaged for germanium, an element of lower polarisability and ionicity, and less prone to kinetic lability, than its heavier congeners.

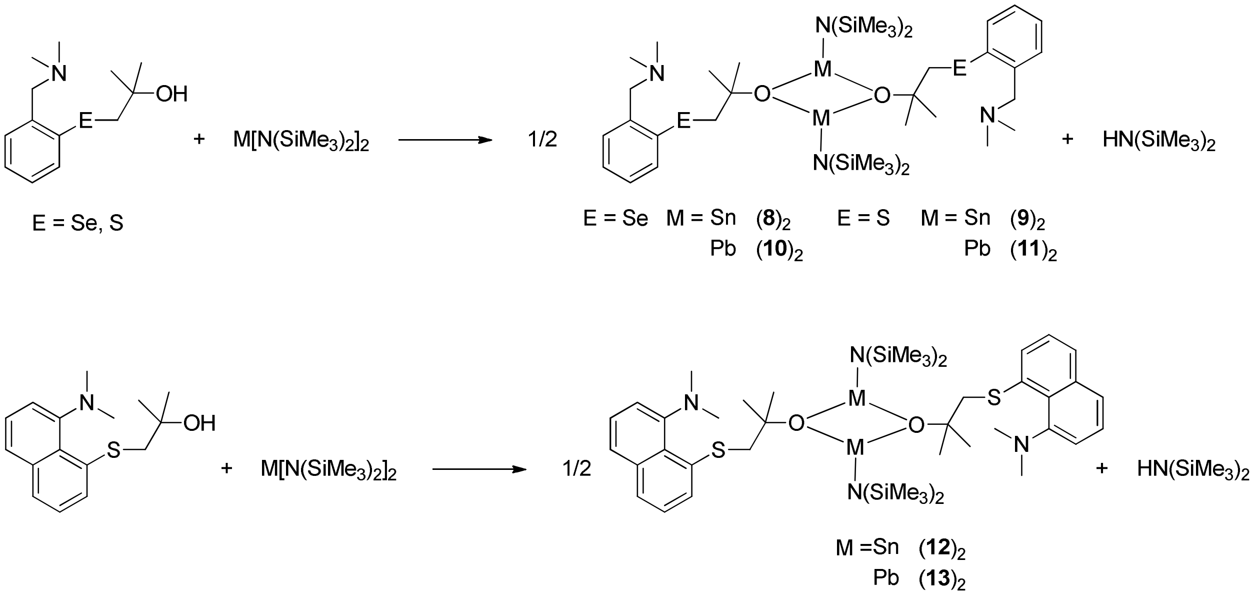


Scheme 3. Potential mechanism leading to the formation of **1–6**.

Synthesis and characterisation of organo-thioyl and -selenoyl alkoxide complexes

The ability of the recently described protio-ligands $2\text{-}(Me_2NCH_2)C_6H_4ECH_2C(R)_2OH$ (E = S, Se; R = Me, Ph)[25] to stabilise heteroleptic tetrelene complexes was investigated, with the aim of assessing the behaviour of the potentially tridentate alkoxide ligands *vis-a-vis* the increasingly polarisable group 14 elements, and comparing it to the organoselenolate and organothiolate employed to obtain **1–6**. To our surprise, the reaction of the *gem*-diphenyl 2-

$(Me_2NCH_2)C_6H_4SeCH_2C(Ph)_2OH$ with $Pb[N(SiMe_3)_2]_2$ afforded a mixture of products, from which only **5** could be isolated in substantial yields following decomposition of the ligand through a yet unidentified process.[26] Attempts to shed light on the involved mechanism by monitoring NMR-scale reactions by VT NMR spectroscopy proved to be unhelpful and efforts in this direction were not pursued. On the other hand, the protonolysis of $M[N(SiMe_3)_2]_2$ with an equimolar amount of the *gem*-dimethyl 2-$(Me_2NCH_2)C_6H_4SeCH_2C(Me)_2OH$ afforded the heteroleptic complexes-$M[OC(Me)_2CH_2EC_6H_4(CH_2NMe_2)-2][N(SiMe_3)_2]$ [M = Sn, E = Se (**8**) or S (**9**); M = Pb, E = Se (**10**) or S (**11**)] (Scheme 3). The isolated yields were at best moderate (*ca.* 39–56%), because of the formation of substantial amounts of the homoleptic derivatives.



Scheme 3. Synthesis of heteroleptic thioyl- and selenoyl-alkoxide Sn^{II} and Pb^{II} complexes **8–13**, with formulations as bridged dimers, as identified in the molecular solid-state.

Although **8–11** could be characterised by NMR spectroscopy, at room temperature the complexes are involved in Schlenk equilibria, which favour the formation of the homoleptic species with increasing temperature owing to entropic factors. Even at –60 °C, the samples are contaminated by *ca.* 5–10% of the homoleptic species, namely M[N(SiMe$_3$)$_2$]$_2$ and M[OC(Me)$_2$CH$_2$EC$_6$H$_4$(CH$_2$NMe$_2$)-2]$_2$; the latter has been otherwise authenticated by ^{119}Sn{^{1}H} NMR spectroscopy (for M = Sn and E = Se) during NMR-scale reactions.[27] Yet, the presence of impurity in these samples was positively ruled out, as NMR characterisation was performed on single crystals also used for XRD studies while the purity of the bulk samples was corroborated by combustion analyses. The molecular structures of (**8**)$_2$–(**11**)$_2$ were established by X-ray diffraction crystallography, and showed that all crystallise as bridged *O*-dimers. The structures of the four compounds are very similar (ESI), and only that of the plumbylene **10**, crystallised as the dimeric (**10**)$_2$, is detailed here. The complex forms a centro-symmetric bridged dimer, with a rhomboidal Pb$_2$O$_2$ core and bridging O$_{\text{alkoxo}}$ atoms (Figure 4).

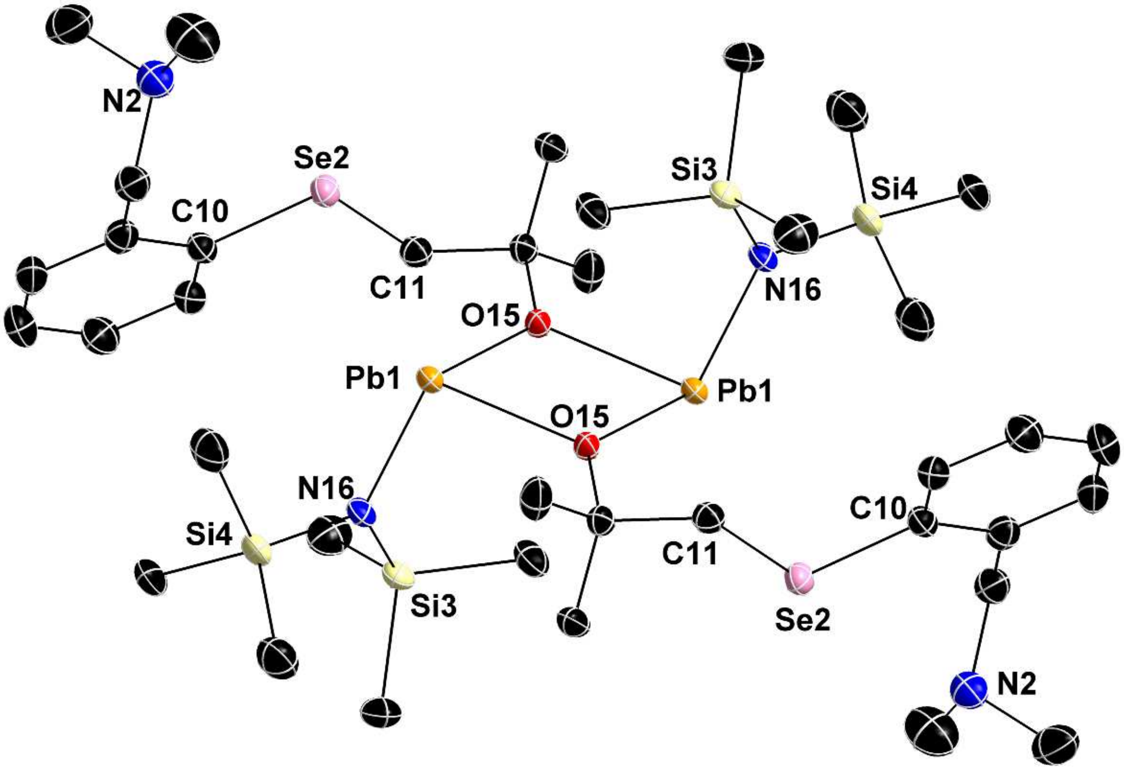


Figure 4. ORTEP representation of the molecular structure of the dimer of Pb[OC(Me)$_2$CH$_2$SeC$_6$H$_4$(CH$_2$NMe$_2$)-2][N(SiMe$_3$)$_2$] [(**10**)$_2$], with thermal ellipsoids set at 50% probability. Hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Pb(1)–N(16) 2.258(2), Pb(1)–O(15) = 2.269(2), Pb(1)–O(15)$^{\#1}$ = 2.357(2), Se(2)–C(10) = 1.926(3), Se(2)–C(11) = 1.964(3); N(16)–Pb(1)–O(15) = 103.37(8), N(16)–Pb(1)–O(15)$^{\#1}$ = 98.66(8), O(15)–Pb(1)–O(15)$^{\#1}$ = 71.39(9), C(10)–Se(2)–C(11) = 100.83(13).

Each lead(II) atom in (**10**)$_2$ is 3-coordinated, and each selenoyl-alkoxide moiety acts as a $\mu^2:\kappa^1,\kappa^1$ ligand. The coordination sphere around Pb^{II} is completed by the sole N(SiMe$_3$)$_2^-$ amide, whereas the Se and N$_{\text{side-arm}}$ atoms do not interact with the Pb^{II} atoms: if the Pb(1)···Se(2) distance (3.41 Å) is relatively short (*vide supra*), the rather large C(10)–Se(2)–C(11) angle militates against significant interactions between Pb^{II} and the chalcogen. The long Se(2)···N(2) distance (3.12 Å) also argues against interactions between these two atoms. The CCDC crystallographic database does not contain other examples of similar unsupported alkoxide/amido lead(II) dimeric complexes, but the metric parameters about the metal atoms in (**10**)$_2$ are nearly identical to those measured in the structurally related [Pb[N(SiMe$_3$)$_2$](O*i*Pr)]$_2$.[28] The Pb–N$_{\text{amide}}$ and Pb–O bond lengths in (**10**)$_2$ are also comparable to those in [MeC(CH$_2$NSiMe$_3$)$_2${CH$_2$O(Li)}Pb]$_2$.[29]

We reasoned that perhaps the hard N$_{\text{side-arm}}$ atoms do not bind to the metal atoms in (**8**)$_2$–(**11**)$_2$, which all form *O*-bridged dimers, because of the excessive flexibility in the side-arm of the ligand framework and large size of the metallacycle that would be formed. Yet, the protio-ligand 1-[8-(NMe$_2$)naphthalen-1-yl]SCH$_2$C(Me)$_2$OH rigidified by introduction of a naphthalene core similarly reacts with M[N(SiMe$_3$)$_2$]$_2$ to give the heteroleptic M[OC(Me)$_2$CH$_2$S{1-(8-(NMe$_2$)naphthalen-1-yl)}][N(SiMe$_3$)$_2$] [M = Sn (**12**); Pb (**13**)] *via* elimination of one equivalent of HN(SiMe$_3$)$_2$ (see Scheme 3). The molecular solid-state structure of (**13**)$_2$ depicted in Figure 5 shows a dimeric complex with O-bridging atoms, and an environment and metric parameters about the metal atoms identical to those in (**10**)$_2$ and (**11**)$_2$.

The use of these N,S,O- and N,Se,O-containing organo-thioyl and -selenoyl alkoxides for the preparation of heteroleptic tin(II) and lead(II) complexes hence results in the formation of bimetallic dimers bridged through the hard O_{alkoxo} atoms; note that the attempts at determining the nuclearity of these heteroleptic complexes in solution by diffusion measurements (DOSY / PGSE NMR spectroscopy) were thwarted by their propensity to participate in reversible ligand distribution reactions, giving a mixture of heteroleptic and homoleptic species. We were never able to detect the coordination of the soft chalcogen (be it S or Se) onto the metal, and even the coordination of the pendant amino arm was not detected; evidently, the electron-rich O_{alkoxo} atom in these ligands is too good a π donor and takes precedence in the coordination chemistry of the charge-neutral stannylenes and plumbylenes considered here. If coordination of both pairs of O_{alkoxo} and Se atoms in the homoleptic bis[*N,N*-diethyl-*N*′-naphthoylselenoureato]lead(II) complex was observed,[30] we are not aware of such occurrence in a structurally characterised heteroleptic complex. The only related molecular structure of a tin complex bearing a N,Se,O-containing ligand is that of bis[2-(2-selenidophenyl)imino-methylphenolate]$_2$tin, an homoleptic tin(IV) complex.[31]

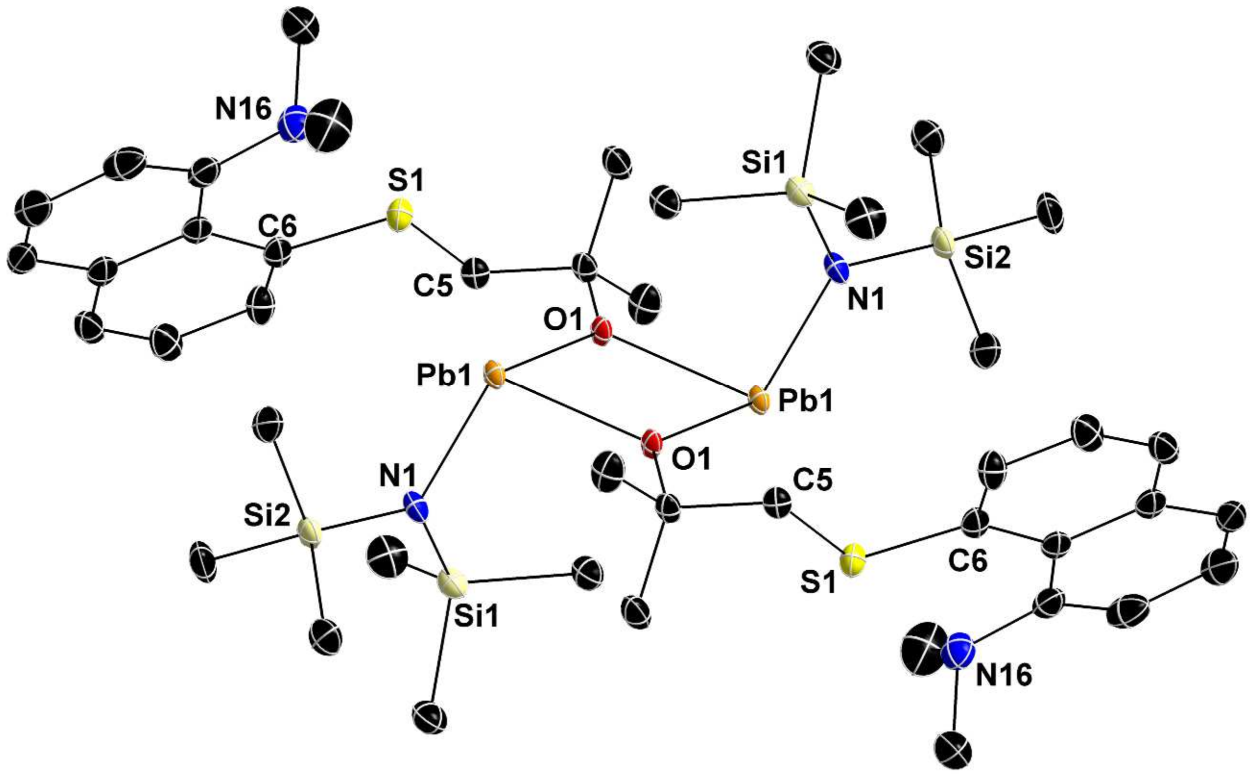
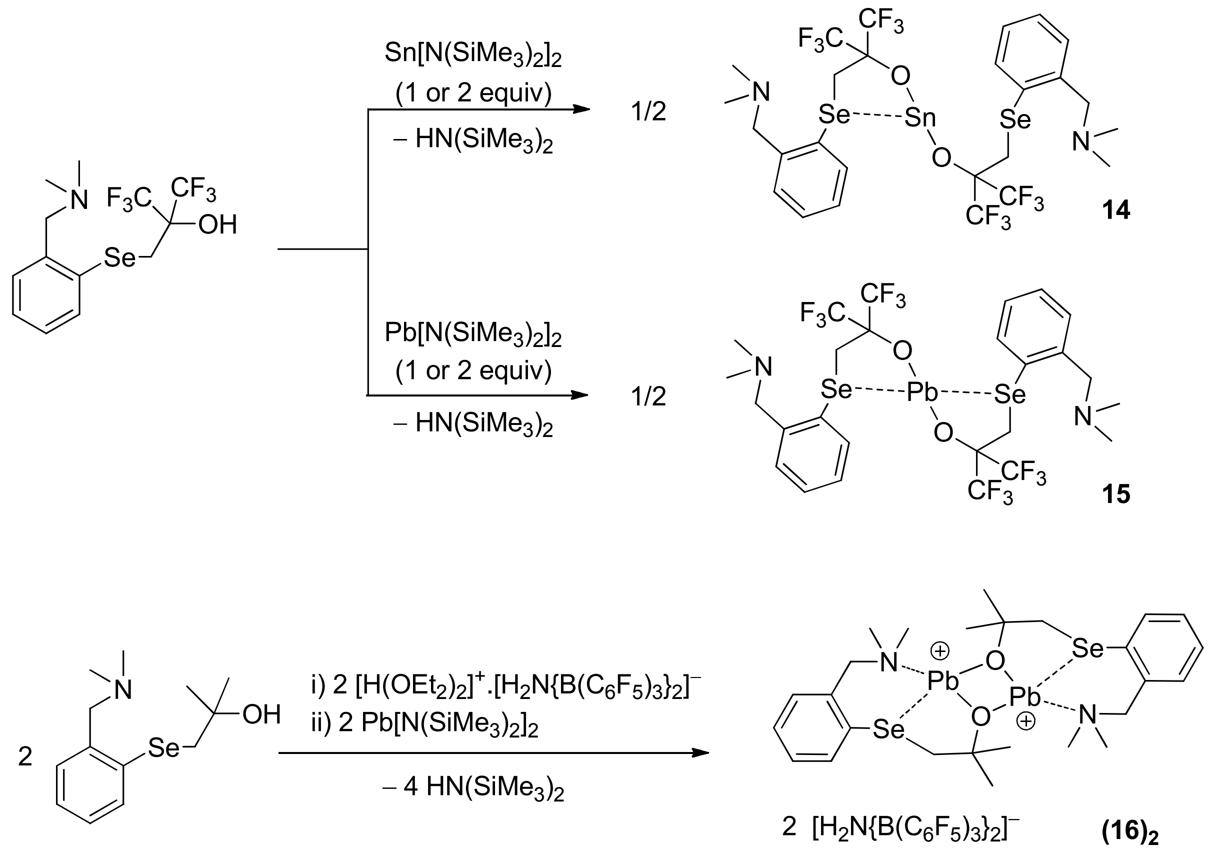


Figure 5. ORTEP representation of the molecular structure of the dimer of Pb[OC(Me)$_2$CH$_2$S{1-(8-(NMe$_2$)naphthalen-1-yl)}][N(SiMe$_3$)$_2$] [(**13**)$_2$], with thermal ellipsoids set at 50% probability. Hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Pb(1)–N(1) = 2.259(3), Pb(1)–O(1) = 2.276(2), Pb(1)–O(1)$^{\#1}$ = 2.389(2); N(1)–Pb(1)–O(1) = 103.05(9), N(1)–Pb(1)–O(1)$^{\#1}$ = 100.88(8), O(1)–Pb(1)–O(1)$^{\#1}$ = 72.06(8), Pb(1)–O(1)–Pb(1)$^{\#1}$ = 107.94(8).

On the preparation of electron-poor stannylenes and plumbylenes

In order to enforce coordination of the N and/or Se atoms as well as that of the O$_{\text{alkoxo}}$ in organoselenoyl-alcoholato ligands onto the metal atom in heavier tetrelenes, two different strategies were implemented (Scheme 4): (*i*) the utilisation of fluorinated alkoxides bearing CF$_3$ electron-withdrawing groups in α position to the alkoxide, and (*ii*) the recourse to ionising agents for the preparation of cationic, even more electrophilic lead(II) species.



Scheme 4. Synthesis of electron-poor tin(II) and lead(II) complexes.

We have employed fluorinated alkoxides with CF_3 substituents in α position to the hydroxide in order to prepare well-defined heteroleptic complexes of large, electrophilic divalent elements (Ca, Sr and Ba) because the electron-withdrawing groups reduce the ability of the alkoxide and act as a π donor, thus limiting the propensity to form aggregates otherwise observed for these metals with regular alkoxides.[32] The reaction of $2\text{-}(Me_2NCH_2)C_6H_4SeCH_2C(CF_3)_2OH$ with one equivalent of $M[N(SiMe_3)_2]_2$ only afforded the corresponding homoleptic complexes $M[OC(CF_3)_2CH_2SeC_6H_4(CH_2NMe_2)\text{-}2]_2$ [M = Sn (**14**); Pb (**15**)], regardless of reaction conditions (Scheme 4). These complexes, which have been structurally identified, were also prepared by using 2 equivalents of the metal precursors *vs*. the protio-ligand (ESI). The sought coordination of one (for M = Sn in **14**, Sn–Se = 2.9248(2) Å, Figure 6) or two (for M = Pb in **15**, Pb–Se =

2.9885(4) and 3.2030(3) Å, Figure 7) atoms of Se onto the metal is observed in these monometallic complexes, giving 5-membered metallacycles; on the other hand, the N atoms still do not bind to the metal. The Pb–O$_{alkoxo}$ bond distances in **15** are shorter than in **8–11**.

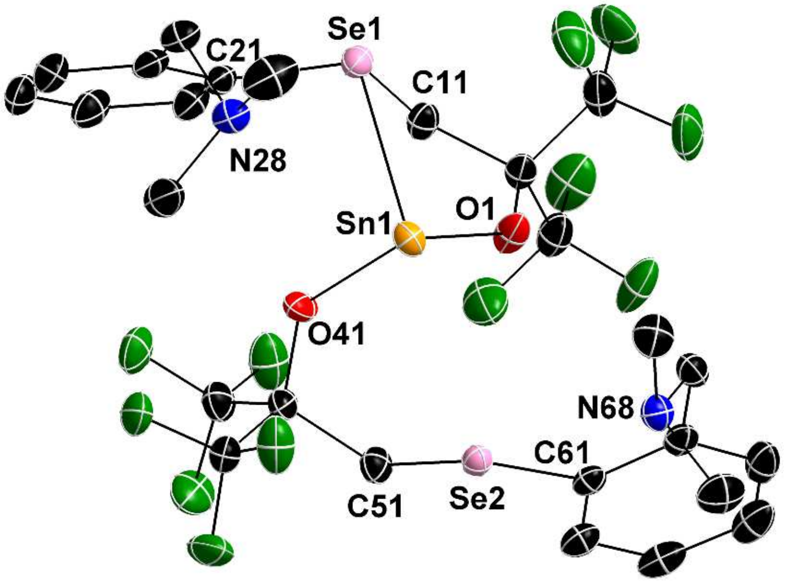


Figure 6. ORTEP representation of Sn[OC(CF$_3$)$_2$CH$_2$SeC$_6$H$_4$(CH$_2$NMe$_2$)-2]$_2$ (**14**) in the molecular solid-state, with thermal ellipsoids set at 50% probability. Hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Sn(1)–O(41) = 2.0519(13), Sn(1)–O(1) = 2.0833(14), Sn(1)–Se(1) = 2.9248(2), Sn(1)–Se(2) = 3.1550(3); O(41)–Sn(1)–O(1) = 95.52(6), O(41)–Sn(1)–Se(1) = 85.16(4), O(1)–Sn(1)–Se(1) = 74.95(4).

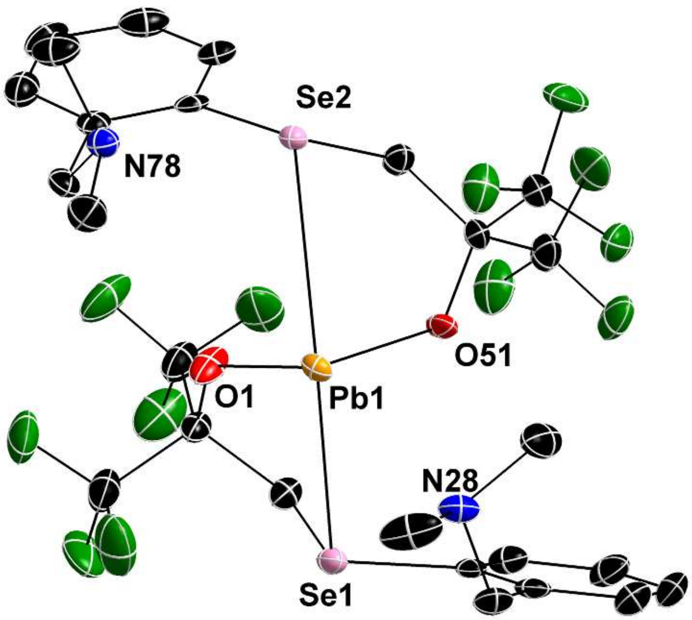


Figure 7. ORTEP representation of Pb[OC(CF_3)$_2$$CH_2SeC_6H_4$($CH_2NMe_2$)-2]$_2$ (**15**) in the molecular solid-sate, with thermal ellipsoids set at 50% probability. Hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Pb(1)–O(51) = 2.161(2), Pb(1)–O(1) = 2.205(2), Pb(1)–Se(1) = 2.9885(4), Pb(1)–Se(2) = 3.2030(3); O(51)–Pb(1)–O(1) = 95.71(10), O(51)–Pb(1)–Se(1) = 84.46(6), O(1)–Pb(1)–Se(1) = 72.47(6), O(51)–Pb(1)–Se(2) = 72.89(6), O(1)–Pb(1)–Se(2) = 76.41(7), Se(1)–Pb(1)–Se(2) = 139.142(9).

Multinuclear NMR data for organoselenoyl alkoxide complexes are summarised in Table 2. The data for **14** recorded in benzene-d_6 are indicative of a symmetrical environment in solution, with two equivalent Se atoms. In particular, single resonances in the ^{19}F{^{1}H} (δ_{19F} = –76.4 ppm, $^4J_{F\text{-}119Sn}$ = 35.4 Hz, $^4J_{F\text{-}Se} \approx 18$ Hz) and ^{77}Se{^{1}H} (multiplet at δ_{77Se} = +234 ppm, $^4J_{Se\text{-}F}$ = 18.2 Hz) NMR spectra. The multiplet in the ^{77}Se{^{1}H} spectrum of **14** appears at a similar chemical shift to that in **8** (δ_{77Se} = +227 ppm) but is deshielded compared to the protio-ligand (heptet at δ_{77Se} = +200 ppm, $^4J_{Se\text{-}F}$ = 14.5 Hz). The ^{119}Sn{^{1}H} spectrum of the complex exhibits a sole multiplet at δ_{119Sn} = –392 ppm, with $^4J_{119Sn\text{-}F}$ = 35.4 Hz indicating coupling to F atoms; this chemical shift is in the range of those measured for other 3-coordinated tin(II) complexes bearing aminophenoxide ligands and alkoxide or siloxide co-ligands.[7,8] That the coupling between ^{119}Sn and ^{77}Se atoms cannot be detected in solution together with the similarity of the ^{77}Se chemical shifts for **8** and **14** suggests the binding of Se and Sn atoms in **14** is weak and does not persist in solution. One should however guard against over-interpretation of ^{77}Se NMR data: for instance, $Sn[OC(Me)_2CH_2SeC_6H_4(CH_2NMe_2)\text{-}2]_2$ features a resonance at δ_{77Se} = +214 ppm with $^{1}J_{Se\text{-}119Sn}$ = 152 Hz in its ^{77}Se{^{1}H} NMR spectrum (and correspondingly, it is manifested as a sharp resonance at δ_{119Sn} = –199 ppm with $^{1}J_{119Sn\text{-}Se}$ = 152 Hz in the ^{119}Sn{^{1}H} NMR spectrum), that is, the coupling with ^{119}Sn indicates a trivalent Se atom due to Se···Sn interaction in this complex, and yet its ^{77}Se chemical shift is close to those in **8** and **14**.

The ^{207}Pb{^{1}H} resonance for lead(II) complex **15** (δ_{207Pb} = +665 ppm) is much more shielded than that in the 3-coordinated **10** (+2124 ppm), suggesting that **15** remains 4-coordinated in solution. However, the ^{77}Se resonances for these two complexes are located in the same range (δ_{77Se} = +205 and +212 ppm, respectively), and no coupling between ^{77}Se and ^{207}Pb could be detected, suggesting that the two Pb···Se interactions found in the molecular solid-state structure of **15** may be replaced by two Pb···N interactions in solution.

Table 2. Multinuclear NMR data for charge-neutral organoselenoyl alkoxide complexes.[a]

		C.N. [b]	$\delta_{^{77}Se}$ [ppm]	$\delta_{^{119}Sn}$ [ppm]	$\delta_{^{207}Pb}$ [ppm]	$\delta_{^{29}Si}$ [ppm]	$\delta_{^{19}F}$ [ppm]
$Sn[OC(Me)_2CH_2SeC_6H_4(CH_2NMe_2)\text{-}2][N(SiMe_3)_2]$ [c]	**8**	3	+227	–14	-	–0.10, –3.25	-
$Sn[OC(Me)_2CH_2SC_6H_4(CH_2NMe_2)\text{-}2][N(SiMe_3)_2]$ [c]	**9**	3	-	–40	-	–0.33, –3.30	-
$Pb[OC(Me)_2CH_2SeC_6H_4(CH_2NMe_2)\text{-}2][N(SiMe_3)_2]$	**10**	3	+205	-	+2124	–2.37, –4.44	-
$Pb[OC(Me)_2CH_2SC_6H_4(CH_2NMe_2)\text{-}2][N(SiMe_3)_2]$	**11**	3	-	-	+2092	–2.37, –4.45	-
$Sn[OC(Me)_2CH_2S\{1\text{-}(8\text{-}(NMe_2)naphthalen\text{-}1\text{-}yl)\}][N(SiMe_3)_2]$ [c]	**12**	3	-	–69	-	–0.64, –3.86	-
$Pb[OC(Me)_2CH_2S\{1\text{-}(8\text{-}(NMe_2)naphthalen\text{-}1\text{-}yl)\}][N(SiMe_3)_2]$ [d]	**13**	3	-	-	+2005	–3.56, –5.18	-
$Sn[OC(CF_3)_2CH_2SeC_6H_4(CH_2NMe_2)\text{-}2]_2$	**14**	3	+234	–392	-	-	–76.4 [e]
$Pb[OC(CF_3)_2CH_2SeC_6H_4(CH_2NMe_2)\text{-}2]_2$	**15**	4	+212	-	+665	-	–76.0 [f]
$Sn[OC(Me)_2CH_2SeC_6H_4(CH_2NMe_2)\text{-}2]_2$ [g]		n.d.	+214 [h]	–199 [h]	-	-	-

[a] Data for $\{^1H\}$ heterodecoupled NMR in benzene-d_6 at 298 K unless otherwise specified. [b] Coordination number of the metal atom in the molecular solid-state. [c] Recorded in toluene-d_8. [d] Recorded in tetrahydrofurane-d_8. [e] $^1J_{C\text{-}F}$ = 291 Hz, $^2J_{C\text{-}F}$ = 28.7 Hz, $^4J_{Se\text{-}F}$ = 18.2 Hz, $^4J_{119Sn\text{-}F}$ = 35.4 Hz. [f] $^1J_{C\text{-}F}$ = 294 Hz, $^2J_{C\text{-}F}$ = 27.8 Hz. [g] Complex prepared and characterised *in situ* and not isolated. [h] $^1J_{119Sn\text{-}Se}$ = 152 Hz. n.d. = not determined.

Following established procedures,[33] treatment of 2-(Me_2NCH_2)$C_6H_4SeCH_2C(Me)_2OH$ with an equimolar amount of Bochmann's acid,[34] $[H(OEt_2)_2]^+\cdot[H_2N\{B(C_6F_5)_3\}_2]^-$, followed by further addition of one equivalent of $Pb[N(SiMe_3)_2]_2$, generated $[\{2\text{-}(Me_2NCH_2)C_6H_4SeCH_2C(Me)_2O\}Pb]^+\cdot[H_2N\{B(C_6F_5)_3\}_2]^-$ (**16**), a cationic complex paired with a weakly-coordinating anion which crystallised as the bimetallic (**16**)$_2$ (Scheme 4). Complex **16** can also be prepared by mixing $[\{2\text{-}(Me_2NCH_2)C_6H_4SeCH_2C(Me)_2OH\}H^+]$ $[H_2N\{B(C_6F_5)_3\}_2{}^-]$ (prepared by reacting the protio-ligand with Bochmann's acid) with $Pb[N(SiMe_3)_2]_2$. The cationic fragment displayed in Figure 8 show an *O*-bridged dimeric dication with a non-symmetrical central Pb_2O_2 core, with 4-coordinated lead(II) atoms where the Se, N and O atoms effectively bind to the metals. The bond distances to the coordinated heteroatoms vary little between the two lead(II) atoms Pb1 and Pb2 in (**16**)$_2$ (average distances: d_{Pb-O} = 2.28 Å; d_{Pb-N} = 2.46 Å; d_{Pb-Se} = 3.13 Å). Presumably due to its dimeric structure, the bonding Pb−O distances in (**16**)$_2$ are longer than those in the monomeric **15** (2.16 and 2.20 Å), and are in fact more comparable to those in the charge-neutral dimers (**10**)$_2$ and (**13**)$_2$ (2.27 and 2.28 Å). On the other hand, the Pb−Se bond length in (**16**)$_2$ falls in the same range as those measured in **15** and in the pseudo polymorph $[Pb\{Se_2P(O\textit{i}Pr)_2\}_2]_n$, the only compound with 4-coordinated Pb^{II} and 3-coordinated Se atoms in the CCDC database.[35] Owing to the poorly coordinating nature of the counter-ion, there is no interaction between the metals and the neighbouring fluorine atoms on the anions in the solid-state. The ^{19}F (δ_{19F} = −132.8 (d), −160.0 (t) and −165.6 (t) ppm) and ^{11}B (δ_{11B} = −8.4 ppm) NMR data recorded in dichloromethane-d_2 are consistent with this observation, and also testify to the integrity of the anion. Despite repeated attempts at various temperatures, we were not able to detect any resonance in the $^{207}Pb\{^1H\}$ NMR spectra of this complex; its $^{77}Se\{^1H\}$ NMR spectrum features a broad singlet at δ_{77Se} = +187 ppm.

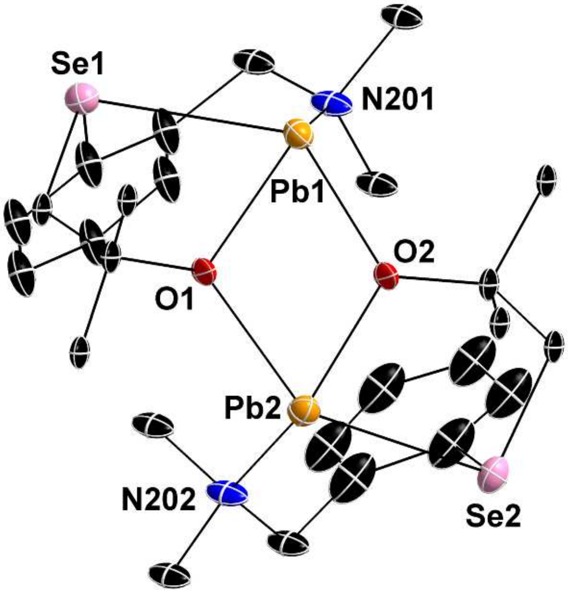


Figure 8. ORTEP representation of the cationic fragment in the molecular structure of (**16**)$_2$, the crystallised dimer of [{2-(Me$_2$NCH$_2$)C$_6$H$_4$SeCH$_2$C(Me)$_2$O}Pb]$_2^{2+}$, showing the connectivity around lead(II) atoms. Hydrogen atoms and counter-anions omitted for clarity. Selected bond lengths (Å) and angles (°): Pb(1)–O(2) = 2.272(5), Pb(1)–O(1) = 2.273(4), Pb(1)–N(201) = 2.455(5), Pb(1)–Se(1) = 3.1153(12), Pb(2)–O(2) = 2.260(4), Pb(2)–O(1) = 2.318(5), Pb(2)–N(202) = 2.475(5), Pb(2)–Se(2) = 3.1504(12); O(2)–Pb(1)–O(1) = 68.03(13), O(2)–Pb(1)–N(201) = 87.55(15), O(1)–Pb(1)–N(201) = 113.94(19), O(2)–Pb(1)–Se(1) = 127.32(12), O(1)–Pb(1)–Se(1) = 69.43(12), N(201)–Pb(1)–Se(1) = 82.53(11), O(2)–Pb(2)–O(1) = 67.46(13), O(2)–Pb(2)–N(202) = 109.22(18), O(1)–Pb(2)–N(202) = 94.98(17), O(2)–Pb(2)–Se(2) = 69.92(12), O(1)–Pb(2)–Se(2) = 132.08(11), N(202)–Pb(2)–Se(2) = 79.16(10), Pb(1)–O(1)–Pb(2) = 110.52(18), Pb(2)–O(2)–Pb(1) = 112.71(18).

Conclusion

The combinations of $\{R^{NMe2}^{E}\}^-$ and $\{R^{NMe2}$^E^O$\}^-$ organochalcogenolato ligands with divalent germanium, tin and lead amides yields unusual heteroleptic tetrelene complexes. Multinuclear NMR spectroscopy and XRD studies show that the metal preferably remains 3-coordinated in these complexes unless severe depletion of electronic density onto the metal is enforced.

The simple aminoarylchalcogenolates $\{R^{NMe2}{}^\wedge E\}^-$ afford chiral monometallic complexes upon coordination of the NMe_2 moiety onto the tetrel atom and formation of a 6-membered metallacycle, be it with M = Ge^{II}, Sn^{II} or Pb^{II}, and equally so for E = S or Se. The mechanism leading to the production of these heteroleptic complexes starting from diorganodichalcogenides and $M[N(SiMe_3)_2]_2$ is not yet elucidated, but in view of the different course (ligand metathesis *vs.* oxidative addition) followed in the reaction of $M[N(SiMe_3)_2]_2$ (M = Ge, Sn) and Ph_2Se_2, the stabilising role of the amino side-arm towards the low oxidation state of the metals, and the redox active nature of the tetrel elements can certainly be invoked.

The scenario for $\{R^{NMe2}{}^\wedge E^\wedge O\}^-$ alkoxides is more subtle. With the regular $\{2\text{-}(Me_2NCH_2)C_6H_4ECH_2C(Me)_2O\}^-$ (E = S, Se), heteroleptic complexes are also obtained, but a propensity to achieve the 3-coordinated environment through the formation of $O_{alkoxide}$-bridged dimers ahead of chelation using the available N and/or S/Se atoms is detected both for tin(II) and lead(II). The use of a rigid amino side-arm does not help the formation of a chelate in these systems. With the fluorinated $\{2\text{-}(Me_2NCH_2)C_6H_4SeCH_2C(CF_3)_2O\}^-$, the π-donating ability of the $O_{alkoxide}$ atom is reduced, thus preventing the formation of dimeric species; instead, homoleptic complexes with 3- (for Sn^{II}) and 4-coordinated (for Pb^{II}) metal atoms are generated upon binding of one or two selenium atoms onto the metal, respectively. Coordination of all heteroatoms onto the metal in is ensured in the cationic $[\{2\text{-}(Me_2NCH_2)C_6H_4SeCH_2C(Me)_2O\}Pb]_2{}^{2+}$, where yet again the ability of the $O_{alkoxide}$ atoms to act as a bridge between the two electron-deficient metal atoms is expressed. Our attempts at preparing the related cationic species using the fluoroalcohol $2\text{-}(Me_2NCH_2)C_6H_4SeCH_2C(CF_3)_2OH$ have been unsuccessful.

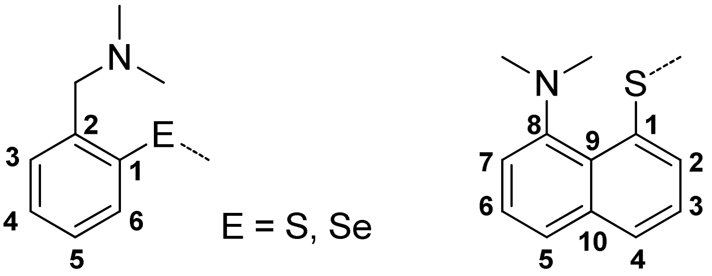
Because it contains both hard (O and N) and soft (S or Se) donors, different coordination patterns for the ligand $\{2\text{-}(Me_2NCH_2)C_6H_4ECH_2C(Me)_2O\}^-$ (E = S, Se) were expected upon coordination onto divalent tetrel elements, according to the varying size, polarisability, Lewis acidity and electrostatic surface potential on moving from germanium(II) to lead(II). Yet, it turns out that the main features across these complexes are remarkably similar, regardless of the nature of the tetrel element. Hence, considerations based on HSAB theory are simply not sufficient to predict reliably the potentially rich coordination chemistry of these ligands onto main-group elements of the same column in the Periodic Table. We will now build on these observations, and future efforts will probe the behaviour of these and related $\{R^{NMe2}\text{\^{}}E\text{\^{}}O\}^-$ alkoxides onto group 12 metals, and on tetrel elements in their preferred +4 oxidation state.

Experimental Section

General procedures. All manipulations were performed under inert atmosphere using standard Schlenk techniques or in a dry, solvent-free glove-box (Jacomex; $O_2 < 1$ ppm, $H_2O < 5$ ppm) for catalyst loading. Ph_2Se_2 (Aldrich), $SnCl_2$ (Acros, 98%), $PbCl_2$ (Strem) and $GeCl_2 \cdot$dioxane (Acros) were used as received. $HN(SiMe_3)_2$ (Acros) was dried over activated molecular sieves and distilled prior to use. The compounds $M[N(SiMe_3)_2]_2$, (M = Ge,[36] Sn,[37] Pb[36]), $[2\text{-}(Me_2NCH_2)C_6H_4]Li$,[9] $[2\text{-}(Me_2NCH_2)C_6H_4]_2Se_2$ [9] and $2\text{-}(Me_2NCH_2)C_6H_4ECH_2C(R)_2OH$ (E = S, Se; R = Me, Ph)[25] were prepared following literature procedures. Solvents (THF, Et_2O, CH_2Cl_2, pentane and toluene) were purified and dried (water contents below 8 ppm) over alumina columns (MBraun SPS). THF was further distilled under argon from sodium mirror/benzophenone ketyl. All deuterated solvents (Eurisotop, Saclay, France) were stored in sealed ampoules over activated 3 Å molecular sieves and were thoroughly degassed by several freeze-thaw-vacuum cycles.

Elemental analyses were performed on a CHN-FlashAE 1112 (Co. Thermo) Analyser (Cluj-Napoca), or a Carlo Erba 1108 Elemental Analyzer instrument at the London Metropolitan University by Stephen Boyer and were the average of a minimum of two independent measurements.

NMR spectra were recorded on Bruker AM-400 and AM-500 spectrometers. All ^{1}H and $^{13}C\{^{1}H\}$ chemical shifts were assigned according to the numbering scheme shown in Scheme 4 using residual signals of the deuterated solvents and were calibrated *vs*. Me_4Si. Assignment of the signals was carried out using 1D (^{1}H, $^{13}C\{^{1}H\}$) and 2D (COSY, HMBC, HMQC) NMR experiments. $^{19}F\{^{1}H\}$ chemical shifts were determined by external reference to an aqueous solution of $NaBF_4$. ^{207}Pb NMR spectra were referenced against a solution of $Pb[N(SiMe_3)_2]_2$ in benzene-d_6 (δ_{207Pb} = +4916 ppm). $^{119}Sn\{^{1}H\}$, $^{29}Si\{^{1}H\}$ and $^{77}Se\{^{1}H\}$ NMR spectra were externally calibrated *vs.* Me_4Si, Me_4Sn and Ph_2Se_2 (δ_{77Se} = +461 ppm).[38]



Scheme 4.

X-ray diffraction crystallography. Crystals of **5–16** and $M(EPh)_2[N(SiMe_3)_2]_2$ (M = Ge, Sn; E = Se, Te) suitable for X-ray diffraction analysis were obtained by recrystallization of the purified products. Diffraction data were collected at 150 K using a Bruker APEX CCD diffractometer with graphite-monochromated MoKα radiation (λ = 0.71073 Å). A combination of ω and Φ scans was carried out to obtain at least a unique data set. The crystal structures were solved by direct methods, remaining atoms were located from difference Fourier synthesis followed by full-matrix least-squares refinement based on F2 (programs SIR97 and SHELXL-97).[39] Many hydrogen atoms could be found from the Fourier difference analysis. Carbon- and oxygen-bound hydrogen atoms were placed at calculated positions and forced to ride on the attached atom. The hydrogen atom contributions were calculated but not refined. All non-hydrogen atoms were refined with anisotropic displacement parameters. The locations of the largest peaks in the final difference Fourier map calculation as well as the magnitude of the residual electron densities were of no chemical significance. Relevant collection and refinement data are summarised in the Electronic Supporting Information. Crystal data and details of data collection and structure refinement for all complexes (CCDC 1006879–1006894) can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[2-(Me_2NCH_2)C_6H_4]$_2S_2$. Elemental sulfur (0.227 g, 7.0 mmol) was added to a solution of 2-(Me_2NCH_2)C_6H_4Li (1.00 g, 7.0 mmol) in anhydrous THF (50 mL) and the reaction mixture was stirred for 2 h at room temperature. The resulting yellow solution was poured into a beaker containing water (100 mL) and left overnight in an efficient fume hood for a complete oxidation. The organic phase was separated and the aqueous phase was extracted several times with dichloromethane. The combined organic phases were dried over $MgSO_4$. Evaporation of the solvent gave a yellow oil. The title compound was purified by column chromatography (CH_2Cl_2 / EtOH = 1:1) and was isolated as a pale yellow oil. Yield 0.65 g (57%). ^{1}H NMR (benzene-d_6, 300.11 MHz, 298 K): δ = 7.93 (d, 1H, $^3J_{H\text{-}H}$ = 7.6 Hz, arom-C_6H), 7.13 (d, 1H, $^3J_{H\text{-}H}$ = 7.4 Hz, arom-C_3*H*), 6.96 (t, 1H, $^3J_{\text{H-H}}$ = 7.4 Hz, arom-C_5*H*), 6.91 (t, 1H, $^3J_{\text{H-H}}$ = 7.4 Hz, arom-C_4*H*), 3.44 (s, 2H, ArCH_2N), 2.07 (s, 6H, N(CH_3)$_2$) ppm. ^{13}C{^{1}H} NMR (benzene-d_6, 75.47 MHz, 298 K): δ = 139.29 (arom-C_1), 138.74 (arom-C_6), 129.58 (arom-C_3), 128.33 (arom-C_2), 128.17 (arom-C_4), 126.27 (arom-C_5), 62.7 (Ar*C*H$_2$N), 44.79 (N(*C*H$_3$)$_2$) ppm. Anal. Calcd for $C_{18}H_{24}N_2S_2$ (332.53 g·mol^{-1}): C 65.0, H 7.3, N 8.4 %. Found: C 65.2, H 7.5, N 8.3 %.

1-{8-(N(CH$_3$)$_2$)naphthalen-1-yl}SCH$_2$C(CH$_3$)$_2$OH. 1-*N,N*-dimethylnaphtalene (14.2 g, 80.0 mmol) and *n*BuLi (52.5 mL of a 1.6 M solution in hexanes, 84.0 mmol) were reacted overnight in Et$_2$O at room temperature. The volatiles were then pumped off. Elemental sulfur (0.77 g, 24.0 mmol) was then added with a bent glass finger to a solution of 1-{8-(dimethylamino)naphthalen-1-yl}Li·Et$_2$O (6.03 g, 24.0 mmol) in THF (100 ml) at room temperature. The resulting yellow solution was stirred at room temperature for 12 h. The mixture was then cooled down with an ice bath, and a solution of 1-chloro-2-methyl-2-propanol (2.59 g, 24.0 mmol) in THF (10 mL) was added slowly with a cannula. The reaction mixture was next warmed to room temperature and stirred overnight. The solvents were evaporated under vacuum, and the crude product was extracted with toluene (100 mL). Removal of the volatiles gave a dark oily material. The title compound was purified as a dark yellow oil by column chromatography (petroleum-ether / ethyl acetate = 3:1). Yield 5.00 g (76%). ^{1}H NMR (benzene-d_6, 400.16 MHz, 298 K): δ = 7.45 (dd, 2H, $^3J_{\text{HH}}$ = 8.0 Hz, $^4J_{\text{H-H}}$ = 1.2 Hz, arom-C_4*H* and -C_5*H*), 7.30 (d, 1H, $^3J_{\text{H-H}}$ = 7.6 Hz, arom-C_2*H*), 7.22−7.17 (m, 2H, arom-C_3*H* and -C_6*H*), 7.02 (d, $^3J_{\text{H-H}}$ = 7.6 Hz, 1H, arom-C_7*H*), 2.89 (s, 2H, ArSCH_2), 2.55 (s, 6H, N(CH_3)$_2$), 2.16 (br, 1H, O*H*), 1.29 (s, 6H, C(CH_3)$_2$OH) ppm. ^{13}C{^{1}H} NMR (benzene-d_6, 100.62 MHz, 298 K): δ = 152.43 (arom-C_8), 137.35 (arom-C_1), 137.21 (arom-C_{10}), 129.68 (arom-C_9), 126.65 and 126.29 (arom-C_3 and -C_6), 125.94 and 125.82 (arom-C_4 and -

C$_5$), 124.01 (arom-*C*$_2$), 118.96 (arom-*C*$_7$), 71.02 (*C*(CH$_3$)$_2$OH), 47.78 (S*C*H$_2$), 45.95 (N(*C*H$_3$)$_2$), 30.01 (C(*C*H$_3$)$_2$OH) ppm. Anal. Calcd for $C_{16}H_{21}NOS$ (275.41 g·mol^{-1}): C 69.8, H 7.7, N 5.1 %. Found: C 69.8, H 7.8, N 5.1 %.

2-(Me$_2$NCH$_2$)C$_6$H$_4$SeCH$_2$C(CF$_3$)$_2$OH. *N,N*-dimethylbenzylamine (13.5 g, 100 mmol) and *n*BuLi (63.1 mL of a 1.6 M solution in hexanes, 101 mmol) were reacted overnight in Et$_2$O at room temperature. The volatiles were then pumped off. Selenium (0.76 g, 9.6 mmol) was then added with a bent glass finger to a solution of [2-(Me$_2$NCH$_2$)C$_6$H$_4$]Li·Et$_2$O (2.06 g, 9.6 mmol in THF (50 mL) at room temperature. The resulting yellow solution was stirred at room temperature for 12 h. The mixture was then cooled down with ice bath, and a solution of 2,2-bis(trifluoromethyl)oxirane (1.73 g, 9.6 mmol) in THF (10 mL) was added by cannula. The reaction mixture was warmed to room temperature and further stirred overnight. Removal of all the volatiles gave a sticky residue to which a saturated aqueous solution of NH$_4$Cl (50 ml) was added upon fast stirring. Extraction with toluene (3 × 30 mL) was then performed, and after evaporation followed by purification by column chromatography (petroleum ether / ethyl acetate = 5:1), the title compound was obtained as a yellow oil. Yield 1.78 g (47%). ^{1}H NMR (benzene-*d*$_6$, 500.13 MHz, 298 K): δ = 10.24 (br, 1H, O*H*), 7.45–7.43 (m, 1H, arom-C$_3$*H*), 6.92–6.86 (m, 2H, arom-C$_4$*H* and -C$_5$*H*), 6.65–6.32 (m, 1H, arom-C$_6$*H*), 3.22 (s, 2H, ArC*H*$_2$N), 3.10 (s, 2H, SeC*H*$_2$), 1.83 (s, 6H, N(C*H*$_3$)$_2$) ppm. ^{13}C{^{1}H}NMR (benzene-*d*$_6$, 125.76 MHz, 298 K): δ = 140.81 (arom-*C*$_2$), 139.14 (arom-*C*$_3$), 133.49 (arom- *C*$_1$), 132.07 (arom-*C*$_6$), 130.15 (arom-*C*$_5$), 129.49 (arom-*C*$_4$), 124.55 (q, $^1J_{\text{C-F}}$ = 290 Hz, CF$_3$), 77.63 (h, $^2J_{\text{C-F}}$ = 27.9 Hz, *C*(CF$_3$)$_2$), 65.30 (Ar*C*H$_2$), 44.54 (s, N(*C*H$_3$)$_2$), 32.04 (Se*C*H$_2$) ppm. ^{19}F{^{1}H} NMR (benzene-*d*$_6$, 376.53 MHz, 298 K): δ = −76.5 (s) ppm. ^{77}Se{^{1}H} NMR (benzene-*d*$_6$, 76.31 MHz, 298 K): δ = +200 (h, $^4J_{\text{Se-F}}$ = 14.5 Hz) ppm. Anal. Calcd. for $C_{13}H_{15}F_6NOSe$ (394.21 g·mol^{-1}): C 39.6, H 3.8, N 3.5 %. Found: C 39.7, H 3.7, N 3.7 %.

Ge[SeC$_6$H$_4$(CH$_2$NMe$_2$)-2][N(SiMe$_3$)$_2$] (1). A solution of [2-(Me$_2$NCH$_2$)C$_6$H$_4$]$_2$Se$_2$ (0.15 g, 0.35 mmol) in diethyl ether (15 mL) was added dropwise at −78 °C over a period of 1 h to a solution of Ge[N(SiMe$_3$)$_2$]$_2$ (0.28 g, 0.70 mmol) in diethyl ether (20 mL). The resulting yellow solution was warmed to room temperature (1 h) and stirred overnight. The solution was filtered off and the solvent was removed in vacuum to give the title compound as a pale yellow oil which was washed with pentane (5 × 3 mL) and dried in vacuum to constant weight. Yield 0.27 g (87%). ^{1}H NMR (benzene-d_6, 400.13 MHz, 298 K): δ = 8.18 (d, 1H, $^3J_{\text{H-H}}$ = 7.2 Hz, arom-C$_6$*H*), 7.24 (d, 1H, $^3J_{\text{H-H}}$ = 8.3 Hz, arom-C$_3$*H*), 6.98 (m, 2H, arom-C$_4$*H* and arom-C$_5$*H*), 3.41 (s, 2H, ArC*H*$_2$N), 2.10 (s, 6H, N(C*H*$_3$)$_2$), 0.49 (s, 18H, N(Si(C*H*$_3$)$_3$)$_2$) ppm. ^{13}C{^{1}H} NMR (benzene-d_6, 100.62 MHz, 298 K): δ = 142.04 (arom-*C*$_1$), 136.09 (arom-*C*$_6$), 132.62 (arom-*C*$_3$), 130.17 (arom-*C*$_2$), 127.15 (arom-*C*$_4$), 126.79 (arom-*C*$_5$), 64.45 (Ar*C*H$_2$N), 44.76 (N(*C*H$_3$)$_2$), 6.7 (N(Si(*C*H$_3$)$_3$)$_2$) ppm. ^{77}Se{^{1}H} NMR (benzene-d_6, 76.31 MHz, 298 K): δ = +258 ppm. ^{29}Si{^{1}H} NMR (benzene-d_6, 79.49 MHz, 298 K): δ= +5.7 ppm. Anal. Calcd for $C_{15}H_{30}GeN_2SeSi_2$ (446.18 g·mol^{-1}): C 40.4, H 6.8, N 6.3 %. Found: C 40.5, H 6.7, N 6.5 %.

Ge[SC$_6$H$_4$(CH$_2$NMe$_2$)-2][N(SiMe$_3$)$_2$] (2). Following the same protocol as that described for **1**, the reaction of [2-(Me$_2$NCH$_2$)C$_6$H$_4$]$_2$S$_2$ (0.07 g, 0.21 mmol) and Ge[N(SiMe$_3$)$_2$]$_2$ (0.16 g, 0.42 mmol) afforded **2** as a pale yellow oil. Yield 0.89 g (53%). ^{1}H NMR (benzene-d_6, 300.11 MHz, 298 K): δ= 7.95 (d, 1H, $^3J_{\text{H-H}}$ = 7.7 Hz, arom-C$_6$*H*), 7.41 (d, 1H, $^3J_{\text{H-H}}$ = 8.7 Hz, arom-C$_3$*H*), 7.07 (br, 2H, arom-C$_4$*H* and arom-C$_5$*H*), 3.41 (s, 2H, ArC*H*$_2$N), 2.11 (s, 6H, N(C*H*$_3$)$_2$), 0.47 (s, 18H,

$\mathrm{N(Si(C}H_3)_3)_2$) ppm. $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (benzene-d_6, 75.47 MHz, 298 K): δ = 142.27 (arom-C_1), 135.7 (arom-C_6), 133.69 (arom-C_3), 130.51 (arom-C_2), 127.12 (arom-C_4 and arom-C_5), 62.28 ($\mathrm{Ar}C\mathrm{H_2N}$), 45.36 ($\mathrm{N(}C\mathrm{H_3)_2}$), 7.33 ($\mathrm{N(Si(}C\mathrm{H_3)_3)_2}$) ppm. Anal. Calcd for $\mathrm{C_{15}H_{30}GeN_2SSi_2}$ (399.29 g·mol^{-1}): C 45.1, H 7.6, N 7.0 %. Found: C 45.3, H 7.4, N 7.0 %.

$\mathrm{Sn[SeC_6H_4(CH_2NMe_2)\text{-}2][N(SiMe_3)_2]}$ (3). Following the same protocol as that described for **1**, the reaction of $\mathrm{[2\text{-}(Me_2NCH_2)C_6H_4]_2Se_2}$ (0.15 g, 0.35 mmol) and $\mathrm{Sn[N(SiMe_3)_2]_2}$ (0.31 g, 0.70 mmol) yielded **3** as a yellow solid. Yield 0.29 g (84%). ^{1}H NMR (benzene-d_6, 400.13 MHz, 298 K): δ = 8.10 (d, 1H, $^3J_{\text{H-H}}$ = 7.1 Hz, arom-$\mathrm{C_6}H$), 7.31 (d, 1H, $^3J_{\text{H-H}}$ = 7.1 Hz, arom-$\mathrm{C_3}H$), 7.02 (t, 2H, $^3J_{\text{H-H}}$ = 7.5 Hz, arom-$\mathrm{C_4}H$ and arom-$\mathrm{C_5}H$), 3.49 (s, 2H, $\mathrm{ArC}H_2\mathrm{N}$), 2.13 (s, 6H, $\mathrm{N(C}H_3)_2$), 0.43 (s, 18H, $\mathrm{N(Si(C}H_3)_3)_2$) ppm. $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (benzene-d_6, 100.62 MHz, 298 K): δ = 143.78 (arom-C_1), 138.58 (arom-C_6), 130.67 (arom-C_3), 129.97 (arom-C_2), 127.78 (arom-C_4), 127.70 (arom-C_5), 65.17 ($\mathrm{Ar}C\mathrm{H_2N}$), 45.22 ($\mathrm{N(}C\mathrm{H_3)_2}$), 6.64 ($\mathrm{N(Si(}C\mathrm{H_3)_3)_2}$) ppm. $^{77}\mathrm{Se}\{^1\mathrm{H}\}$ NMR (benzene-d_6, 76.31 MHz, 298 K): δ = +188 ($^1J_{\text{Se-119Sn}}$ = 865 Hz, $^1J_{\text{Se-117Sn}}$ = 815 Hz) ppm. $^{29}\mathrm{Si}\{^1\mathrm{H}\}$ NMR (benzene-d_6, 79.49 MHz, 298 K): δ = +6.5 ppm. $^{119}\mathrm{Sn}\{^1\mathrm{H}\}$ NMR (benzene-d_6, 149.21 MHz, 298 K): δ = +196 ($^1J_{\text{119Sn-Se}}$ = 865 Hz) ppm. Anal. Calcd for $\mathrm{C_{15}H_{30}SnN_2SeSi_2}$ (492.25 g·mol^{-1}): C 36.6, H 6.1, N 5.7 %. Found: C 36.4, H 6.0, N 5.8 %.

$\mathrm{Sn[SC_6H_4(CH_2NMe_2)\text{-}2][N(SiMe_3)_2]}$ (4). Following the same protocol as that described for **1**, the reaction of $\mathrm{[2\text{-}(Me_2NCH_2)C_6H_4]_2S_2}$ (0.11 g, 0.32 mmol) and $\mathrm{Sn[N(SiMe_3)_2]_2}$ (0.28 g, 0.64 mmol) yielded **4** as a pale yellow solid. Yield 0.21 g (74%). ^{1}H NMR (benzene-d_6, 400.13 MHz, 298 K): δ = 7.95 (m, 1H, arom-$\mathrm{C_6}H$), 7.47 (m, 1H, arom-$\mathrm{C_3}H$), 7.04 (m, 2H, arom-$\mathrm{C_4}H$ and arom-$\mathrm{C_5}H$), 3.62 (s, 2H, $\mathrm{ArC}H_2\mathrm{N}$), 2.16 (s, 6H, $\mathrm{N(C}H_3)_2$), 0.4 (s, 18H, $\mathrm{N(Si(C}H_3)_3)_2$) ppm.

$^{13}C\{^1H\}$ NMR (benzene-d_6, 100.62 MHz, 298 K): δ = 143.37 (arom-C_1), 136.99 (arom-C_6), 132.38 (arom-C_3), 130.63 (arom-C_2), 127.32 (arom-C_4 and arom-C_5), 63.02 (ArCH$_2$N), 45.60 (N(CH$_3$)$_2$), 6.69 (N(Si(CH$_3$)$_3$)$_2$) ppm. $^{29}Si\{^1H\}$ NMR (benzene-d_6, 79.49 MHz, 298 K): δ = 7.19 ppm. $^{119}Sn\{^1H\}$ NMR (benzene-d_6, 149.21 MHz, 298 K): δ = −78 ppm. Anal. Calcd for $C_{15}H_{30}SnN_2SSi_2$ (445.36 g·mol^{-1}): C 40.4, H 6.8, N 6.3 %. Found: C 40.6, H 7.0, N 6.0 %.

Pb[SeC$_6$H$_4$(CH$_2$NMe$_2$)-2][N(SiMe$_3$)$_2$] (5). Following the same protocol as that described for **1**, the reaction of [2-(Me$_2$NCH$_2$)C$_6$H$_4$]$_2$Se$_2$ (0.10 g, 0.24 mmol) with Pb[N(SiMe$_3$)$_2$]$_2$ (0.25 g, 0.48 mmol) yielded **5** as a yellow solid. Yield 0.21 g (87%). ^1H NMR (toluene-d_8, 400.13 MHz, 298 K): δ = 7.93 (d, 1H, $^3J_{H\text{-}H}$ = 7.5 Hz, arom-C$_6$$H$), 6.91 (t, 1H, $^3J_{H\text{-}H}$ = 7.6 Hz, arom-C$_5$$H$), 6.79 (t, 1H, $^3J_{H\text{-}H}$ = 7.7 Hz, arom-C$_4$$H$), 6.64 (d, 1H, $^3J_{H\text{-}H}$ = 7.9 Hz, arom-C$_3$$H$), 3.54 (br s, 2H, ArC$H_2$N), 1.84 (br, s, 6H, N(C$H_3$)$_2$), 0.28 (s, 18H, N[Si(C$H_3$)$_3$)$_2$]) ppm. $^{13}C\{^1H\}$ NMR (toluene-d_8, 100.62 MHz, 298 K): δ = 140.64 (arom-C_1), 140.12 (arom-C_6), 131.29 (arom-C_3), 128.22 (arom-C_2), 125.67 (br, arom-C_4 and arom-C_5), 66.30 (ArCH$_2$N), 45.99 (N(CH$_3$)$_2$), 6.89 (N(Si(CH$_3$)$_3$)$_2$) ppm. $^{77}Se\{^1H\}$ NMR (toluene-d_8, 76.31 MHz, 298 K): δ = +264 ppm. $^{29}Si\{^1H\}$ NMR (toluene-d_8, 79.49 MHz, 298 K): δ = −1.7 ppm. $^{207}Pb\{^1H\}$ NMR (toluene-d_8, 83.97 MHz, 298 K): δ = +3230 ppm. Anal. Calcd for $C_{15}H_{30}PbN_2SeSi_2$ (580.74 g·mol^{-1}): C 31.0, H 5.2, N 4.8 %. Found: C 30.9, H 5.0, N 5.0 %. Single-crystals suitable for XRD studies were grown by recrystallisation from a concentrated solution in pentane.

Pb[SC$_6$H$_4$(CH$_2$NMe$_2$)-2][N(SiMe$_3$)$_2$] (6). Following the same protocol as that described for **1**, the reaction of [2-(Me$_2$NCH$_2$)C$_6$H$_4$]$_2$S$_2$ (0.09 g, 0.27 mmol) with Pb[N(SiMe$_3$)$_2$]$_2$ (0.28 g, 0.51 mmol) yielded **6** as a yellow solid. Yield 0.22 g (76%). ^1H NMR (benzene-d_6, 400.13 MHz, 298

K): δ = 7.84 (d, 1H, $^3J_{H\text{-}H}$ = 8.0 Hz, arom-C_6H), 7.11 (br. m, 1H, arom-C_3H), 6.83 (t, 1H, $^3J_{H\text{-}H}$ = 7.5 Hz, arom-C_5H), 6.74 (br m, 1H, arom-C_4H), 3.69 (br s, 2H, $ArCH_2N$), 2.05 (br s, 6H, $N(CH_3)_2$), 0.4 (s, 18H, $N[Si(CH_3)_3)_2]$ ppm. $^{13}C\{^1H\}$ NMR (benzene-d_6, 100.62 MHz, 298 K): δ = 139.32 (arom-C_1), 137.09 (arom-C_6), 131.40 (arom-C_3), 128.85 (arom-C_2), 124.74 (br, arom-C_4 and arom-C_5), 63.97 ($ArCH_2N$), 45.77 ($N(CH_3)_2$), 4.95 ($N(Si(CH_3)_3)_2$) ppm. $^{29}Si\{^1H\}$ NMR (benzene-d_6, 79.49 MHz, 298 K): δ = −1.79 ppm. $^{207}Pb\{^1H\}$ NMR (benzene-d_6, 83.97 MHz, 298 K): δ = +2927 ppm. Anal. Calcd for $C_{15}H_{30}PbN_2SSi_2$ (533.85 g·mol^{-1}): C 33.7, H 5.7, N 5.2 %. Found: C 33.8, H 5.6, N 5.3 %. Single-crystals suitable for XRD studies were grown by recrystallisation from a concentrated solution in pentane.

$Sn(SePh)_2[N(SiMe_3)_2]_2$ (7). A mixture of Ph_2Se_2 (0.19 g, 0.60 mmol) and $Sn[N(SiMe_3)_2]_2$ (0.26 g, 0.60 mmol) was dissolved in toluene (30 ml) and stirred overnight at room temperature. Removal of the volatile fraction *in vacuo* afforded analytically pure **7** as a pale yellow solid. Recrystallisation the crude product in pentane afforded large colourless blocks that were suitable for X-ray diffraction crystallography. Yield (after crystallization) 0.37 g (82%). ^1H NMR (benzene-d_6, 300.13 MHz, 298 K): δ = 7.77–7.75 (m, 4H, arom–H), 7.00–6.99 (m, 6H, arom–H), 0.35 (s, 36H, $N(Si(CH_3)_3)$ ppm. $^{13}C\{^1H\}$ NMR (benzene-d_6, 74.57 MHz, 298 K): δ = 138.77 (o-C_6H_5), 129.78 (m-C_6H_5), 128.91 (p-C_6H_5), 126.20 (i-C_6H_5), 7.07 ($^1J_{C\text{-}Si}$ = 55.7 Hz, $^3J_{C\text{-}119Sn}$ = 12.5 Hz, $N(Si(CH_3)_3)_2$) ppm. $^{29}Si\{^1H\}$ NMR (benzene-d_6, 79.49 MHz, 25 °C): δ = 6.15 ($^2J_{Si\text{-}119Sn}$ = 12.3 Hz, $^1J_{Si\text{-}C}$ = 55.7 Hz) ppm. $^{119}Sn\{^1H\}$ NMR (benzene-d_6, 149.21 MHz, 25 °C): δ = –183 ($^1J_{119Sn\text{-}Se}$ = 1688 Hz) ppm. $^{77}Se\{^1H\}$ NMR (benzene-d_6, 76.31 MHz, 25 °C): δ = +206 ($^1J_{Se\text{-}117Sn}$ = 1614 Hz, $^1J_{Se\text{-}119Sn}$ = 1688 Hz) ppm. Anal. Calcd for $C_{24}H_{46}N_2Se_2Si_4Sn$ (751.61 g·mol^{-1}): C 38.4, H 6.1, N 3.7 %. Found: C 38.1, H 6.3, N 3.7 %.

$Sn[OC(Me)_2CH_2SeC_6H_4(CH_2NMe_2)$-2]$[N(SiMe_3)_2]$ (8). A solution of 2-$(Me_2NCH_2)C_6H_4SeCH_2C(Me)_2OH$ (0.21 g, 0.73 mmol) in Et_2O (15 mL) was added dropwise at −78 °C to a solution of $Sn[N(SiMe_3)_2]_2$ (0.33 g, 0.75 mmol) in Et_2O (30 mL). The reaction mixture was stirred while it was allowed to warm slowly to −40 °C (*ca.* 90 min). The volatiles were then removed under reduced pressure to give a foam which was purified by stripping with pentane (2 mL). Recrystallisation of the resulting solid in a 1:2 mixture of toluene and pentane at −30 °C afforded colourless single crystals of the title compound. Yield 0.23 g (56%). The compound is kinetically labile in solution at room temperature, hence the NMR data were recorded at low temperature. ^{1}H NMR (toluene-d_8, 400.13 MHz, 233 K): δ = 7.55 (d, 1H, $^3J_{\text{H-H}}$ = 7.6 Hz, arom-C_6H), 7.06–7.03 (m, 2H, arom-C_3H and arom-C_5H), 6.97–6.93 (m, 1H, arom-C_4H), 3.43–3.28 (br m, 4H, $ArCH_2N$ and $SeCH_2$), 2.09 (s, 6H, $N(CH_3)_2$), 1.53–1.51 (br m, 6H, $C(CH_3)_2O$), 0.54–0.42 (br overlapping s, 9H + 9H, $N(Si(CH_3)_3)_2$) ppm. ^{13}C{^{1}H} NMR (toluene-d_8, 100.61 MHz, 233 K): δ = 140.98 (arom-C_1), 134.99 (arom-C_2), 131.56 (arom-C_6), 130.35 (arom-C_3), 128.65 (arom-C_5), 126.48 (arom-C_4), 78.79 ($C(CH_3)_2O$), 65.25 ($ArCH_2N$), 44.96 ($N(CH_3)_2$), 43.04 ($SeCH_2$), 31.44 ($C(CH_3)_2O$), 7.62, 6.64 (both $N(Si(CH_3)_3)_2$) ppm. ^{77}Se{^{1}H} NMR (toluene-d_8, 76.31 MHz, 233 K): δ = +227 ppm. ^{29}Si{^{1}H} NMR (toluene-d_8, 149.21 MHz, 233 K): δ = −0.10, −3.25 ppm. ^{119}Sn{^{1}H} NMR (toluene-d_8, 149.21 MHz, 233 K): δ = −14 ppm. Satisfactory elemental analysis for $C_{19}H_{38}N_2OSeSi_2Sn$ (564.36 g·mol^{-1}) could not be obtained for this compound despite repeated attempts.

$Sn[OC(Me)_2CH_2SC_6H_4(CH_2NMe_2)$-2]$[N(SiMe_3)_2]$ (9). Following the same protocol as that given for **8**, 2-$(Me_2NCH_2)C_6H_4SCH_2C(Me)_2OH$ (0.13 g, 0.54 mmol) and $Sn[N(SiMe_3)_2]_2$ (0.24 g, 0.56 mmol) were reacted to give **8** as a colourless crystalline solid. Yield 0.12 g (43%). This complex is kinetically labile in solution at room temperature, hence the NMR data were recorded at low temperature. ^{1}H NMR (toluene-d_8, 400.13 MHz, 233 K): δ = 7.35 (d, 1H, $^3J_{\text{H-H}}$ = 8.0 Hz, arom-C$_6$*H*), 7.31 (d, 1H, $^3J_{\text{H-H}}$ = 7.6 Hz, arom-C$_3$*H*), 7.06 (t, 1H, $^3J_{\text{H-H}}$ = 7.6 Hz, arom-C$_5$*H*), 6.97 (dt, 1H, $^3J_{\text{H-H}}$ = 7.2 Hz, arom-C$_4$*H*), 3.60 (AB spin, $^2J_{\text{H-H}}$ = 13.2 Hz, 1H, ArC*H*(H)N), 3.49 (AB spin, $^2J_{\text{H-H}}$ = 13.2 Hz, 1H, ArC*H*(H)N), 3.27 (AB spin, $^2J_{\text{H-H}}$ = 12.0 Hz, 1H, SC*H*(H)), 3.21 (AB spin, $^2J_{\text{H-H}}$ = 12.4 Hz, 1H, SCH(*H*)), 2.17 (s, 6H, N(C*H*$_3$)$_2$), 1.52 (s, 3H, C(C*H*$_3$)$_2$O), 1.49 (s, 3H, C(C*H*$_3$)$_2$O), 0.55–0.44 (br overlapping s, 9H + 9H, N(Si(C*H*$_3$)$_3$)$_2$) ppm. ^{13}C{^{1}H} NMR (toluene-d_8, 100.61 MHz, 233 K): δ = 139.55 (arom-*C*$_1$), 136.79 (arom-*C*$_2$), 130.38 (arom-*C*$_3$), 129.45 (arom-*C*$_6$), 128.14 (arom-*C*$_4$), 126.39 (arom-*C*$_5$), 78.11 (*C*(CH$_3$)$_2$O), 62.65 (Ar*C*H$_2$N), 48.68 (S*C*H$_2$), 45.60 (N(*C*H$_3$)$_2$), 31.21 (C(*C*H$_3$)$_2$O), 7.61, 6.64 (both N(Si(*C*H$_3$)$_3$)$_2$) ppm. ^{29}Si{^{1}H} NMR (toluene-d_8, 79.49 MHz, 233 K): δ = −0.33, −3.30 ppm. ^{119}Sn{^{1}H} NMR (toluene-d_8, 149.21 MHz, 213 K): δ = –40 ppm. Anal. Calcd for $C_{19}H_{38}N_2OSSi_2Sn$ (517.46 g·mol^{-1}): C 44.1, H 7.4, N 5.4 %. Found: C 43.9, H 7.3, N 5.3 %.

Pb[OC(Me)$_2$CH$_2$SeC$_6$H$_4$(CH$_2$NMe$_2$)-2][N(SiMe$_3$)$_2$] (10). Following the same protocol as that given for **8**, the reaction of 2-(Me$_2$NCH$_2$)C$_6$H$_4$SeCH$_2$C(Me)$_2$OH (0.17 g, 0.60 mmol) with Pb[N(SiMe$_3$)$_2$]$_2$ (0.33 g, 0.60 mmol) afforded colourless single crystals of the title compound. Yield 0.31 g (40%). ^{1}H NMR (benzene-d_6, 500.13 MHz, 298 K): δ = 7.53 (d, 1H, $^3J_{\text{H-H}}$ = 7.5 Hz, arom-C$_6$*H*), 7.18 (d, 1H, $^3J_{\text{H-H}}$ = 7.0 Hz, arom-C$_3$*H*), 7.07 (dt, 1H, $^4J_{\text{H-H}}$ = 1.5 Hz, $^3J_{\text{H-H}}$ = 7.5 Hz, arom-C$_5$*H*), 6.99 (dt, 1H, $^4J_{\text{H-H}}$ = 1.0 Hz, $^3J_{\text{H-H}}$ = 7.0 Hz, arom-C$_4$*H*), 3.47 (s, 2H, ArC*H*$_2$N), 3.28 (br, 2H, SeC*H*$_2$), 2.12 (s, 6H, N(C*H*$_3$)$_2$), 1.45 (s, 6H, C(C*H*$_3$)$_2$O), 0.51–0.36 (overlapping br s, 18H, N(Si(C*H*$_3$)$_3$)$_2$) ppm. ^{13}C{^{1}H} NMR (benzene-d_6, 125.76 MHz, 298 K): δ = 141.33 (arom-

C$_1$), 133.99 (arom-*C*$_2$), 131.89 (arom-*C*$_6$), 130.75 (arom-*C*$_3$), 128.79 (arom-*C*$_5$), 127.08 (arom-*C*$_4$), 76.45 (*C*(CH$_3$)$_2$O), 65.39 (Ar*C*H$_2$N), 46.62 (Se*C*H$_2$), 45.41 (N(*C*H$_3$)$_2$), 33.01 (C(*C*H$_3$)$_2$O), 8.88, 6.06 (both N(Si(*C*H$_3$)$_3$)$_2$) ppm. ^{29}Si{^{1}H} NMR (benzene-*d*$_6$, 79.49 MHz, 298 K): $\delta = -2.37$, -4.44 ppm. ^{207}Pb{^{1}H}NMR (benzene-*d*$_6$, 83.71 MHz, 298 K): $\delta = +2124$ ppm. ^{77}Se{^{1}H} NMR (benzene-*d*$_6$, 76.32 MHz, 298 K): $\delta = +205$ ppm. Anal. Calcd for $C_{19}H_{38}N_2OPbSeSi_2$ (652.85 g·mol^{-1}): C 34.9, H 5.9, N 4.3. Found: C 34.7, H 5.9, N 4.1 %.

Pb[OC(Me)$_2$CH$_2$SC$_6$H$_4$(CH$_2$NMe$_2$)-2][N(SiMe$_3$)$_2$] (11). Following the same protocol as that given for **8**, the reaction of 2-(Me$_2$NCH$_2$)C$_6$H$_4$SCH$_2$C(Me)$_2$OH (0.14 g, 0.60 mmol) with Pb[N(SiMe$_3$)$_2$]$_2$ (0.33 g, 0.60 mmol) afforded colourless single crystals of the title compound. Yield 0.28 g (39%). ^{1}H NMR (benzene-*d*$_6$, 500.13 MHz, 298 K): $\delta = 7.41$ (d, 1H, $^3J_{\text{H-H}} = 8.0$ Hz, arom-C$_6$*H*), 7.37 (d, 1H, $^3J_{\text{H-H}} = 7.0$ Hz, arom-C$_3$*H*), 7.10 (dt, 1H, $^4J_{\text{H-H}} = 1.0$ Hz, $^3J_{\text{H-H}} = 7.5$ Hz, arom-C$_4$*H*), 7.00 (dt, 1H, $^4J_{\text{H-H}} = 1.0$ Hz, $^3J_{\text{H-H}} = 7.5$ Hz, arom-C$_5$*H*), 3.60–3.52 (br m, 2H, ArC*H*$_2$N), 3.26–3.21 (br s, 2H, SC*H*$_2$), 2.17 (s, 6H, N(C*H*$_3$)$_2$), 1.46 (s, 6H, C(C*H*$_3$)$_2$O), 0.52–0.32 (overlapping br s, 18H, N(Si(C*H*$_3$)$_3$)$_2$) ppm. ^{13}C{^{1}H} NMR (benzene-*d*$_6$, 125.76 MHz, 298 K): $\delta = 140.03$ (arom-*C*$_1$), 136.57 (arom-*C*$_2$), 130.76 (arom-*C*$_6$), 129.37 (arom-*C*$_3$), 128.42 (arom-*C*$_4$), 126.79 (arom-*C*$_5$), 75.96 (*C*(CH$_3$)$_2$O), 62.93 (Ar*C*H$_2$N), 52.04 (S*C*H$_2$), 45.91 (N(*C*H$_3$)$_2$), 32.51 (C(*C*H$_3$)$_2$O), 6.28, 6.05 (both N(Si(*C*H$_3$)$_3$)$_2$) ppm. ^{29}Si{^{1}H} NMR (benzene-*d*$_6$, 79.49 MHz, 298 K): $\delta = -2.37$, -4.45 ppm. ^{207}Pb{^{1}H} NMR (benzene-*d*$_6$, 83.71 MHz, 298 K): $\delta = +2092$ ppm. Anal. Calcd for $C_{19}H_{38}N_2OPbSSi_2$ (605.95 g·mol^{-1}): C 37.7, H 6.3, N 4.6. Found: C 37.5, H 6.4, N 4.5 %.

Sn[OC(Me)$_2$CH$_2$S{1-(8-(NMe$_2$)naphthalen-1-yl)}][N(SiMe$_3$)$_2$] (12). Following the same protocol as that given for **8**, the reaction of [1-{8-(N(CH$_3$)$_2$)naphthalen-1-yl}S]CH$_2$C(CH$_3$)$_2$OH (0.18 g, 0.64 mmol) with Sn[N(SiMe$_3$)$_2$]$_2$ (0.29 g, 0.66 mmol) afforded colourless single crystals of (**12**)$_2$. Yield 0.24 g (68%). ^{1}H NMR (toluene-d_8, 400.13 MHz, 213 K): δ = 7.41 (d, 2H, $^3J_{\text{H-H}}$ = 7.6 Hz, arom-C$_4$*H* and -C$_5$*H*), 7.27 (t, 1H, $^3J_{\text{H-H}}$ = 7.6 Hz, arom-C$_3$*H*), 7.23−7.18 (m, 2H, arom-C$_2$*H* and -C$_6$*H*), 6.92 (d, $^3J_{\text{H-H}}$ = 7.2 Hz, 1H, arom-C$_7$*H*), 3.43 (AB spin, $^2J_{\text{H-H}}$ = 10.8 Hz, 1H, SC*H*(H)), 2.83 (AB spin, $^2J_{\text{H-H}}$ = 10.4 Hz, 1H, SCH(*H*)), 2.67 (s, 3H, NC*H*$_3$), 2.36 (s, 3H, NC*H*$_3$), 1.77 (s, 3H, C(C*H*$_3$)$_2$), 1.70 (s, 3H, C(C*H*$_3$)$_2$), 0.64 (br s, 9H, Si(*C*H$_3$)$_3$), 0.20 (br s, 9H, Si(*C*H$_3$)$_3$) ppm. ^{13}C{^{1}H} NMR (toluene-d_8, 100.61 MHz, 213 K): δ = 151.87 (arom-*C*$_8$), 136.61 (arom-*C*$_1$), 134.59 (arom-*C*$_{10}$), 134.92 (arom-*C*$_9$), 126.53 (arom-*C*$_3$), 126.08 (arom-*C*$_4$) and 125.84(arom-*C*$_5$ and -*C*$_6$), 122.62 (arom-*C*$_2$), 118.92 (arom-*C*$_7$), 77.28 (*C*(CH$_3$)$_2$O), 47.01 (S*C*H$_2$), 46.82, 44.85 (both N(*C*H$_3$)$_2$), 32.73, 31.53 (both C(*C*H$_3$)$_2$O), 7.87, 6.53 (both N(Si(*C*H$_3$)$_3$)$_2$) ppm. ^{29}Si{^{1}H} NMR (toluene-d_8, 79.49 MHz, 213 K): δ = −0.64, −3.86 ppm. ^{119}Sn{^{1}H} NMR (toluene-d_8, 149.20 MHz, 213 K): δ = −69 ppm. Anal. Calcd for C$_{22}$H$_{38}$N$_2$OSSi$_2$Sn (553.50 g·mol^{-1}): C 47.7, H 6.9, N 5.1 %. Found: C 47.6, H 7.0, N 4.9 %.

Pb[OC(Me)$_2$CH$_2$S{1-(8-(NMe$_2$)naphthalen-1-yl)}][N(SiMe$_3$)$_2$] (13). Following the same protocol as that given for **8**, the reaction of [1-{8-(N(CH$_3$)$_2$)naphthalen-1-yl}S]CH$_2$C(CH$_3$)$_2$OH (0.18 g,0.64 mmol) with Pb[N(SiMe$_3$)$_2$]$_2$ (0.34 g, 0.65 mmol) afforded colourless crystals of the title compound. Yield 0.38 g (46%). ^{1}H NMR (THF-d_8, 500.13 MHz, 298 K): δ = 7.56 (dt, 2H, $^4J_{\text{H-H}}$ = 1.0 Hz, $^3J_{\text{H-H}}$ = 7.5Hz, arom-C$_3$*H* and -C$_6$*H*), 7.36 (t, 1H, $^3J_{\text{H-H}}$ = 7.5 Hz, arom-C$_5$*H*), 7.33 (t, 1H, $^3J_{\text{H-H}}$ = 7.5 Hz, arom-C$_4$*H*), 7.28 (d, 2H, $^3J_{\text{H-H}}$ = 7.5Hz, arom-C$_2$*H* and -C$_7$*H*), 3.90 (AB system, 1H, $^2J_{\text{H-H}}$ = 10.0 Hz, SC(H)*H*), 3.27 (AB system, 1H, $^2J_{\text{H-H}}$ = 10.0 Hz, SC(*H*)H, 2.74–2.65 (br. overlapping s, 6H, N(CH_3)$_2$), 1.67–1.61 (br overlapping s, 6H, C(CH_3)$_2$O), 0.29 (br s, 9H, Si(CH$_3$)$_3$), –0.24 (br s, 9H, Si(CH$_3$)$_3$) ppm. ^{13}C{^{1}H} NMR (THF-d_8, 125.76 MHz, 298 K): δ = 152.15 (arom-C_8), 137.06 (arom-C_1), 134.84 (arom-C_{10}), 129.28 (arom-C_9), 126.52 (arom-C_5), 126.06 and 126.05 (arom-C_3 and -C_6), 125.96 (arom-C_4), 123.20 (arom-C_2), 119.11 (arom-C_7), 75.60 (C(CH$_3$)$_2$O), 50.54 (SCH$_2$), 47.20, 44.59 (both N(CH$_3$)$_2$), 33.46, 32.15 (both C(CH$_3$)$_2$O), 7.83, 5.29 (both N(Si(CH$_3$)$_3$)$_2$) ppm. ^{29}Si{^{1}H} NMR (THF-d_8, 79.49 MHz, 298 K): δ = –3.56, –5.18 ppm. ^{207}Pb{^{1}H} NMR (THF-d_8, 83.71 MHz, 298 K): δ = +2006 ppm. Anal. Calcd for $C_{22}H_{38}N_2OPbSSi_2$ (641.99 g·mol^{-1}): C 41.2, H 6.0, N 4.4. Found: C 41.0, H 5.9, N 4.3 %.

Sn[OC(CF$_3$)$_2$CH$_2$SeC$_6$H$_4$(CH$_2$NMe$_2$)-2]$_2$ (14). 2-(Me$_2$NCH$_2$)C$_6$H$_4$SeCH$_2$C(CF$_3$)$_2$OH (0.19 g, 0.48 mmol) was dissolved in Et$_2$O (25 ml) and added dropwise to a solution of Sn[N(SiMe$_3$)$_2$]$_2$ (0.22 g, 0.49 mmol) in Et$_2$O (30 mL) at –78 °C. The reaction mixture was stirred until it gradually warmed to –40 °C (*ca.* 90 min). The volatiles were then removed under reduced pressure and the resulting foam was crystallised in a mixture of toluene and pentane (1:2) at –30 °C. A small crop of colourless crystals suitable for X-ray diffraction studies was collected and submitted to characterisation. Isolated yield 0.06 g (27%). ^{1}H NMR (benzene-d_6, 400.16 MHz, 298 K): δ = 7.11 (d, 2H, $^3J_{H\text{-}H}$ = 7.6 Hz, arom-C$_6$$H$), 6.98–6.90 (m, 4H, arom-C$_4$$H$ and -C$_5$$H$), 6.83 (d, 2H, $^3J_{H\text{-}H}$ = 7.6 Hz, arom-C$_3$$H$), 3.43 (s, 4H, ArSeC$H_2$), 3.29 (s, 4H, ArC$H_2$N), 1.99 (s, 12H, N(C$H_3$)$_2$) ppm. ^{13}C{^{1}H} NMR (benzene-d_6, 125.76 MHz, 298 K): 139.80 (arom-C_1), 132.55 (arom-C_2), 131.26 (arom-C_6), 130.86 (arom-C_3), 129.56 (arom-C_5), 127.81 (arom-C_4), 125.62 (q, $^1J_{C\text{-}F}$ = 291 Hz, CF$_3$), 82.64 (h, $^2J_{C\text{-}F}$ = 28.7 Hz, C(CF$_3$)$_2$), 65.22 (ArCH$_2$N), 44.84 (N(CH$_3$)$_2$), 32.40 (SeCH$_2$) ppm. ^{119}Sn{^{1}H} NMR (benzene-d_6, 149.20 MHz, 25 °C): δ = –392 (m, $^4J_{119Sn\text{-}F}$ = 35.4 Hz) ppm. ^{19}F{^{1}H} NMR (benzene-d_6, 376.53 MHz, 298 K): δ = –76.4 ($^4J_{F\text{-}119Sn}$ = 35.4 Hz, $^4J_{F\text{-}Se}$ ≈ 18 Hz) ppm. ^{77}Se{^{1}H} NMR (benzene-d_6, 76.31 MHz, 298 K): δ = +234 (h, $^4J_{\text{F-Se}}$ = 18.2 Hz) ppm. Anal.Calcd for $C_{26}H_{28}F_{12}N_2O_2SnSe_2$ (905.12 g·mol^{-1}): C 34.5, H 3.1, N 3.1. Found: C 34.4, H 3.2, N 3.1.

Pb[OC(CF$_3$)$_2$CH$_2$SeC$_6$H$_4$(CH$_2$NMe$_2$)-2]$_2$ (15). A solution of Pb[N(SiMe$_3$)$_2$]$_2$ (0.24 g, 0.45 mmol) in Et$_2$O (30 mL) was added dropwise to a solution of 2-(Me$_2$NCH$_2$)C$_6$H$_4$SeCH$_2$C(CF$_3$)$_2$OH (0.35 g, 0.89 mmol) in Et$_2$O (35 mL) at –78 °C. The reaction mixture was stirred until it gradually warmed to –40 °C (*ca.* 90 min). The volatiles were then removed under vacuum and the resulting foam was crystallized in a mixture of toluene and pentane (1:1) at –30 °C. A small crop of colourless crystals suitable for X-ray diffraction studies was collected and submitted to characterisation. Isolated yield 0.14 g (32%). ^{1}H NMR (benzene-d_6, 500.13 MHz, 298 K): δ = 7.33 (dd, 2H, $^3J_{\text{H-H}}$= 8.0 Hz, $^4J_{\text{H-H}}$= 1.0 Hz, arom-C$_6$*H*), 7.09 (dt, 2H, $^3J_{\text{H-H}}$= 7.5 Hz, $^4J_{\text{H-H}}$= 1.5 Hz, arom-C$_5$*H*), 6.93 (dt, 2H, $^3J_{\text{H-H}}$= 7.5 Hz, $^4J_{\text{H-H}}$= 1.0 Hz, arom-C$_4$*H*), 6.81 (dd, 2H, $^3J_{\text{H-H}}$= 7.5 Hz, $^4J_{\text{H-H}}$= 1.5 Hz, arom-C$_3$*H*), 3.67 (s, 4H, ArSeC*H*$_2$), 3.14 (s, 4H, ArC*H*$_2$N), 1.85 (s, 12H, N(CH$_3$)$_2$) ppm. ^{13}C{^{1}H} NMR (benzene-d_6, 125.76 MHz, 298 K): δ = 138.50 (arom-*C*$_1$), 131.58 (arom-*C*$_{2,3}$), 131.15 (arom-*C*$_6$), 129.88 (arom-*C*$_5$), 127.77 (q, $^1J_{\text{C-F}}$ = 294 Hz, *C*F$_3$), 127.66 (arom-*C*$_4$), 84.35 (h, $^2J_{\text{C-F}}$ = 27.8 Hz, *C*(CF$_3$)$_2$), 64.53 (Ar*C*H$_2$N), 45.09 (N(*C*H$_3$)$_2$), 32.93 (Se*C*H$_2$) ppm. ^{207}Pb{^{1}H} NMR (benzene-d_6, 83.71 MHz, 298 K): δ = +665 (br m) ppm. ^{19}F{^{1}H} NMR (benzene-d_6, 376.53 MHz, 298 K): δ = –76.0 (s) ppm. ^{77}Se{^{1}H}NMR (benzene-d_6, 76.31 MHz, 298 K): δ = +212 (br m) ppm. Anal.Calcd for $C_{26}H_{28}F_{12}N_2O_2PbSe_2$ (993.61 g·mol^{-1}): C 31.4, H 2.8, N 2.8. Found: C 31.3, H 2.7, N 2.9.

$[\{2\text{-}(Me_2NCH_2)C_6H_4SeCH_2C(Me)_2O\}Pb^+]\cdot[H_2N\{B(C_6F_5)_3\}_2^-]$ (16). With a bent glass finger, $H(OEt_2)_2^+\cdot H_2N\{B(C_6F_5)_3\}_2^-$ (0.58 g, 0.50 mmol) was added in small aliquots to a colourless solution of $[2\text{-}(CH_2NMe_2)C_6H_4Se]CH_2C(R)_2OH$ (0.14 g, 0.50 mmol) in Et_2O (30 mL). The resulting pale yellow solution was stirred at room temperature for 1 h. The mixture was then added dropwise with a cannula to a solution of $Pb[N(SiMe_3)_2]_2$ (0.27 g, 0.50 mmol) in Et_2O (30 mL) at –78 °C. The resulting solution was warmed to room temperature and stirred for 6 h. The volatiles were removed *in vacuo* to afford an oily material which was washed with pentane (2 × 20 ml). A small crop of colourless X-ray quality crystals were grown at room temperature by recrystallisation from a 1:1 mixture of dichloromethane and pentane. Crystals (0.11 g) containing CH_2Cl_2 and pentane were isolated from a mixture these solvents. ^1H NMR (CD_2Cl_2, 500.13 MHz, 298 K): δ = 7.62 (d, 1H, $^3J_{\text{H-H}}$ = 6.8 Hz, arom-C_6H), 7.56 (t, 1H, $^3J_{\text{H-H}}$ = 7.2 Hz, arom-C_5H), 7.46 (m, 1H, arom-C_4H), 7.33 (d, 1H, $^3J_{\text{H-H}}$ = 7.6 Hz, arom-C_3H), 5.67 (br, 2H, $H_2N\{B(C_6F_5)_3\}_2$), 4.31–4.13 (br m, 2H, $ArCH_2N$), 3.71 (br, 2H, $SeCH_2$), 2.39 (s, 6H, $N(CH_3)_2$), 1.44 (s, 6H, $C(CH_3)_2O$) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 100.62 MHz, 298 K): δ = 149.51, 147.14, 140.78, 138.31, 135.82, 120.92 (all C_6F_5), 138.80 (arom-C_1), 135.30 (arom-C_3), 134.59 (arom-C_6), 132.59 (arom-C_5), 131.52 (arom-C_4), 130.16 (arom-C_2), 78.13 ($C(CH_3)_2O$), 63.36 ($ArCH_2N$), 50.38 ($SeCH_2$), 45.49 ($N(CH_3)_2$), 34.19 ($C(CH_3)_2O$) ppm. $^{19}F\{^1H\}$ NMR (CD_2Cl_2, 376.53 MHz, 298 K): δ = –132.79 (d, 12F, $^3J_{\text{F-F}}$ = 18.8 Hz, *o*-F), –160.0 (t, 6F, $^3J_{\text{F-F}}$ = 19.6 Hz, *p*-F), –165.6 (t, 12F, $^3J_{\text{F-F}}$ = 19. 6 Hz, *m*-F) ppm. ^{11}B NMR (CD_2Cl_2, 128.39 MHz, 298 K): δ = –8.4 ppm. $^{77}Se\{^1H\}$ NMR (CD_2Cl_2, 76.31 MHz, 298 K): δ = +187 ppm. $^{207}Pb\{^1H\}$NMR (CD_2Cl_2, 83.71 MHz, 298 K): the resonance for the complex could not be detected. Satisfactory elemental analysis could not be obtained for this compound, presumably due to its high air- and moisture-sensitivity, and to the presence of lattice solvent molecules in the crystalline material.

Electronic Supporting Information (ESI) available: syntheses of Ge(TePh)$_2$[N(SiMe$_3$)$_2$]$_2$, Ge(SePh)$_2$[N(SiMe$_3$)$_2$]$_2$ and Ge(TePh)$_2$[N(SiMe$_3$)$_2$]$_2$; X-ray structures of **6**, (**8**)$_2$, (**9**)$_2$, (**11**)$_2$, (**12**)$_2$, Ge(EPh)$_2$[N(SiMe$_3$)$_2$]$_2$ (E = Se, Te) and Sn(TePh)$_2$[N(SiMe$_3$)$_2$]$_2$; Tables of crystallographic data.

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