

Cadmium complexes bearing $\text{Me}_2\text{N}^+\text{E}^-\text{O}^-$ (E = S, Se)

organochalcogenoalkoxides and their zinc and mercury analogues[†]

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Dedicated to Professor Ionel Haiduc on the occasion of his 80th anniversary.

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Abstract

Heteroleptic zinc and cadmium complexes of the type $[\{\text{Me}_2\text{N}^{\wedge}\text{E}^{\wedge}\text{O}^{\text{R}2}\}\text{M}-\text{Nu}]_n$ (M = Zn, Cd; E = S, Se; R = CH₃, CF₃; Nu = N(SiMe₃)₂, I, Cl; $n = 1-2$) were prepared by reacting the alcohol proteo-ligands $\{\text{Me}_2\text{N}^{\wedge}\text{E}^{\wedge}\text{O}^{\text{R}2}\}\text{H}$ with $[\text{M}(\text{N}(\text{SiMe}_3)_2)_2]$ (M = Zn, Cd) or $[\text{XMN}(\text{SiMe}_3)_2]$ (M = Zn, X = Cl; M = Cd, X = I) in anequimolar ratio. These group 12 metal complexes were characterised in solution by multinuclear NMR spectroscopy and their solid-state structures were determined by X-ray diffractometry. The ligands $\{\text{Me}_2\text{N}^{\wedge}\text{E}^{\wedge}\text{O}^{(\text{CH}_3)_2}\}^-$ bearing CH₃ groups in α position to the alkoxide behave as κ^2 -*O,E*-bidentate moieties (E = S, Se) and form centro-symmetric dinuclear *O*-bridged heteroleptic alkoxo-amido complexes both with zinc and cadmium, with four-coordinate metalcentres resting in tetrahedral environments. By contrast, complexes supported by the CF₃-substituted $\{\text{Me}_2\text{N}^{\wedge}\text{E}^{\wedge}\text{O}^{(\text{CF}_3)_2}\}^-$ crystallise as tetrahedral mononuclear species, with tridentate κ^3 -*N,O,E*-coordinated ligands. These structural differences resulting from changes in the ligand skeleton and in the electron-donating properties of the alkoxide were also observed in solution. Attempts to prepare congeneric heteroleptic mercury complexes from $[\text{Hg}(\text{N}(\text{SiMe}_3)_2)_2]$ unexpectedly only afforded homoleptic bis(alkoxide)s such as $[\{\text{Me}_2\text{N}^{\wedge}\text{S}^{\wedge}\text{O}^{(\text{CF}_3)_2}\}]_2\text{Hg}$. Owing to the strong Hg–C bond, treatment of $[\text{PhHgN}(\text{SiMe}_3)_2]$ with $\{\text{Me}_2\text{N}^{\wedge}\text{S}^{\wedge}\text{O}^{(\text{CF}_3)_2}\}\text{H}$ afforded the heteroleptic, T-shaped $[\{\text{Me}_2\text{N}^{\wedge}\text{S}^{\wedge}\text{O}^{(\text{CF}_3)_2}\}\text{HgPh}]$ mercuric alkoxide upon elimination of hexamethyldisilazane. $[\{\text{Me}_2\text{N}^{\wedge}\text{S}^{\wedge}\text{O}^{(\text{CF}_3)_2}\}]_2\text{Hg}$ and $\{\text{Me}_2\text{N}^{\wedge}\text{S}^{\wedge}\text{O}^{(\text{CF}_3)_2}\}\text{HgPh}$ constitute very rare examples of structurally characterised mercuric alkoxides.

Introduction

Heteroleptic zinc amides of the type $\{\text{LX}\}\text{ZnNR}_2$ supported by a monoanionic ligand $\{\text{LX}\}^-$, and amongst these most prominently $\{\text{LX}\}\text{ZnN}(\text{SiMe}_3)_2$, have of late enjoyed considerable popularity, for instance as excellent precatalysts for the ring-opening polymerisation of cyclic esters.¹ Many such complexes have been structurally authenticated,² and the main features of their coordination chemistry are well established. By contrast, the numbers of pertaining d^{10} cadmium and mercury amido complexes are rather limited. Boyle's heteroleptic alkoxide and aryloxides $[\text{Cd}(\mu^2\text{-OR})(\text{N}(\text{SiMe}_3)_2)(\text{solvent})]_2$ dinuclear cadmium compounds are representative of the thirteen $\{\{\text{LX}\}\text{CdN}(\text{SiMe}_3)_2\}$ species referenced to date in the Cambridge Structural Database.³ Other examples include the four-coordinate tris(pyrazolyl)methanide $[\{\text{C}(\text{Me}_2\text{pz})_3\}\text{CdN}(\text{SiMe}_3)_2]$ reported by Mountford,⁴ the three-coordinate, sterically congested β -diketiminate $[\{\text{BDI}^{\text{Pr}}\}\text{CdN}(\text{SiMe}_3)_2]$ described by Fulton,⁵ and Parkin's five-coordinate tris(2-pyridylthio)methanide $[\{\text{Tptm}\}\text{CdN}(\text{SiMe}_3)_2]$.⁶ Moreover, the sole cases of mercury disilazides have linear geometry about the metal, as in $[\text{Hg}\{\text{N}(\text{SiMe}_3)(\text{SiPh}_2^t\text{Bu})\}_2]$,⁷ in the α -mercurio-substituted phosphorus ylide $[\text{Ph}_3\text{P}=\text{CMe}\{\text{HgN}(\text{SiMe}_3)_2\}]$,⁸ and in $[\text{Hg}\{\text{cyclo-N}[\text{Si}(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{Si}(\text{CH}_3)_2]\}_2]$.⁹

Whereas aryloxocomplexes of zinc, cadmium and mercury are well-known especially for the non-toxic zinc,¹⁰ far fewer examples of alkoxo complexes have been reported.¹¹ The number of structurally characterised alkoxides decreases drastically upon descending group 12. With the soft mercury metal, the poorly characterised homoleptic $\text{Hg}(\text{OMe})_2$ and $\text{Hg}(\text{OEt})_2$ form yellow, poorly soluble materials,¹² while authenticated mercury alkoxides are not referenced in the CSD database. Only a handful of complexes with *O,O*-chelating ligands, *e.g.* in a (1-phenyl-3-

methyl-4-benzoyl-pyrazol-5-onato)phenyl mercury β -diketonato complex¹³ or in a bis(tropolonato) mercury coordination polymer,¹⁴ are known.

We have recently developed hemi-labile, potentially tridentate alcohol proteo-ligands $\{L^{E,R2}\}H$ ($E = S, Se; R = Me, CF_3$) containing a nitrogen and a chalcogen heteroatoms, and we have explored their coordination chemistry with coinage metals¹⁵ and with tetrelenes (Scheme 1).¹⁶ By varying the nature of the substituent in α position to the hydroxyl and the electronic density at the metal centre, we have been able to tune the coordination patterns in tin(II) and lead(II) complexes, notably by enforcing coordination of the heteroelements onto the metal atom. Compared to their congeners $\{L^{E,(CH_3)_2}\}^-$ having methyl groups in α position to the alkoxide, the presence of electron-withdrawing CF_3 groups in $\{L^{E,(CF_3)_2}\}^-$ (and the likes of these) has been shown to reduce the propensity to yield polymetallic aggregated species,¹⁷ and to favour intramolecular coordination of heteroatoms in discrete complexes of electrophilic metals.¹⁶

Scheme 1. Varying coordination patterns in tetrelene complexes stabilised by $\{L^{E,R2}\}^-$ ligands.¹⁶

As a continuation of these investigations, we are now reporting of the utilisation of $\{L^{E,R2}\}H$ alcoholsto synthesise zinc and cadmium amides and halides, and related phenylmercuric derivatives. Variations in the respective coordination spheres and geometries are probed in relation with the identity of the metal and the substitution pattern in $[\{L^{E,R2}\}MNu]$ compounds ($E = S, Se$; $R = CH_3, CF_3$; $M = Zn, Cd, Hg$; $Nu = N(SiMe_3)_2, Cl, Ph$), and the synthesis and characterisation of an unusual $(C_{sp3-})O-Hg$ phenyl mercury alkoxide are detailed.

Results and Discussion

Synthesis of complexes

The organochalcogenoalcohols $\{L^{E,R2}\}H$, where $E = S$ or Se and $R = CH_3$ or CF_3 , were utilised in alcoholysis reactions with equimolar quantities of the group 12 monomeric precursors $[M(N(SiMe_3)_2)_2]$ to obtain the heteroleptic amido complexes $[\{L^{E,R2}\}MN(SiMe_3)_2]$ ($M = Zn, Cd, Hg$; Schemes 2-4). The reactions proceeded cleanly upon quantitative release of $HN(SiMe_3)_2$ in the cases of cadmium and zinc to afford the heteroleptic complexes $[\{L^{E,R2}\}CdN(SiMe_3)_2]_n$ ($R = CH_3, E = S, n = 2, [1]_2$; $R = CH_3, E = Se, n = 2, [2]_2$; $R = CF_3, E = S, n = 1, 3$; $R = CF_3, E = Se, 4$) and $[\{L^{E,R2}\}ZnN(SiMe_3)_2]$ ($R = CH_3, E = Se, n = 2, [6]_2$; $R = CF_3, E = Se, n = 1, 7$) (Schemes 2 and 3). Because the coordination features of the cadmium complexes with sulphur-containing ligands **1** and **3** matched closely those of the congeneric selenium-containing **2** and **4** (*vide infra*), $\{L^{S,R2}\}H$ were not subsequently used to prepare zinc-amido complexes, and only the selenium-containing zinc complexes $[\{L^{Se,R2}\}CdN(SiMe_3)_2]_n$ were prepared for $R = CH_3$ and CF_3 (Scheme 3). The formulations for the dimeric $[1]_2, [2]_2$ and $[6]_2$ were established on the basis of their crystallographic data (*vide infra*). Their NMR data, with single sets of clearly resolved resonances for each complex, testify to a high level of symmetry in benzene- d_6 solution.

The heteroleptic starting materials [ICdN(SiMe₃)₂] and [ClZnN(SiMe₃)₂] were utilised to obtain the halide complexes [{L^{Se,(CH₃)₂}}CdI] (**5**) and [{L^{Se,(CH₃)₂}}ZnCl] (**8**), respectively, upon treatment with one equivalent of {L^{Se,(CH₃)₂}}H (Schemes 2 and 3). They were first synthesised in good yields upon ligand redistribution in diethyl ether between stoichiometric amounts of the bis(amido) precursors and CdI₂ or ZnCl₂. Compounds **1-8** were all isolated as colourless solids. All amido complexes are readily soluble in aromatic hydrocarbons and ethers. However, the iodo and chloro complexes **5** and **8** are only sparingly soluble in toluene and benzene; their NMR data were hence recorded in THF-*d*₈. The isolated yields for the cadmium compounds (typically 60-80%) were generally higher than those for their zinc counterparts (*ca.* 50%).



Scheme 2. Syntheses of the cadmium complexes [**1**]₂-**5**. All drawings are representative of their molecular solid-state structures, except for **5**, for which it could not be ascertained.

Compounds **1-4** are rare terminal amido cadmium complexes, and their molecular structures were determined by X-ray diffraction analysis. To our knowledge, the only other example of a structurally characterised amido/alkoxo cadmium complex is Boyle's $[\text{Cd}(\mu\text{-O}^t\text{Bu})_2(\text{N}(\text{SiMe}_3)_2)\cdot\text{pyridine}]_2$.³ The amine elimination route starting from $[\text{ICdN}(\text{SiMe}_3)_2]$ afforded the iodo complex **5** in good yield and free of alkali salts. This protocol is more convenient than salt metathesis, which when performed in ethers with bidentate β -diketiminates led to the heterobimetallic $[\{\text{BDI}^{\text{iPr}}\}\text{Cd}(\mu\text{-Cl})_2\text{Li}\cdot(\text{THF})_2]$,⁵ $[\{\text{BDI}^{\text{F}}\}\text{Cd}(\mu\text{-I})_2\text{Li}\cdot(\text{Et}_2\text{O})_2]$ ¹⁸ or $[\{\text{BDI}^{\text{iPr}}\}\text{Cd}(\mu\text{-Cl})_2\text{Li}\cdot(\text{Et}_2\text{O})_2]$.^{19,20}

Scheme 3. Syntheses of the zinc complexes [**6**]₂-**8**. Drawings are representative of the molecular solid-state structures, except for **8**, for which it could not be ascertained.

In comparison, mixed amido/alkoxo zinc compounds akin to **6** and **7** are relatively more common. Reported mononuclear complexes include bulky $[\text{Zn}(\kappa^3\text{-NNO})\text{N}(\text{SiMe}_3)_2]$ heteroscorpionates²¹ and $[\text{Zn}(\mu\text{-O}^{\wedge\wedge\wedge}\text{NHC}^{\text{Dipp}})\text{N}(\text{SiMe}_3)_2]$ bearing an *N*-heterocyclic ligand anchored to the alkoxide (Dipp = 2,6-diisopropylphenyl),²² while dinuclear complexes are also known, *e.g.* $[\text{Zn}(\mu\text{-OCeEt}_3)\text{N}(\text{SiMe}_3)_2\cdot\text{pyridine}]_2$ featuring three-coordinate zinc atoms,²³ and $[\text{Zn}(\mu\text{-O}^{\wedge\wedge}\text{NHC}^{\text{R}})\text{N}(\text{SiMe}_3)_2]_2$ (R = ^{*i*}Pr, mesityl) with four-coordinate metal atoms.²²

By contrast with zinc and cadmium bis(amide)s, $[\text{Hg}(\text{N}(\text{SiMe}_3)_2)_2]$ failed to deliver the targeted heteroleptic mercury amido compound through alcoholysis. Hence, equimolar reaction with $\{\text{L}^{\text{S},(\text{CF}_3)_2}\}\text{H}$ returned the colourless bis(alkoxide) $[\{\text{L}^{\text{S},(\text{CF}_3)_2}\}_2\text{Hg}]$ (**9**) as the main product together with unreacted $[\text{Hg}(\text{N}(\text{SiMe}_3)_2)_2]$. Compound **9** was obtained in 72% yield by using two equivalents of proteo-ligand (Scheme 4), and its molecular structure was determined. We are not aware of another example of mercury bis(alkoxide) that has been structurally authenticated. Instead, we took advantage of the strength of the Hg–C bond in $[\text{PhHgN}(\text{SiMe}_3)_2]$ to treat this precursor with an equimolar amount of $\{\text{L}^{\text{S},(\text{CF}_3)_2}\}\text{H}$. This reaction led to the isolation of the colourless $[\{\text{L}^{\text{S},(\text{CF}_3)_2}\}\text{HgPh}]$ (**10**) in 45% yield (Scheme 4), and its molecular structure was established. $\{\text{L}^{\text{Se},(\text{CF}_3)_2}\}\text{H}$ also reacted with $[\text{PhHgN}(\text{SiMe}_3)_2]$ to give $[\{\text{L}^{\text{Se},(\text{CF}_3)_2}\}\text{HgPh}]$ (**11**) in similar yields. These two compounds are, to our knowledge, the first examples of heteroleptic amido/alkoxo mercury complexes, and even, for **10**, of structurally characterised mercury alkoxides. They are soluble in common organic solvents, including aromatic hydrocarbons, and are stable in such solutions for weeks.

Scheme 4. Syntheses of the mercury complexes **9-11**. Drawings are representative of the molecular solid-state structures, except for **11**, the structure of which could not be ascertained.

Structural characterisation

The solid-state structures of complexes **1-4** (Cd), **6-7** (Zn) and **9-10** (Hg) were determined by X-ray diffraction crystallography. The structures for **1** and **3** are isomorphous with those of their selenium-containing analogues **2** and **4**, respectively, and therefore their structures will not be discussed in detail. They are given as Electronic Supporting Information. Key metric parameters for all these complexes are collated in Table 1.

There are four molecules *per* asymmetric unit in the molecular structure of **2**, which crystallised as the dinuclear [**2**]₂. Only one of the four independent but roughly equivalent molecules is depicted in Figure 1, which shows the complex to exist in the solid state as a

crystallographically centrosymmetric *O*-bridged dimer with a classical rhomboidal Cd₂O₂ core. Each cadmium atom rests in a distorted four-coordinate tetrahedral arrangement ($\tau_4 = 0.69$),²⁴ with Cd1 sitting *ca.* 0.47 Å above the mean plane defined by O1, O1' and N1, and with Se1 in apical position. The $d_{\text{Cd1-Se1}}$ bond length of 2.8086(4) Å is well below the sum of Van der Waals radii for Cd (1.58 Å) and Se (1.90 Å).

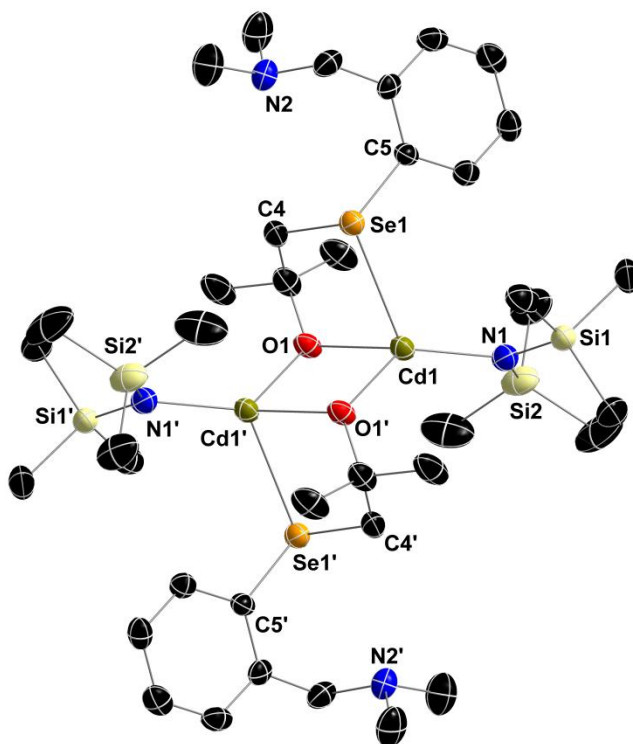


Figure 1. ORTEP rendering of the molecular solid-state structure of $[\{L^{\text{Se},(\text{CH}_3)_2}\}\text{CdN}(\text{SiMe}_3)_2\}_2$ ($[\mathbf{2}]_2$). Ellipsoids at the 50% probability level. Only one of four independent molecules represented. H atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Cd1–N1 = 2.108(3), Cd1–O1' = 2.187(2), Cd1–O1 = 2.209(2), Cd1–Se1 = 2.8086(4), Se1–C5 = 1.939(3), Se1–C4 = 1.966(3); N1–Cd1–O1' = 128.64(9), N1–Cd1–O1 = 134.25(9), O1'–Cd1–O1 = 81.40(8), N1–Cd1–Se1 = 119.55(8), O1'–Cd1–Se1 = 99.34(6), O1–Cd1–Se1 = 79.73(6); C5–Se1–C4 = 103.37(13), C5–Se1–Cd1 = 108.06(9), C4–Se1–Cd1 = 89.94(10).

On the other hand, the amino side-arm does not bind to the metal atom, with the $d_{\text{Cd1-N2}}$ distance (6.105(3) Å) far exceeding the sum of the van der Waals radii for these elements. The $d_{\text{Cd1-N1}}$ bond distance (2.108(3) Å) is typical of terminal [Cd]–N(SiMe₃)₂ amides.³⁻⁶ The geometry about the cadmium atoms in [2]₂ resembles that in [Cd(μ²-OCH₂^tBu)N(SiMe₃)₂•(pyridine)]₂,³ the only other structurally identified mixed amido/alkoxo cadmium complex ($d_{\text{Cd-O}} = 2.184(1)$ – $2.211(2)$ Å; $d_{\text{Cd-Nterminal}} = 2.123(2)$ Å). The Lewis acidity of the metal centres in these two complexes is pronounced. It is satisfied by coordination of pyridine in Boyle's compound, and by the intramolecular binding of the selenoether in [2]₂. As a result of coordination to cadmium, the selenium atoms in [2]₂ are three-coordinate, with the geometry forming a distorted trigonal pyramid ($\Sigma_{\theta}(\text{Se}) = 301.4^\circ$).²⁵ It is similar to that in the cadmium selenoether [{L}Cd(μ-Cl)Cl]₂, where L is a neutral bis(pyridin-2-ylmethyl)selane,²⁶ and where the average $d_{\text{Cd-Se}}$ distance to the three-coordinate selenium atom of *ca.* 2.85 ± 0.02 Å is slightly longer than in [2]₂ (2.8086(4) Å).

The bonding pattern is very different in **4**, which crystallised as a mononuclear complex with a four-coordinate tetrahedral cadmium centre in a distorted tetrahedral geometry ($\tau_4 = 0.69$) upon coordination on the selenoether and the flanking amine (Figure 2). Formation of the monomeric **4** results from the presence of the two CF₃ electron-withdrawing groups in α position to the alkoxide in the ligand, which restricts its capacity to act as a π donor and to form polymetallic species.¹⁷ Binding of the amine (N31) onto Cd1 maintains a coordination number of four for the electron-precise central cadmium atom. The $d_{\text{Cd1-O11}}$ distance to the terminal alkoxide in **4** (2.145(2) Å) is expectedly shorter than the corresponding distances to the two bridging O-atoms in [2]₂, but the distances to the terminal amides match in the two complexes. The dative bond with the N_{amine} atom ($d_{\text{Cd1-N31}} = 2.341(3)$ Å) is longer than that to N_{amide} ($d_{\text{Cd1-N1}} = 2.085(3)$ Å), but it falls well below the sum of Van der Waals radii (3.45 Å). There is no close contact

between Cd1 and fluorine atoms. The shorter Cd–Se distance in **4** ($d_{\text{Cd1-Se1}} = 2.7348(4)$ Å) than in **[2]₂** ($d_{\text{Cd1-Se1}} = 2.8086(4)$ Å) testifies to a stronger bond in **4**, again a consequence of electronic depletion at the metal ensuing from the presence of the CF₃ groups. The other geometrical features around the selenium atom in **4** (distorted trigonal pyramid, $\Sigma_{\theta}(\text{Se}) = 295.8$ °) are comparable to those in **[2]₂**.

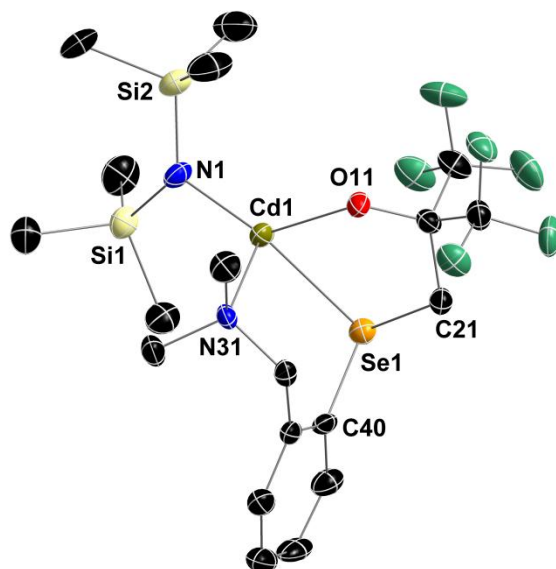


Figure 2. ORTEP rendering of the molecular solid-state structure of $[\{\text{L}^{\text{Se},(\text{CF}_3)_2}\}\text{CdN}(\text{SiMe}_3)_2]$ (**4**). Ellipsoids at the 50% probability level. Only one of four independent molecules represented. H atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Cd1–N1 = 2.085(3), Cd1–O11 = 2.145(2), Cd1–N31 = 2.341(3), Cd1–Se1 = 2.7348(4), Se1–C40 = 1.942(3), Se1–C21 = 1.962(3); N1–Cd1–O11 = 134.37(10), N1–Cd1–N31 = 117.76(10), O11–Cd1–N31 = 89.29(9), N1–Cd1–Se1 = 128.43(8), O11–Cd1–Se1 = 80.64(6), N31–Cd1–Se1 = 94.02(6), C40–Se1–C21 = 104.16(14), C40–Se1–Cd1 = 99.22(9), C21–Se1–Cd1 = 92.43(9).

The structure of the centrosymmetric *O*-bridged dimeric complex **[6]₂** displayed in Figure 3 resembles very closely that of its cadmium congener **[2]₂**, and shows each metal atom to be in a

distorted tetrahedral environment ($\tau_4 = 0.70$). Such four-coordinate arrangement is typical for alkoxo complexes of the more Lewis acidic zinc ions. Whereas zinc selenides are very common, we are not aware of crystallographic data for a similar Se \rightarrow Zn adduct. The $d_{\text{Zn1-Se1}} = 2.6868(4)$ Å bond distance is shorter than seen for cadmium, in line with the smaller ionic radius of Zn $^{2+}$ compared to that of Cd $^{2+}$ (0.60 and 0.78 Å for C.N. = 4, respectively). The Se–C bond lengths in [6] $_2$ are almost identical to those in [2] $_2$, with the selenium atom in a distorted pyramidal geometry.

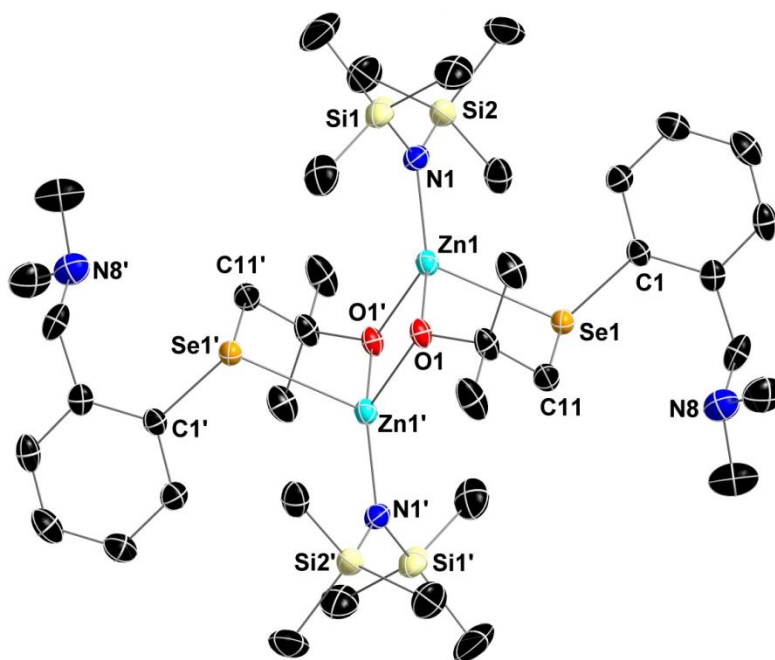


Figure 3. ORTEP rendering of the molecular solid-state structure of $[\{L^{\text{Se},(\text{CH}_3)_2}\}\text{ZnN}(\text{SiMe}_3)_2\}_2$ ([6] $_2$). Ellipsoids at the 50% probability level. Only one of two independent molecules represented. H atoms omitted for clarity. Selected bond lengths (Å) and angles ($^\circ$): Zn1–N1 = 1.910(2), Zn1–O1' = 1.9881(18), Zn1–O1 = 2.0027(17), Zn1–Se1 = 2.6868(4), Se1–C1 = 1.929(3), Se1–C11 = 1.972(3) ; N1–Zn1–O1' = 128.79(8), N1–Zn1–O1 = 132.01(8), O1'–Zn1–

O1 = 84.02(7), N1–Zn1–Se1 = 118.95(7), O1'–Zn1–Se1 = 97.19(5), O1–Zn1–Se1 = 83.01(5), C1–Se1–C11 = 101.64(11), C1–Se1–Zn1 = 111.41(8), C11–Se1–Zn1 = 88.96(8).

The replacement of CH₃ by CF₃ α -substituents in **7** again generates a mononuclear, four-coordinate complex (Figure 4). The geometry about Zn1 forms a characteristic distorted tetrahedron ($\tau_4 = 0.77$) upon coordination of the amino side-arm ($d_{\text{Zn1-N19}} = 2.1203(12)$ Å). The $d_{\text{Zn1-O18}}$ and $d_{\text{Zn1-Se1}}$ distances (1.9339(10) and 2.5742(2) Å, respectively) are shorter than in the dimeric [2]₂ as a result of monomeric structure of **7** and the presence of the electron-withdrawing CF₃ groups. The $d_{\text{Zn1-O18}}$ distance is in the range expected for a terminal zinc alkoxide.²⁷

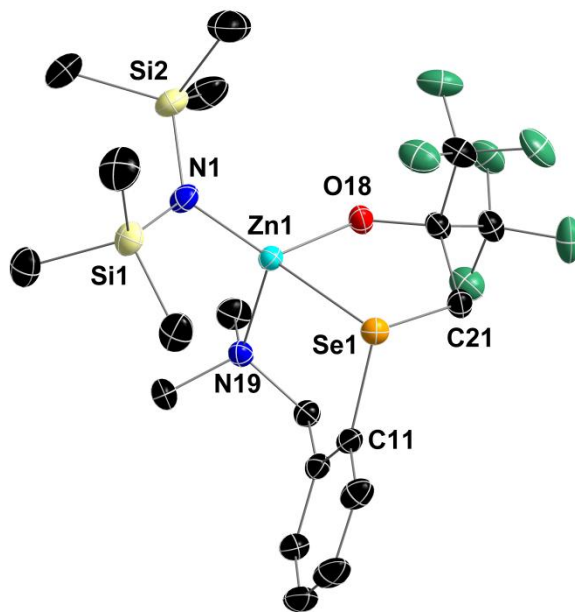


Figure 4. ORTEP rendering of the molecular solid-state structure of [$\{\text{L}^{\text{Se},(\text{CF}_3)_2}\}\text{ZnN}(\text{SiMe}_3)_2$] (**7**). Ellipsoids at the 50% probability level. Only one of two independent molecules represented. H atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Zn1–N1 = 1.9016(12), Zn1–O18 = 1.9339(10), Zn1–N19 = 2.1203(12), Zn1–Se1 = 2.5742(2), Se1–C11 = 1.9273(14),

Se1–C21 = 1.9639(14); N1–Zn1–O18 = 128.81(5), N1–Zn1–N19 = 117.05(5), O18–Zn1–N19 = 96.05(4), N1–Zn1–Se1 = 122.65(4), O18–Zn1–Se1 = 85.73(3), N19–Zn1–Se1 = 98.79(3), C11–Se1–C21 = 103.43(6), C11–Se1–Zn1 = 99.72(4), C21–Se1–Zn1 = 90.59(4).

The molecular structure of the homoleptic mercury bis(alkoxide) **9** is displayed in Figure 5. The five-coordinate metal atom is surrounded by two oxygen, two sulphur and only one nitrogen atoms. It adopts a distorted trigonal bipyramidal geometry ($\tau_5 = 0.31$),²⁸ with N21, S1 and S2 in equatorial positions (note the large \angle S1–Hg–S2 angle, 152.275(19) °), and the oxygen atoms O1 and O51 at the apices (\angle O1–Hg–O51 = 170.67(7) °). No Hg⋯F interaction is seen, and the second nitrogen atom is also very far from the metal centre ($d_{\text{Hg1–N71}} = 4.1892(26)$ Å).

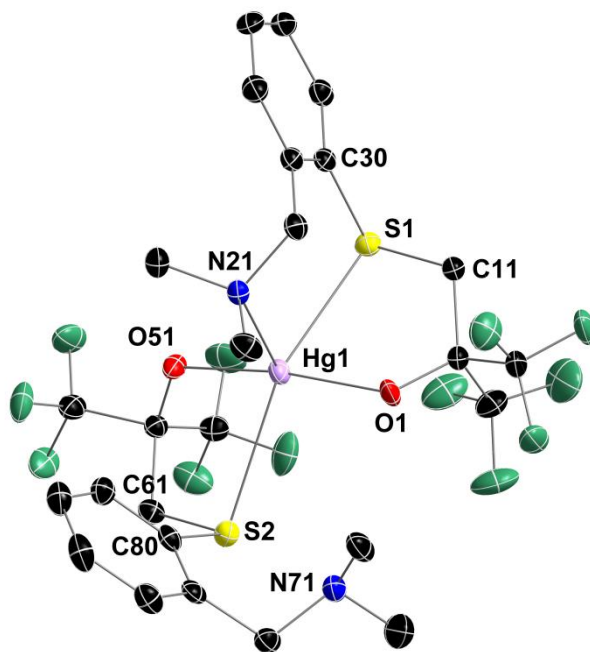


Figure 5. ORTEP rendering of the molecular solid-state structure of $[\{\text{L}^{\text{S},(\text{CF}_3)_2}\}_2\text{Hg}]$ (**9**). Ellipsoids at the 50% probability level. Only one of two independent molecules represented. H atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Hg1–O51 = 2.1135(17),

Hg1–O1 = 2.1322(18), Hg1–N21 = 2.479(2), Hg1–S1 = 2.7718(6), Hg1–S2 = 2.8753(7), S1–C30 = 1.784(3), S1–C11 = 1.818(2), S2–C80 = 1.790(3), S2–C61 = 1.814(2); O51–Hg1–O1 = 170.67(7), O51–Hg1–N21 = 99.69(7), O1–Hg1–N21 = 89.22(7), O51–Hg1–S1 = 104.65(5), O1–Hg1–S1 = 78.06(5), N21–Hg1–S1 = 89.17(5), O51–Hg1–S2 = 75.16(5), O1–Hg1–S2 = 98.22(5), N21–Hg1–S2 = 118.41(5), S1–Hg1–S2 = 152.275(19).

The two bond lengths to the oxygen atoms are comparable (2.1135(17) and 2.1322(18) Å), but there is a substantial discrepancy in the distances to the sulphur atoms, $d_{\text{Hg1-S1}} = 2.7718(6)$ Å and $d_{\text{Hg1-S2}} = 2.8753(7)$ Å. The two pairs of S–C bond distances for the two sulphur atoms are almost identical for S1 and S2. Five-coordinate mercury compounds are well-known, but we could not find structurally related mercury alkoxo or aryloxo compounds in the CSD database. The Hg–O bond lengths in **9** are noticeably longer than in the two-coordinate {2-Cl-4-Br-C₆H₃-O}HgPh (2.0060 Å),²⁹ but much shorter than in the three-coordinate {*o*-(MeN=CH)-C₆H₄-O}HgPh (2.4210(13) and 2.4392(9) Å) mercury aryloxides.³⁰

By contrast with **9**, the metal atom is only three-coordinate in the heteroleptic phenyl complex **10** (Figure 6), with coordination of the sulphur atom S3 but without coordination of the amine (N1) onto the metal. The $\angle\text{C14-Hg1-O1}$ (173.3(3) °) angle is close to the expected 180 °, with a T-shape geometry about Hg1 featuring a $\angle\text{S3-Hg1-O1}$ angle much narrower than the $\angle\text{S3-Hg1-C14}$ one. The $d_{\text{Hg1-S3}}$ distance (3.008(3) Å) is much lower than the sum of Van der Waals radii for mercury (1.55 Å) and sulphur (1.80 Å). The $d_{\text{Hg1-C14}}$ bond length in **10** (2.039(9) Å) matches closely that of 2.046 Å in the dimeric [{C₁₀H₈NO}HgPh]₂ ({C₁₀H₈NO}[−] = quinaldinate), but the $d_{\text{Hg1-O1}}$ bond distance to the *O*_{alkoxide} atom in **10** (2.044(6) Å) is much shorter than in this other *O*-bridged dimer (2.161 and 2.790 Å).³¹ Compared to Skelton's quinaldinate compound, we attribute the mononuclear structure of **10** to the presence of the CF₃

moieties, resulting in a poorly π -donating O_{alkoxide} . The prominent solid-state structural features of these zinc, cadmium and mercury complexes are collated in Table 1.

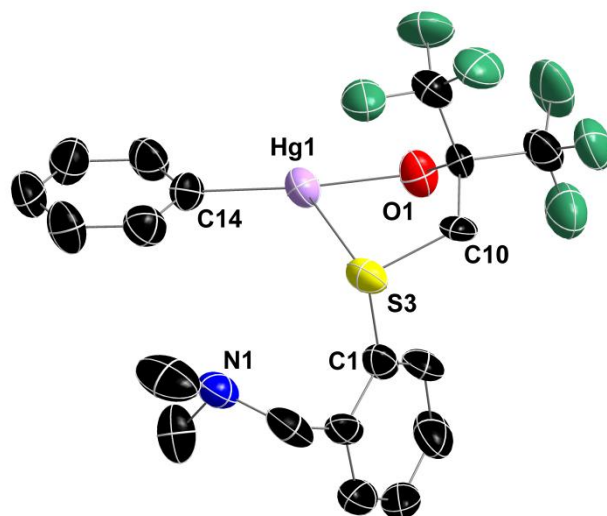


Figure 6. ORTEP rendering of the molecular solid-state structure of $[\{L^{S,(CF_3)_2}\}HgPh]$ (**10**). Ellipsoids at the 50% probability level. Only one of two independent molecules represented. H atoms omitted for clarity. Selected bond lengths (\AA) and angles ($^\circ$): C14–Hg1 = 2.039(9), Hg1–O1 = 2.044(6), Hg1–S3 = 3.008(3); C14–Hg1–O1 = 173.3(3), C14–Hg1–S3 = 114.4(3), O1–Hg1–S3 = 72.18(17).

Table 1. Summary of crystallographic data and selected metric parameters for **[1]₂-4, [6]₂, 7, 9 and 10**

Complex	Geometry	C.N. ^a	$d_{\text{met-O}}^b$	$d_{\text{met-E}}^b$	$d_{\text{met-Namide}}^b$	$d_{\text{met-Namine}}^b$
				E = S, Se		
$[\{\text{L}^{\text{S, (CH}_3\text{)}_2}\}\text{CdN}(\text{SiMe}_3)_2]_2(\mathbf{1})_2$	distorted tetrahedral	4	2.1903(16) 2.1975(17)	2.7390(6)	2.099(2)	
$[\{\text{L}^{\text{Se, (CH}_3\text{)}_2}\}\text{CdN}(\text{SiMe}_3)_2]_2(\mathbf{2})_2$	distorted tetrahedral	4	2.187(2) 2.209(2)	2.8086(4)	2.108(3)	
$[\{\text{L}^{\text{S, (CF}_3\text{)}_2}\}\text{CdN}(\text{SiMe}_3)_2](\mathbf{3})$	distorted tetrahedral	4	2.1504(13)	2.6563(5)	2.0849(15)	2.3384(15)
$[\{\text{L}^{\text{Se, (CF}_3\text{)}_2}\}\text{CdN}(\text{SiMe}_3)_2](\mathbf{4})$	distorted tetrahedral	4	2.145(2)	2.7348(4)	2.085(3)	2.341(3)
$[\{\text{L}^{\text{Se, (CH}_3\text{)}_2}\}\text{ZnN}(\text{SiMe}_3)_2]_2(\mathbf{6})_2$	distorted tetrahedral	4	1.9881(18) 2.0027(17)	2.6868(4)	1.910(2)	
$[\{\text{L}^{\text{Se, (CF}_3\text{)}_2}\}\text{ZnN}(\text{SiMe}_3)_2](\mathbf{7})$	distorted tetrahedral	4	1.9339(1)	2.5742(2)	1.9016(12)	2.1203(12)
$[\{\text{L}^{\text{S, (CF}_3\text{)}_2}\}_2\text{Hg}](\mathbf{9})$	distorted trigonal bipyramidal	5	2.1135(17) 2.1322(18)	2.7718(6) 2.8753(7)		2.479(2)
$[\{\text{L}^{\text{S, (CF}_3\text{)}_2}\}\text{HgPh}](\mathbf{10})$	T-shape	3	2.044(6)	3.008(3)		

^a Coordination number. ^b Distances in angstrom.

Solution behaviour

The multinuclear NMR data of the investigated compounds correspond to the solid-state structures.

At room temperature, a significant difference was observed in the solution behaviour of the $L^{E,(CH_3)_2}$ complexes **1**, **2**, **6**, and, respectively, the $L^{E,(CF_3)_2}$ congeners **3**, **4** and **7**. With the former set of complexes, the resonances in the aliphatic region (four sharp singlets) are consistent with species containing equivalent CH_2 hydrogens and CH_3 groups, both in the CH_2NMe_2 and the $ECH_2C(O)Me_2$ fragments. On the other hand, for **3**, **4** and **7**, AB spin systems are observed in the 1H NMR spectrum for the non-equivalent protons in each CHH group and two broad CH_3 resonances for the $N(CH_3)_2$ methyl groups; accordingly, the ^{19}F NMR spectra contain two resonances of equal intensities in each case for the two CF_3 groups in the $ECH_2C(O)(CF_3)_2$ fragments. In addition, somewhat broad resonances were diagnostic of fluxional phenomena. In order to further investigate the dynamic behaviour of **4**, VT NMR experiments and line-shape analysis were conducted for this compound. At 253 K, all resonances in the aliphatic region of the 1H NMR spectrum were sharp and well resolved and, as expected, the ^{19}F resonances appear as two quartets of equal intensity at $\delta_{^{19}F} = -76.60$ and -77.85 ppm ($^4J_{FF} = 8.5$ Hz). Free activation energies (ΔG^\ddagger) of 81.5 kJ mol $^{-1}$ (at 343 K) and 78.3 kJ mol $^{-1}$ (at 323 K) were determined for the dynamic processes experienced by the CF_3 and the $N(CH_3)_2$ groups, respectively. Besides, ΔG^\ddagger values of 65.8 and 80.1 kJ mol $^{-1}$ were also evaluated at 333 K for the fluxional phenomena for the $CHHSe$ and $CHHN$ hydrogen atoms. These observations suggest that in solution, $\{L^{Se,(CF_3)_2}\}^-$ behaves as a hemilabile *N,Se,O*-tridentate ligand in **4**, with reversible coordination-dissociation of the NMe_2 side-arm; a similar conclusion most likely also applies to **3** and **7**.

The room temperature NMR spectra for the homoleptic mercury complex **9** feature only one set of characteristic resonances. This observation suggests that the two $\{\text{L}^{\text{S},(\text{CF}_3)_2}\}^-$ ligands are equivalent in solution on the NMR timescale. It contrasts with the solid state structure, where one ligand acts as κ^2 -*O,S*-bidentate and the other as κ^3 -*N,O,S*-tridentate towards mercury, and reflects fast fluxionality of the ligands (*N* moieties) in solution at room temperature.

^1H DOSY studies were performed for complex **[2]₂** to ascertain its nuclearity in solution. The diffusion-molecular weight analysis gave an estimated molecular weight of 1173 $\text{g}\cdot\text{mol}^{-1}$, close to the value of 1116.1 $\text{g}\cdot\text{mol}^{-1}$ expected for a dinuclear compound.³² The hydrodynamic radii of the complex evaluated by PGSE NMR spectroscopy ($r_{\text{PGSE}} = 5.49 \text{ \AA}$) and from the crystallographic data ($r_{\text{XRD}} = 6.34 \text{ \AA}$) also match reasonably well. Both sets of data suggest a dimeric structure for **[2]₂** in solution in benzene-*d*₆. It is assumed that the scenario is similar for the other complexes **[1]₂** and **[6]₂**.

A summary of ^{77}Se , ^{113}Cd and ^{199}Hg NMR data for **1-10** is collected in Table 2. They were recorded in benzene-*d*₆, except for complexes **5** and **8**, which showed insufficient solubility in this solvent and for which THF-*d*₈ was used instead. Since the use of THF-*d*₈ can greatly impact multinuclear NMR chemical shifts,³³ the values should only be compared with caution to the values for the other compounds. Note that the utilisation of sulphur- or selenium-containing ligands bears little influence on the chemical shifts of the resulting cadmium or mercury complexes, compare for instance the near-identical ^{113}Cd chemical shifts of complexes **[1]₂** (−344 ppm) and **[2]₂** (−336 ppm), or the equally matching ^{199}Hg chemical shifts of **10** (−1238 ppm) and **11** (−1217 ppm). On the other hand, the ^{77}Se NMR chemical shifts for the cadmium complexes **[1]₂** (+127 ppm) and especially **4** (+105 ppm) are shifted significantly upfield with respect to the corresponding proteo-ligands (+193 for $\{\text{L}^{\text{Se},(\text{CH}_3)_2}\}\text{H}$ and +200 ppm for $\{\text{L}^{\text{Se},(\text{CF}_3)_2}\}\text{H}$,

respectively). This observation reflects the coordination of selenium onto cadmium in these two complexes. However, the variation of ^{77}Se NMR chemical shifts are more erratic in the case of the zinc and mercury complexes. This may tentatively be related to the different coordination environments in these complexes.³⁴ The geometry in the mercury compound **11** is unfortunately not known. One may however hypothesise that the more highfield ^{77}Se chemical shift for **7** (+124 ppm) may reflect its mononuclear nature and short Zn–Se distance (2.5742(2) Å), whereas the resonances are more deshielded in the dinuclear complex [**6**]₂ with its longer Zn–Se bond length (2.6868(4) Å) and in **8** (probably also dimeric in the solid state) bearing the $\{\text{L}^{\text{Se},(\text{CH}_3)_2}\}^-$ ligand.

Table 2. Summary of solution ^{77}Se , ^{113}Cd and ^{199}Hg multinuclear NMR data for **1-10**.

Complex	Solvent	^{77}Se NMR ^a	^{113}Cd NMR ^a	^{199}Hg NMR ^a
$\{\text{L}^{\text{Se},(\text{CH}_3)_2}\}\text{H}$	benzene- <i>d</i> ₆	+193	n/a	n/a
$\{\text{L}^{\text{Se},(\text{CF}_3)_2}\}\text{H}$	benzene- <i>d</i> ₆	+200	n/a	n/a
$[\{\text{L}^{\text{S},(\text{CH}_3)_2}\}\text{CdN}(\text{SiMe}_3)_2]_2([\mathbf{1}]_2)$	benzene- <i>d</i> ₆	n/a	–344	n/a
$[\{\text{L}^{\text{Se},(\text{CH}_3)_2}\}\text{CdN}(\text{SiMe}_3)_2]_2([\mathbf{2}]_2)$	benzene- <i>d</i> ₆	+127	–336	n/a
$[\{\text{L}^{\text{S},(\text{CF}_3)_2}\}\text{CdN}(\text{SiMe}_3)_2](\mathbf{3})$	benzene- <i>d</i> ₆	n/a	not observed	n/a
$[\{\text{L}^{\text{Se},(\text{CF}_3)_2}\}\text{CdN}(\text{SiMe}_3)_2](\mathbf{4})$	benzene- <i>d</i> ₆	+105	–275	n/a
$[\{\text{L}^{\text{Se},(\text{CH}_3)_2}\}\text{CdI}](\mathbf{5})$	THF- <i>d</i> ₈	+158	–462	n/a
$[\{\text{L}^{\text{Se},(\text{CH}_3)_2}\}\text{ZnN}(\text{SiMe}_3)_2]_2([\mathbf{6}]_2)$	benzene- <i>d</i> ₆	+236	n/a	n/a
$[\{\text{L}^{\text{Se},(\text{CF}_3)_2}\}\text{ZnN}(\text{SiMe}_3)_2](\mathbf{7})$	benzene- <i>d</i> ₆	+124	n/a	n/a
$[\{\text{L}^{\text{Se},(\text{CH}_3)_2}\}\text{ZnCl}](\mathbf{8})$	THF- <i>d</i> ₈	+199	n/a	n/a
$[\{\text{L}^{\text{S},(\text{CF}_3)_2}\}]_2\text{Hg}(\mathbf{9})$	benzene- <i>d</i> ₆	n/a	n/a	–2003

$[\{L^{S,(CF_3)_2}\}HgPh](\mathbf{10})$	benzene- d_6	n/a	n/a	-1238
$[\{L^{Se,(CF_3)_2}\}HgPh](\mathbf{11})$	benzene- d_6	+184	n/a	-1217

^a Chemical shifts given in ppm.

Conclusion

The chalcogen-containing heteroleptic zinc(II) and cadmium(II) complexes $[\{L^{E,R^2}\}MN(SiMe_3)_2]$ (E = S, Se) are obtained by equimolar treatment of $[M(N(SiMe_3)_2)_2]$ with the alcohol proteo-ligands $\{L^{E,R^2}\}H$. The coordination behaviour of the alkoxides $\{L^{E,R^2}\}^-$ is dictated by the substitution pattern. In the dinuclear $[\{L^{E,(CH_3)_2}\}MN(SiMe_3)_2]_2$, the metal centres (M = Zn, Cd) lie in a distorted tetrahedral environment and the ligand acts as a bidentate, κ^2 -O,Se-bridging moiety; these structural features are maintained in solution. By contrast, the electron-withdrawing CF_3 groups in α position to the alkoxide in $[\{L^{E,(CF_3)_2}\}MN(SiMe_3)_2]$ induces a κ^3 -O,Se,N-tridentate binding mode, resulting in mononuclear structures in the solid state and in solution.

The same proteo-ligands behave differently towards mercuric precursors. In particular, the reaction of $[Hg(N(SiMe_3)_2)_2]$ with one equivalent of $\{L^{S,(CF_3)_2}\}H$ resulted in the homoleptic $[\{L^{S,(CF_3)_2}\}_2Hg]$ (**9**); the corresponding heteroleptic $[\{L^{S,(CF_3)_2}\}HgN(SiMe_3)_2]$ could not be synthesised. However, the alkoxides act as κ^2 -O,S-bidentate moieties in the mononuclear, tricoordinated heteroleptic complexes $[\{L^{E,(CF_3)_2}\}HgPh]$ **10** (E = S) and **11** (E = Se). Their syntheses were accomplished from $[PhHgN(SiMe_3)_2]$, and they testify to the robustness of the Hg–C bond (C_6H_6 , $pK_a(H_2O) = 43$; $HN(SiMe_3)_2$, $pK_a(THF) = 25.8$). One should in particular note that **9–11** constitute unprecedented examples of structurally authenticated mercury alkoxides.³⁵ The related mercury complexes $[\{L^{E,(CH_3)_2}\}HgPh]$ (E = S, **12**; Se, **13**. See the ESI for detail) were also prepared, but we failed so far to obtain X-ray quality crystals; besides, they are

only soluble in THF-*d*₈, and therefore we could not use their ⁷⁷Se ($\delta_{77\text{Se}} = +202$ ppm for **13**) and ¹⁹⁹Hg ($\delta_{199\text{Hg}} = -801$ and -798 ppm for **12** and **13**, respectively) NMR data for comparison.

For a given R group (CH₃ or CF₃), there is essentially no difference in the coordination patterns of the $\{\text{L}^{\text{S,R}2}\}^-$ and $\{\text{L}^{\text{Se,R}2}\}^-$ ligands containing sulphur and selenium atoms, respectively. Whether with zinc or cadmium, the $[\{\text{L}^{\text{E,CF}_3}_2\}\text{MN}(\text{SiMe}_3)_2]$ and $[\{\text{L}^{\text{E,CH}_3}_2\}\text{MN}(\text{SiMe}_3)_2]_2$ complexes display very similar structural features for E = S or Se. On the other hand, for a given ligand, the coordination differs largely between divalent metals of groups 12 and 14 from the same row of the Periodic Table. For instance, whereas $[\{\text{L}^{\text{Se,CH}_3}_2\}\text{CdN}(\text{SiMe}_3)_2]_2$ (**[2]**) adopts a distorted tetrahedral geometry as a result of the coordination of the selenium atom onto the metal centre (*vide supra*), it was shown that in the corresponding tetrelene $[\{\text{L}^{\text{Se,CH}_3}_2\}\text{SnN}(\text{SiMe}_3)_2]_2$ (and in the pertaining $[\{\text{L}^{\text{Se,CH}_3}_2\}\text{PbN}(\text{SiMe}_3)_2]_2$) the metal is only three-coordinated and rests in a trigonal pyramidal geometry.¹⁶ Similar observations were made for the sulphur-containing ligands, and this is seen as an evidence of the greater Lewis acidity of group 12 metals. Our current investigations are now aiming at utilising these *O,Se,N*-monoanionic alkoxides for the synthesis of complexes of the alkaline earths.

Experimental Section

General procedures. All manipulations were performed under inert atmosphere using standard Schlenk techniques or in a dry, solvent-free glove-box (Jacomex; O₂ < 1 ppm, H₂O < 5 ppm). ZnCl₂ (Acros, 98%), CdI₂ (Strem) and HgBr₂ (Strem) were used as received. HN(SiMe₃)₂ (Acros) was dried over activated molecular sieves and distilled prior to use. The compounds $[\text{M}[\text{N}(\text{SiMe}_3)_2]_2]$, (M = Zn, ³⁶Cd, ³⁷Hg³⁷), $[\text{PhHgN}(\text{SiMe}_3)_2]^{38}$ and $\{\text{L}^{\text{E,R}2}\}\text{H}$ (E = S, Se; R = Me, CF₃)¹⁵ were prepared following literature procedures. All bis(amido) precursors were obtained in

very good yields after purification by distillation (zinc) or trap-to-trap transfer (cadmium and mercury). Solvents (THF, Et₂O, CH₂Cl₂, 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 Analyser instrument at the London Metropolitan University by Stephen Boyer and were the average of a minimum of two independent measurements.³⁹

NMR spectra were recorded on Bruker AM-400 and AM-500 spectrometers. All ¹H and ¹³C{¹H} chemical shifts were assigned according to the numbering shown in Scheme 5 using residual signals of the deuterated solvents and were calibrated *vs.* Me₄Si. Assignment of the signals was carried out using 1D (¹H, ¹³C{¹H}) and 2D (COSY, HMBC, HMQC) NMR experiments. ¹⁹F chemical shifts were determined by external reference to an aqueous solution of NaBF₄. ¹⁹⁹Hg, ²⁹Si{¹H} and ⁷⁷Se{¹H} NMR spectra were externally calibrated *vs.* Me₂Hg, Me₄Si and Ph₂Se₂ (δ_{77Se} = +461ppm).⁴⁰

Scheme 5.

X-ray diffraction crystallography. Crystals of **1-4, 6, 7, 9** and **10** suitable for X-ray diffraction analysis were obtained by recrystallisation of the purified products. Diffraction data were collected at 150 K using a Bruker APEX CCD diffractometer with graphite-monochromated MoK α radiation ($\lambda = 0.71073 \text{ \AA}$). 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).⁴¹ 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 (CCDC1518552-1518559) can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[ICdN(SiMe₃)₂]. [Cd[N(SiMe₃)₂]₂ (0.48 g, 1.1 mmol) was added to a solution of CdI₂ (0.40 g, 1.1 mmol) in Et₂O (40 mL) and the mixture was stirred for 4 h at room temperature. Removal of the volatiles under vacuum afforded a solid which was washed with pentane to give the title compound as an analytically pure colourless powder. Yield 0.74 g (84%). ¹H NMR (THF-*d*₈, 500.1 MHz, 298 K): $\delta = 0.19$ (s, 18H, SiCH₃) ppm. ¹³C{¹H} NMR (THF-*d*₈, 125.8 MHz, 298 K): $\delta = 5.44$ (SiCH₃) ppm. Anal. Calcd for C₆H₁₈CdINSi₂C₆H₁₈CdINSi₂ (399.7 g mol⁻¹): C 18, H 4.5, N 3.5%) could not be obtained.³⁹

[ClZnN(SiMe₃)₂]. A solution of [Zn(N(SiMe₃)₂)₂] (1.93 g, 5.0 mmol) in Et₂O (25 mL) was added dropwise to a suspension of ZnCl₂ (0.70 g, 5.0 mmol) in Et₂O (50 mL). The reaction mixture was stirred overnight at room temperature, and the solvent was removed under vacuum. The resulting solid was washed with *n*-hexane (3×5 mL, hence reducing the isolated yield) to give the title compound as a colourless powder (0.65 g, 50%). ¹H NMR (THF-*d*₈, 400.1 MHz, 298 K): δ = 0.04 (s, 18H, SiCH₃) ppm. ¹³C{¹H} NMR (THF-*d*₈, 100.6 MHz, 298 K): δ = 2.77 (SiCH₃) ppm. Anal. Calcd. for C₆H₁₈ClNSi₂Zn (261.22 g mol⁻¹; C 27.6, H 7.0, N 5.4%): satisfactory data could not be obtained.³⁹

[[L^{S,(CH₃)₂}]CdN(SiMe₃)₂] (1)}. A solution of {L^{S,(CH₃)₂}H (0.25 g, 1.05 mmol) in Et₂O (15 ml) was added dropwise at -78 °C to a solution of [Cd(N(SiMe₃)₂)₂] (0.46 g, 1.05 mmol) in Et₂O (10 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 yellow oil which was purified by stripping with pentane (3×2 mL). Recrystallisation from pentane at -30 °C afforded colourless crystals of the title compound as the dimeric [1]₂. Yield 0.32 g (59%). ¹H NMR (benzene-*d*₆, 500.1 MHz, 298 K): δ = 8.35 (dd, ⁴J_{HH} = 1.1 Hz, ³J_{HH} = 7.8 Hz, 1H, arom-*H*₆), 7.29 (dd, ⁴J_{HH} = 1.3 Hz, ³J_{HH} = 7.7 Hz, 1H, arom-*H*₃), 7.18 (dt, ⁴J_{HH} = 1.6 Hz, ³J_{HH} = 7.6 Hz, 1H, arom-*H*₅), 7.07 (dt, ⁴J_{HH} = 1.1 Hz, ³J_{HH} = 7.5 Hz, 1H, arom-*H*₅), 3.53 (s, 2H, ArCH₂N), 3.16 (s, 2H, SCH₂), 2.11 (s, 6H, N(CH₃)₂), 1.45 (s, 6H, C(CH₃)₂O), 0.37 (s, 18H, SiCH₃) ppm. ¹³C{¹H} NMR (benzene-*d*₆, 125.8 MHz, 298 K): δ = 143.5 (arom-*C*₂), 136.38 (arom-*C*₆), 132.98 (arom-*C*₁), 131.14 (arom-*C*₃), 129.37 (arom-*C*₄), 128.51 (arom-*C*₅), 71.01 (C(CH₃)₂O), 62.50 (ArCH₂N), 56.37 (SCH₂), 45.25 (N(CH₃)₂), 33.36 (C(CH₃)₂O), 6.46 (SiCH₃) ppm. ²⁹Si{¹H} NMR (benzene-*d*₆, 79.5 MHz, 298 K): δ = -3.16 ppm. ¹¹³Cd{¹H} NMR (benzene-*d*₆, 84.9 MHz, 298 K): δ = -344.9 ppm. Anal.}

Calcd for $C_{19}H_{38}CdN_2OSSi_2$ ($511.17 \text{ g mol}^{-1}$; C 44.6, H 7.5, N 5.5 %):satisfactory data could not be obtained.³⁹

[{L^{Se,(CH₃)₂}}CdN(SiMe₃)₂] (2). Following the same protocol as that detailed for **1**, the reaction of {L^{Se,(CH₃)₂}}H (0.34 g, 1.17 mmol) and Cd(N(SiMe₃)₂)₂ (0.51 g, 1.17 mmol) afforded colourless crystals of the title compound as the dimeric [2]₂. Yield 0.50 g (77%). ¹H NMR (benzene-*d*₆, 500.1 MHz, 298 K): $\delta = 8.44$ (dd, ⁴*J*_{HH}= 1.0 Hz, ³*J*_{HH}= 7.7 Hz, 1H, arom-*H*₆), 7.13-7.17 (overlapping m, 2H, arom-*H*₃ + arom-*H*₄), 7.03 (dt, ⁴*J*_{HH}= 1.0 Hz, ³*J*_{HH}= 7.4 Hz, 1H, arom-*H*₅), 3.40 (s, 2H, ArCH₂N), 3.22 (s, 2H, SeCH₂), 2.07 (s, 6H, NCH₃), 1.46 (s, 6H, C(CH₃)₂O), 0.42 (s, 18H, SiCH₃) ppm. ¹³C{¹H} NMR (benzene-*d*₆, 125.7 MHz, 298 K): $\delta = 143.37$ (arom-*C*₂), 136.85 (arom-*C*₆), 130.52 (arom-*C*₄), 130.14 (arom-*C*₁), 128.60 (arom-*C*₃), 128.36 (arom-*C*₅), 70.58 (C(CH₃)₂O), 64.63 (ArCH₂N), 52.86 (SeCH₂), 44.92 (NCH₃), 33.75 (C(CH₃)₂O), 6.68 (¹*J*_{CSi}= 52.2 Hz, SiCH₃) ppm. ²⁹Si{¹H} NMR (benzene-*d*₆, 79.4 MHz, 298 K): $\delta = -3.35$ ppm. ¹¹³Cd{¹H}NMR (benzene-*d*₆, 84.8 MHz, 298 K): $\delta = -336.7$ ppm. ⁷⁷Se{¹H} NMR (benzene-*d*₆, 76.3 MHz, 298 K): $\delta = +127.3$ ppm (¹*J*_{SeCd}= 42.9 Hz). Anal. Calcd for $C_{19}H_{38}CdN_2OSeSi_2$ ($558.07 \text{ g mol}^{-1}$; C 40.9, H 6.9, N 5.0%):satisfactory data could not be obtained.³⁹

[{L^{S,(CF₃)₂}}CdN(SiMe₃)₂] (3). Following the same protocol as that detailed for **1**, the reaction of {L^{S,(CF₃)₂}}H (0.26 g, 0.70 mmol) with [Cd(N(SiMe₃)₂)₂] (0.32 g, 0.70 mmol) afforded colourless crystals of the title compound. Yield 0.32 g (69%). ¹H NMR (benzene-*d*₆, 500.1 MHz, 298 K): $\delta = 7.26$ (d, ³*J*_{HH}= 7.9 Hz, 1H, arom-*H*₆), 6.84 (dt, ⁴*J*_{HH}= 1.4, ³*J*_{HH}= 7.4 Hz, 1H, arom-*H*₅), 6.74 (dt, ⁴*J*_{HH}= 1.5 Hz, ³*J*_{HH}= 7.5 Hz, 1H, arom-*H*₄), 6.49 (dd, ⁴*J*_{HH}= 1.6 Hz, ³*J*_{HH}= 7.4 Hz, 1H, arom-*H*₃), 4.29 (br m, 1H, SCH₂), 3.50 (d, ²*J*_{HH}= 13.2 Hz, 1H, ArCHHN), 2.54 (d, ²*J*_{HH}= 13.2 Hz, 1H, ArCHHN), 2.19 (overlapping m, 4H, SCH₂ + NCH₃), 1.58 (s, 3H, NCH₃), 0.26 (s, 18H, SiCH₃)

ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (benzene- d_6 , 125.8 MHz, 298 K): $\delta = 137.99$ (arom- C_6), 137.44 (arom- C_2), 135.74 (arom- C_3), 130.71 (arom- C_5), 129.59 (arom- C_4), 128.33 (arom- C_1), 78.85 ($C(\text{CF}_3)_2\text{O}$), 61.7 (SCH_2), 47.81, 44.37 (NCH_3), 41.73 (ArCH_2N), 5.97 ($^1J_{\text{CSi}} = 53.8$ Hz, SiCH_3) ppm; the resonance for CF_3 was not observed. $^{29}\text{Si}\{^1\text{H}\}$ NMR (benzene- d_6 , 79.5 MHz, 298 K): $\delta = -2.90$ ($^2J_{\text{Cd-Si}} = 20.4$ Hz) ppm. $^{113}\text{Cd}\{^1\text{H}\}$ NMR (benzene- d_6 , 84.9 MHz, 298 K): $\delta = -171$ ppm. ^{19}F NMR (benzene- d_6 , 376 MHz, 298 K): $\delta = -76.4$ (br unresolved q, 3F, CF_3) and -77.9 (br unresolved q, 3F, CF_3) ppm, br.; Anal. Calcd for $\text{C}_{19}\text{H}_{32}\text{CdF}_6\text{N}_2\text{OSSi}_2$ (619.11 g mol $^{-1}$; C 36.9, H 5.2, N 4.5%): satisfactory data could not be obtained.³⁹

[$\{\text{L}^{\text{Se}(\text{CF}_3)_2}\}\text{CdN}(\text{SiMe}_3)_2$] (4). Following the same protocol as that given for **1**, the reaction of $\{\text{L}^{\text{Se}(\text{CF}_3)_2}\}\text{H}$ (0.31 g, 0.78 mmol) with $[\text{CdN}(\text{SiMe}_3)_2]_2$ (0.34 g, 0.78 mmol) afforded a colourless solid. Yield 0.43 g (82%). ^1H NMR (benzene- d_6 , 500.1 MHz, 298 K): $\delta = 7.25$ (d, $^3J_{\text{HH}} = 8.0$ Hz, 1H, arom- H_6), 6.83 (dt, $^4J_{\text{HH}} = 1.4$, $^3J_{\text{HH}} = 7.4$ Hz, 1H, arom- H_5), 6.72 (dt, $^4J_{\text{HH}} = 1.6$ Hz, $^3J_{\text{HH}} = 7.6$ Hz, 1H, arom- H_4), 6.47 (dd, $^4J_{\text{HH}} = 1.3$ Hz, $^3J_{\text{HH}} = 7.8$ Hz, 1H, arom- H_3), 4.21 (br s, 1H, SeCHH), 3.52 (d, $^2J_{\text{HH}} = 13.0$ Hz, 1H, ArCHHN), 2.65 (d, $^2J_{\text{HH}} = 13.0$ Hz, 1H, ArCHHN), 2.21 (overlapping m, 4H, $\text{SeCHH} + \text{NCH}_3$), 1.61 (s, 3H, NCH_3), 0.25 (s, 18H, SiCH_3) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (benzene- d_6 , 125.8 MHz, 298 K): $\delta = 137.99$ (arom- C_6), 137.88 (arom- C_2), 135.84 (arom- C_3), 130.42 (arom- C_5), 129.60 (arom- C_4), 128.35 (arom- C_1), 78.0 ($C(\text{CF}_3)_2\text{O}$), 62.23 (SCH_2), 47.82, 44.39 (NCH_3), 38.58 (ArCH_2N), 6.12 ($^1J_{\text{CSi}} = 53.8$ Hz, SiCH_3) ppm; the resonance for CF_3 was not detected. $^{29}\text{Si}\{^1\text{H}\}$ NMR (benzene- d_6 , 79.5 MHz, 298 K): $\delta = -3.05$ ($^2J_{\text{CdSi}} = 20.4$ Hz) ppm. $^{77}\text{Se}\{^1\text{H}\}$ NMR (benzene- d_6 , 76.3 MHz, 298 K): $\delta = +105$ ppm. $^{113}\text{Cd}\{^1\text{H}\}$ NMR (benzene- d_6 , 84.9 MHz, 298 K): $\delta = -275$ ppm. ^{19}F NMR (benzene- d_6 , 376 MHz, 298 K): $\delta = -76.7$ (br unresolved q, 3F, CF_3) and -77.8 ppm (br unresolved q, 3F, CF_3). ^{19}F NMR (toluene- d_8 , 376 MHz, 253 K): $\delta = -76.60$ (q, 3F, $^4J_{\text{FF}} = 8.5$ Hz, CF_3) and -77.85 (q, 3F, $^4J_{\text{FF}} = 8.5$ Hz, CF_3)

ppm. Anal. Calcd. for $C_{19}H_{32}CdF_6N_2OSeSi_2$ ($666.01 \text{ g mol}^{-1}$; C 34.3, H 4.8, N 4.2%): satisfactory data could not be obtained.³⁹

[{L^{Se,(CH₃)₂}}CdI] (5). A solution of $\{L^{Se,(CH_3)_2}\}H$ (0.14 g, 0.47 mmol) in THF (15 mL) was added dropwise at $-78 \text{ }^\circ\text{C}$ to a solution of $[ICdN(SiMe_3)_2]$ (0.19 g, 0.47 mmol) in THF (10 mL). The reaction mixture was stirred at this temperature for 3 h and it was allowed to warm slowly to room temperature. The volatiles were then removed under reduced pressure and **5** was obtained as a solid after purification by stripping with pentane ($3 \times 2 \text{ mL}$). Yield 0.17 g (68%). 1H NMR (THF-*d*₈, 500.1 MHz, 298 K): $\delta = 7.56$ (d, $^3J_{HH} = 8.3 \text{ Hz}$, 1H, arom-*H*₆), 7.22-7.27 (m, 3H, arom-*H*₃ + arom-*H*₄ + arom-*H*₅), 3.67 (s, 2H, ArCH₂N), 3.32 (s, 2H, SeCH₂), 2.34 (s, 6H, NCH₃), 1.35 (s, 6H, C(CH₃)₂O) ppm. $^{13}C\{^1H\}$ NMR (THF-*d*₈, 125.7 MHz, 298 K): $\delta = 138.19$ (arom-*C*₆), 137.46 (arom-*C*₂), 133.25 (arom-*C*₄), 132.79 (arom-*C*₁), 129.99 (arom-*C*₃), 127.82 (arom-*C*₅), 70.29 (ArCH₂N), 65.28 (SeCH₂), 47.74 (NCH₃), 30.41 (C(CH₃)₂O) ppm. $^{113}Cd\{^1H\}$ NMR (THF-*d*₈, 84.9 MHz, 298 K): $\delta = -463$ ppm. $^{77}Se\{^1H\}$ NMR (THF-*d*₈, 76.3 MHz, 298 K): $\delta = +158$ ppm. Anal. Calcd for $C_{13}H_{20}CdINOSe$ ($524.58 \text{ g mol}^{-1}$; C 29.8, H 3.8, N 2.7%): satisfactory data could not be obtained.³⁹

[{L^{Se,(CH₃)₂}}ZnN(SiMe₃)₂] (6). Following the same protocol as that detailed for **1**, the reaction of $\{L^{Se,(CH_3)_2}\}H$ (0.29 g, 1.01 mmol) with $Zn[N(SiMe_3)_2]_2$ (0.39 g, 1.01 mmol) afforded colourless crystals of the title compound as the dimeric $[6]_2$. Yield 0.27 g (52%). 1H NMR (benzene-*d*₆, 500.1 MHz, 298 K): $\delta = 7.89$ (d, 1H, $^3J_{HH} = 8.7 \text{ Hz}$, arom-*H*₆), 7.16 (m, 1H, arom-*H*₃), 7.09 (t, 1H, $^3J_{HH} = 7.7 \text{ Hz}$, arom-*H*₄), 7.02 (t, 1H, $^3J_{HH} = 7.3 \text{ Hz}$, arom-*H*₅), 3.45 (s, 2H, ArCH₂N), 3.20 (s, 2H, SeCH₂), 2.10 (s, 6H, N(CH₃)₂), 1.53 (s, 6H, C(CH₃)₂O), 0.36 (s, 18H, SiCH₃) ppm. $^{13}C\{^1H\}$ NMR (benzene-*d*₆, 125.8 MHz, 298 K): $\delta = 141.98$ (arom-*C*₂), 133.99 (arom-*C*₆), 132.93 (arom-

C_1), 130.41 (arom- C_3), 128.35 (arom- C_4), 127.49 (arom- C_5), 73.95 ($C(CH_3)_2O$), 64.76 ($ArCH_2N$), 47.94 (SCH_2), 44.92 ($N(CH_3)_2$), 32.24 ($C(CH_3)_2O$), 6.03 ($SiCH_3$) ppm. $^{29}Si\{^1H\}$ NMR (benzene- d_6 , 79.5 MHz, 298 K): $\delta = -2.83$ ppm. $^{77}Se\{^1H\}$ NMR (benzene- d_6 , 84.9 MHz, 298 K): $\delta = 236$ ppm. Anal. Calcd for $C_{19}H_{38}N_2OZnSeSi_2$ (511.03 g mol $^{-1}$; C 44.7, H 7.5, N 5.49%): satisfactory data could not be obtained.³⁹

[{L^{Se,(CF₃)₂}}ZnN(SiMe₃)₂] (7). Following the same protocol as that given for **1**, the reaction of $\{L^{Se,(CF_3)_2}\}H$ (0.29 g, 0.73 mmol) with $[Zn(N(SiMe_3)_2)_2]$ (0.28 g, 0.73 mmol) afforded colourless crystals of the title compound. Yield 0.27 g (46%). 1H NMR (benzene- d_6 , 500.1 MHz, 298 K): $\delta = 7.26$ (br m, 1H, arom- H_6), 6.86 (t, $^3J_{HH} = 7.60$ Hz, 1H, arom- H_5), 6.75 (t, $^3J_{HH} = 7.7$ Hz, 1H, arom- H_4), 6.49 (d, $^3J_{HH} = 7.4$ Hz, 1H, arom- H_3), 4.11 (br m, 1H, SeCHH), 3.46 (d, $^2J_{HH} = 13.5$ Hz, 2H, $ArCH_2N$), 2.56 (br m, 1H SeCHH), 2.22 (s, 3H, NCH_3), 1.63 (s, 3H, NCH_3), 0.44 (br, 18H, $SiCH_3$) ppm. $^{13}C\{^1H\}$ NMR (benzene- d_6 , 125.8 MHz, 298 K): $\delta = 137.79$ (arom- C_6), 137.79 (arom- C_2), 135.23 (arom- C_3), 130.75 (arom- C_5), 129.77 (arom- C_4), 128.33 (arom- C_1), 78.72 ($C(CF_3)_2O$), 62.46 (SeCH₂), 47.61, 43.92 (NCH_3), 38.80 ($ArCH_2N$), 6.01 (br, $SiCH_3$) ppm. $^{29}Si\{^1H\}$ NMR (benzene- d_6 , 79.5 MHz, 298 K): $\delta = -2.48$ ppm. $^{77}Se\{^1H\}$ NMR (benzene- d_6 , 76.3 MHz, 298 K): +124 ppm. ^{19}F NMR (benzene- d_6 , 376 MHz, 298 K): $\delta = -76.8$ (br unresolved q, 3F, CF_3) and -77.6 (br unresolved q, 3F, CF_3) ppm; Anal. Calcd for $C_{19}H_{38}N_2OZnSeSi_2$ (618.97 g mol $^{-1}$): C 36.9, H 5.2, N 4.5. Found: C 36.6, H 5.3, N 4.4 %.

[{L^{Se,(CH₃)₂}}ZnCl] (8). $[ClZnN(SiMe_3)_2]$ (0.23 g, 0.87 mmol) was dissolved in dry THF (10 mL), and a solution of $\{L^{Se,(CH_3)_2}\}H$ (0.25 g, 0.87 mmol) in dry THF (15 mL) was added dropwise at -78 °C. The reaction mixture was stirred for 3 h at this temperature, and then the solvent was removed under vacuum to give a colourless solid. Compound **8** was purified by washing with dry

n-hexane (3×5 mL) and isolated as a colourless powder (0.18 g, 52%). ¹H NMR (THF-*d*₈, 400.1 MHz, 298 K): δ = 7.68 (br, 1H, arom-*H*₆), 7.39 (br, 1H, arom-*H*₃), 7.23 (overlapping m, 2H, arom-*H*₄+ arom-*H*₅), 3.96 (s, 2H, ArCH₂N), 3.08 (s, 2H, SeCH₂), 2.46 (br s, 6H, NCH₃), 1.27 (s, 6H, C(CH₃)₂O) ppm. ¹³C{¹H} NMR (THF-*d*₈, 100.6 MHz, 298 K): δ = 136.95 (arom-*C*₁), 136.45 (arom-*C*₂), 135.89 (arom-*C*₆), 132.83 (arom-*C*₃), 130.66 (arom-*C*₄), 128.47 (arom-*C*₅), 71.20 (C(CH₃)₂O), 63.71 (ArCH₂N), 46.30 (SeCH₂), 44.43 (NCH₃), 29.64 (C(CH₃)₂O) ppm. ⁷⁷Se{¹H} NMR (THF-*d*₈, 76.3 MHz, 298 K): δ = +199 ppm. Anal. Calcd. for C₁₃H₂₀ClNOSeZn (386.10 g mol⁻¹; C 40.4; H 5.2; N 3.6%): satisfactory data could not be obtained.³⁹

[{L^{S,(CF₃)₂}]₂Hg] (9).} A solution of {L^{S,(CF₃)₂}H (0.26 g, 0.75 mmol) in Et₂O (15 mL) was added dropwise at -78 °C over a period of 1.5 h to a solution of [Hg(N(SiMe₃)₂)₂] (0.19 g, 0.37 mmol) in Et₂O (10 mL). The resulting yellow solution was warmed to room temperature and the solvent was removed in vacuum to give a pale yellow oil which was washed with pentane (5×3 mL) and dried in vacuum. Recrystallisation from pentane at -30 °C afforded colourless crystals of **9**. Yield 0.24 g (72%). ¹H NMR (benzene-*d*₆, 500.1 MHz, 298 K): δ = 7.43 (br., s, 2H, arom-*H*₆), 6.84 (overlapping m, 6H, arom-*H*₃ + arom-*H*₅ + arom-*H*₄), 3.36 (br s, 4H, SCH₂), 3.24 (br s, 4H, ArCH₂N), 2.06 (br s, 12H, NCH₃) ppm. ¹³C{¹H} NMR (benzene-*d*₆, 125.8 MHz, 298 K): δ = 139.54 (arom-*C*₁), 134.4 (arom-*C*₆), 133.53 (arom-*C*₂), 132.58 (arom-*C*₅), 128.92 (arom-*C*₃), 128.78 (arom-*C*₄), 62.36 (SCH₂), 45.52 (NCH₃), 38.1 (ArCH₂N) ppm. ¹⁹⁹Hg{¹H}NMR (benzene-*d*₆, 71.6 MHz, 298 K): δ = -2003 ppm. ¹⁹F NMR (benzene-*d*₆, 376.0 MHz, 298 K): δ = -76.9 (s, 12F, CF₃) ppm. Anal. Calcd for C₂₆H₂₈HgF₁₂N₂O₂S₂ (893.21 g mol⁻¹; C 35.0, H 3.2, N 3.1%): satisfactory data could not be obtained.³⁹}

$[\{\text{L}^{\text{S},(\text{CF}_3)_2}\}\text{HgPh}]$ (**10**). $[\text{PhHgN}(\text{SiMe}_3)_2]$ (0.17 g, 0.43 mmol) was dissolved in THF (10 mL), and a solution of $\{\text{L}^{\text{S},(\text{CF}_3)_2}\}\text{H}$ (0.14 g, 0.43 mmol) in THF (15 mL) was added dropwise at room temperature. The reaction mixture was stirred overnight at room temperature, and the solvent was removed under vacuum. After washing with hexane (3×5 mL), **10** was isolated as a colourless solid (0.12 g, 45%). Single crystals suitable for X-ray diffraction crystallography were obtained from a concentrated *n*-pentane solution kept overnight at room temperature. ^1H NMR (benzene- d_6 , 400.1 MHz, 298 K): $\delta = 7.47$ (br, 1H, arom- H_6), 6.92 (overlapping m, 4H, *o*- C_6H_5 + *m*- C_6H_5), 6.85 (overlapping m, 2H, arom- H_4 + arom- H_5), 6.72 (overlapping m, 2H, arom- H_3 + *p*- C_6H_5), 3.34 (s, 2H, ArCH_2N), 3.26 (s, 2H, SCH_2), 1.89 (s, 6H, NCH_3) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (benzene- d_6 , 100.6 MHz, 298 K): $\delta = 143.17$ (*i*- C_6H_5), 140.22 (arom- C_1), 137.81 (*o*- C_6H_5), 137.07 (arom- C_2), 134.22 (*p*- C_6H_5), 133.53 (arom- C_6), 131.75 (*m*- C_6H_5), 131.00 (arom- C_3), 129.18 (arom- C_4), 128.72 (arom- C_5), 127.89 (q, $^1J_{\text{CF}} = 220.3$ Hz, $\text{C}(\text{CF}_3)_2\text{O}$), 62.92 (ArCH_2N), 61.03 ($\text{C}(\text{CH}_3)_2\text{O}$), 44.72 (SCH_2), 31.69 (NCH_3) ppm. ^{19}F NMR (benzene- d_6 , 376.0 MHz, 298 K): -76.8 (s, 6F, CF_3) ppm. $^{199}\text{Hg}\{^1\text{H}\}$ NMR (benzene- d_6 , 71.6 MHz, 298 K) : $\delta = -1238$ ppm. Anal. Calcd. for $\text{C}_{19}\text{H}_{19}\text{F}_6\text{HgNOS}$ (624.01 g mol $^{-1}$): C 36.6; H 3.1; N 2.2. Found: C 36.4, H 3.5, N 2.4.

$[\{\text{L}^{\text{Se},(\text{CF}_3)_2}\}\text{HgPh}]$ (**11**). Similarly with **10**, $[\text{PhHgN}(\text{SiMe}_3)_2]$ (0.18 g, 0.41 mmol) was reacted with $\{\text{L}^{\text{Se},(\text{CF}_3)_2}\}\text{H}$ (0.16 g, 0.41 mmol) to yield **11** as a colourless powder (0.12 g, 43%). ^1H NMR (benzene- d_6 , 400.1 MHz, 298 K): $\delta = 7.63$ (d, $^3J_{\text{HH}} = 7.7$ Hz, 1H, arom- CH_6), 6.91 (overlapping m, 4H, *o*- C_6H_5 + *m*- C_6H_5), 6.86 (overlapping m, 2H, arom- H_4 + arom- H_5), 6.83 (d, $^3J_{\text{HH}} = 7.1$ Hz, 1H, arom- H_3), 6.69 (m, 1H, *p*- C_6H_5), 3.26 (s, 2H, ArCH_2N), 3.16 (s, 2H, SeCH_2), 1.84 (s, 6H, NCH_3) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (benzene- d_6 , 100.6 MHz, 298 K): $\delta = 145.53$ (*i*- C_6H_5), 141.08 (arom- C_1), 137.00 (*o*- C_6H_5), 134.73 (arom- C_2), 130.00 (*p*- C_6H_5), 129.33 (arom- C_6), 128.75 (*m*- C_6H_5), 128.65 (arom- C_3), 128.35 (arom- C_4), 128.02 (q, $^1J_{\text{CF}} = 214.3$ Hz, $\text{C}(\text{CF}_3)_2\text{O}$), 126.94 (arom-

C_5), 70.88 ($C(CH_3)_2O$), 64.96 ($ArCH_2N$), 44.26 ($SeCH_2$), 31.69 ($N(CH_3)_2$) ppm. ^{19}F NMR (benzene- d_6 , 376.0 MHz, 298 K): -76.9 (s, 6F, CF_3) ppm. $^{77}Se\{^1H\}$ NMR (benzene- d_6 , 76.3 MHz, 298 K) : $\delta = +184$ ppm. $^{199}Hg\{^1H\}$ NMR (THF- d_8 , 71.6 MHz, 298 K): $\delta = -1217$ ppm. Anal. Calcd. for $C_{19}H_{19}F_6HgNOSe$ (670.91 g mol^{-1}): C 34.0; H 2.9; N 2.1. Found: C 33.9, H 3.1, N 2.1.

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Electronic supporting information. X-ray structures of complexes **1** and **3**; Crystallographic data for all complexes available as CIF files (CCDC 1518552-1518559). NMR data; Syntheses of **12** and **13**; Diffusion-molecular weight analysis for [**2**]₂.

Notes and References

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