

# Analogy of the Coordination Chemistry of Alkaline Earth Metal and Lanthanide $\text{Ln}^{2+}$ Ions: The Isostructural Zoo of Mixed Metal Cages $[\text{IM}(\text{OtBu})_4\{\text{Li}(\text{thf})\}_4(\text{OH})]$ ( $\text{M} = \text{Ca}, \text{Sr}, \text{Ba}, \text{Eu}$ ), $[\text{MM}'_6(\text{OPh})_8(\text{thf})_6]$ ( $\text{M} = \text{Ca}, \text{Sr}, \text{Ba}, \text{Sm}, \text{Eu}, \text{M}' = \text{Li}, \text{Na}$ ), and their Derivatives with 1,2-Dimethoxyethane

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**Abstract:** As previously shown, alkali and alkaline earth metal iodides in nonaqueous, aprotic solvents behave like transition metal halides, forming *cis*- and *trans*-dihalides with various neutral O-donor ligands. These compounds can be used as precursors for the synthesis of new mixed alkali/alkaline earth metal aggregates. We show here that  $\text{Ln}^{2+}$  ions form isostructural

cluster compounds. Thus, with  $\text{LiOtBu}$ , 50% of the initial iodide can be replaced in  $\text{MI}_2$ ,  $\text{M} = \text{Ca}, \text{Sr}, \text{Ba}, \text{Eu}$ , to generate the mixed-metal alkoxide ag-

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gregates  $[\text{IM}(\text{OtBu})_4\{\text{Li}(\text{thf})\}_4(\text{OH})]$ , for which the  $\text{M}-\text{OH}$  contacts were investigated by theoretical methods. With  $\text{M}'\text{OPh}$  ( $\text{M}' = \text{Li}, \text{Na}$ ), a new mixed-metal aryloxide cluster type  $[\text{MM}'_6(\text{OPh})_8(\text{thf})_6]$  is obtained for  $\text{M} = \text{Ca}, \text{Sr}, \text{Ba}, \text{Sm}, \text{Eu}$ . Their stability versus DME (DME = 1,2-dimethoxyethane) as bidentate ligand is studied.

## Introduction

Group 2 metal oxides find applications in a wide range of man-made materials such as catalysts, ferroelectrics, metallic conductors, and superconductor materials. Alkoxides and aryloxides of Group 2 metals are known to be good low-dimensional precursors for the generation of the corresponding oxide materials through sol-gel techniques and CVD (chemical vapor deposition) processes.<sup>[1]</sup> Compounds of the type  $[\text{M}(\text{OR})_n]$  and  $[\text{M}(\text{L})_x(\text{OR})_y]$  ( $\text{R} = \text{alkyl and aryl}$ ;  $\text{L} = \text{neutral or anionic ligand}$ ;  $n = 2$ ;  $x = 1, 2, \dots$ ;  $y = 1, 2$ ) are accessible through several synthetic procedures, and the methods of preparation are often chosen as a function of the electronegativity of the metal.<sup>[1a,2]</sup> We are interested in alkali and alkaline earth metal compounds in order to study their behavior in non-aqueous solvents, their analogy to transition metals, and possible applications in oxide materi-

als, investigating cluster compounds and coordination networks. We have previously shown that Group 2 metal iodides may act as starting materials for both homo-metallic alkaline earth and mixed-metal alkali and alkaline earth metal cage compounds obtained from partial abstraction of iodide.<sup>[3]</sup> Depending of the bulk of the R group on the alkoxide or aryloxide reagent and the nature of the alkali metal and the solvent of crystallization (binding mode, Lewis basicity, and so forth), different structural features can be achieved.<sup>[3b,4]</sup>

The structures and chemical behavior of heavier alkaline earth metal complexes ( $\text{Ca}, \text{Sr}, \text{Ba}$ )<sup>[5]</sup> have been often compared to those of d- and f-block metal complexes.<sup>[6]</sup> The similarities are even stronger with divalent lanthanide metal ions and their complexes in weak polar aprotic solvents.<sup>[7]</sup> Lanthanide ions are  $d^0$  species with a limited radial expansion of their 4f shell. Thus, the f orbitals of the lanthanide ions do not contribute significantly to complex formation. As for alkaline earth metal ions, bonding between lanthanide ions and coordinating ligands depends essentially on the difference of their electronegativity resulting in strongly electrostatic metal–ligand interactions. At the same time, both groups of metal ions show very little structuring effect, and steric factors of the ligands generally guide the structure of the complexes.

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Nearly identical size/charge ratios for  $\text{Yb}^{2+}/\text{Ca}^{2+}$  and  $\text{Eu}^{2+}/\text{Sm}^{2+}/\text{Sr}^{2+}$  (for a coordination number 7:  $r_{\text{Ca}^{2+}}=1.06$ ,  $r_{\text{Yb}^{2+}}=1.02$  Å;  $r_{\text{Eu}^{2+}}=1.20$ ,  $r_{\text{Sm}^{2+}}=1.22$ ,  $r_{\text{Sr}^{2+}}=1.21$  Å)<sup>[8]</sup> prompted us to compare the chemistry of alkaline earth and lanthanide(II) alkoxide and aryloxide metal clusters in organic solvents. Our general reaction scheme is based on the treatment of a divalent metal iodide with an alkali metal (Li or Na) species in order to abstract iodide partially or totally in order to induce aggregate formation.

## Results and Discussion

**The  $[\text{IM}(\text{OtBu})_4\{\text{Li}(\text{thf})\}_4(\text{OH})]$ -type clusters:** First attempts of reactions with  $[\text{CaI}_2(\text{thf})_4]$  as a starting material and  $\text{LiOtBu}$  lead to the crystallization of the homometallic cluster of lithium  $[(\text{thf})_4\text{Li}_4(\text{OtBu})_3\text{I}]$ .<sup>[10]</sup> Although the reaction should be possible in analogy to the synthesis of alkaline earth metal alkoxydes described by Hanusa et al.,<sup>[9]</sup> the calcium compound could not be isolated and characterized at first. However, the  $^1\text{H}$  NMR spectrum of the reaction solution gave hints for two more species containing  $\text{OtBu}$  groups in some form, one of them being most likely  $t\text{BuOH}$ , the product obtained from partial hydrolysis of either the final compound  $[(\text{thf})_4\text{Li}_4(\text{OtBu})_3\text{I}]$ <sup>[10]</sup> or the initial compound  $\text{LiOtBu}$ . When the reaction is carried out under inert atmosphere ( $\text{N}_2$ ) with  $[\text{CaI}_2(\text{thf})_4]$  and a very large excess of a 1 M solution of  $\text{LiOtBu}$  in THF in the presence of  $\text{LiOH}$ , the uncharged, mixed-metal cluster compound  $[\text{Ca}(\text{OtBu})_4\{\text{Li}(\text{thf})\}_4(\text{OH})]\cdot\text{THF}$  (**1**) was isolated. Compound **1** can also be obtained by reaction of the starting material  $[\text{CaI}_2(\text{dme})_2(\text{thf})]$ <sup>[11]</sup> (DME = 1,2-dimethoxyethane) with four equivalents of a 1 M solution of  $\text{LiOtBu}$  in THF, also in presence of  $\text{LiOH}$ , the latter being introduced by partial hydrolysis of the  $\text{LiOtBu}$  solution. Compound **1** crystallizes from the mother liquor at  $-25^\circ\text{C}$  after several days in form of colorless cubic crystals of the tetragonal space group  $P4/nmm$  (No. 129). The structure can be described as a square antiprism formed by four Li atoms in one plane and four O atoms of the  $\text{OtBu}$  ligands in the other square plane, the Li face being capped by an OH group and the O face by a  $\text{Ca}-\text{I}$  unit, leading to an overall almost spherical entity (Figure 1). Its formation can be formally explained by the successful substitution of one iodide and the O-donor THF molecules of  $[\text{CaI}_2(\text{thf})_4]$  for instance, by a  $[\{\text{LiOtBu}\}_4]$  unit and a  $\mu_5$ -capping OH group. The coordination sphere of the calcium ion is built up by one remaining iodide, four  $\text{OtBu}$  groups, and one OH group to give an octahedral geometry. Calcium has thus its common coordination number six and the lithium cations reach their common (distorted) tetrahedral coordination sphere with two  $\text{OtBu}$  groups, the  $\text{OH}^-$  ion, and one terminal THF molecule.

The  $\text{Ca}-\text{I}$  distance (3.072(2) Å) is 0.03 Å shorter than that in  $[\text{CaI}_2(\text{thf})_4]$  (3.106(2) Å) or  $[\text{Ca}(\text{clox})(\text{thf})_4]$  (3.108(3) Å;  $\text{clox} = \text{OCPh}_2\text{CH}_2\text{C}_6\text{H}_4\text{Cl}_4$ )<sup>[10]</sup> while the coordination number and geometry are still the same; however, it corresponds well to the sum of the Shannon ionic radii (for a co-

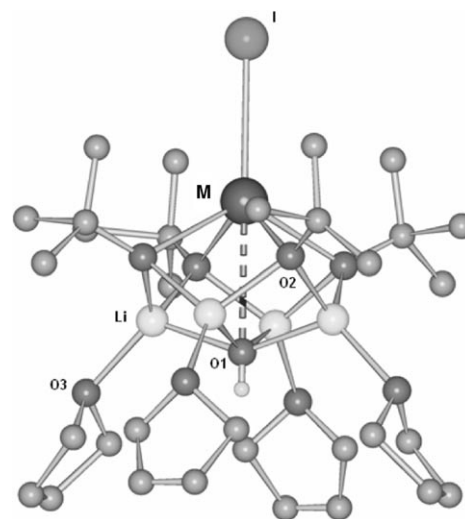
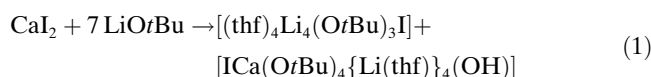


Figure 1. Molecular structure of  $[\text{IM}(\text{OtBu})_4\{\text{Li}(\text{thf})\}_4(\text{OH})]$ ,  $\text{M} = \text{Ca}$  (**1**),  $\text{Sr}$  (**2**),  $\text{Ba}$  (**3**),  $\text{Eu}$  (**4**); H atoms have been omitted for clarity.

ordination number 6:  $r_{\text{Ca}^{2+}}=1.00$ ,  $r_{\text{I}^-}=2.20$  Å).<sup>[8]</sup> It is also shorter by 0.06 Å than in the other possible starting material  $[\text{CaI}_2(\text{dme})_2(\text{thf})]$  ( $\text{Ca}-\text{I}$  3.137(9) Å), due here to a lower coordination number. The  $\text{Ca}-\text{O}(\text{OtBu})$  distances in **1** are 2.352(4) Å, and correspond well with those observed in the heterometallic compounds  $[\text{CaGe}_2(\text{OtBu})_6]$  (average  $\text{Ca}-\text{O}(\text{OtBu})=2.360$  Å) and  $[\text{CaSn}_2(\text{OtBu})_6]$ <sup>[12]</sup> (average  $\text{Ca}-\text{O}(\text{OtBu})=2.368$  Å), although the bridging mode of the  $\text{OtBu}$  groups in these compounds is different. The  $\text{Ca}-\text{O}(\text{OH})$  distance in **1** (2.696(7) Å) is longer than the  $\text{Ca}-\text{O}(\text{OH})$  distances in  $\text{Li}[\{\text{Ca}_7(\mu_3-\text{OH})_8\text{I}_6(\text{thf})_{12}\}_2(\mu-\text{I})]\cdot 3\text{THF}$  (average  $\text{Ca}-\text{O}(\text{OH})=2.323(2)$  Å),<sup>[3a,13]</sup> probably due to the bridging mode of the OH group with five bonding partners. The  $\text{Li}\cdots\text{Li}$  contacts (2.719(1) Å) are shorter than in elemental lithium (3.039 Å), but longer than in similar compounds like  $[\{\text{Ph}_2\text{P}(\text{NSiMe}_3)_2\text{CLi}_2\}]$ <sup>[14]</sup> with 2.393–2.410 Å. The increase relative to the literature data is probably due to the short  $\text{Ca}-\text{OH}$  bond of 2.696(7) Å, in which the alkaline earth cation strongly attracts the OH anion that caps the  $\text{Li}_4$  square.

This leads to the formation of the very flat square antiprism in which the plane containing the four Li atoms is only 1.12 Å from the plane containing the oxygen atoms of the  $\text{OtBu}$  groups. Thus, the  $\text{OH}^-$  group is 0.63 Å above the  $\text{Li}_4$  plane, and the Ca atom is 0.94 Å below the  $\text{O}_4$  plane. The structure can thus be interpreted as insertion of a  $[\{(\text{thf})\text{LiOtBu}\}_4]$  unit into the  $\text{Ca}-\text{OH}$  bond of a linear  $\text{I}-\text{Ca}-\text{OH}$  fragment. This confirms the data derived from the NMR spectrum of the mother solution from which **1** can be obtained,<sup>[10a]</sup> and the final reaction equation can thus be written as Equation (1).



The alkaline earth metal  $\text{Ca}^{2+}$  is found on a crystallographic  $4mm$  site ( $1/4, 1/4, z$  ( $c$ )), as is the halide I and the O1-hydroxy group. The Li atom is found on a crystallographic mirror plane  $m$  ( $1/4, y, z$  ( $i$ )) together with the attached C1 atom and one of the three methyl groups C2. The main symmetry features of the molecule are thus the fourfold axis through I, Ca, and O1, and the two mirror planes through Li and O2. In the crystal, the neutral clusters are arranged along the  $C_4$  axis with rather long  $\text{I}\cdots\text{O1(H)}$  hydrogen bonds of 3.612(5) Å (Figure 2). The analogue Sr and Ba clusters (**2** and **3**, respectively) have been synthesized from  $\text{MI}_2$  and  $\text{LiOtBu}$  in THF, and present in principle the same structure with the alkaline earth metal ions being exchanged formally.<sup>[3a,15]</sup>

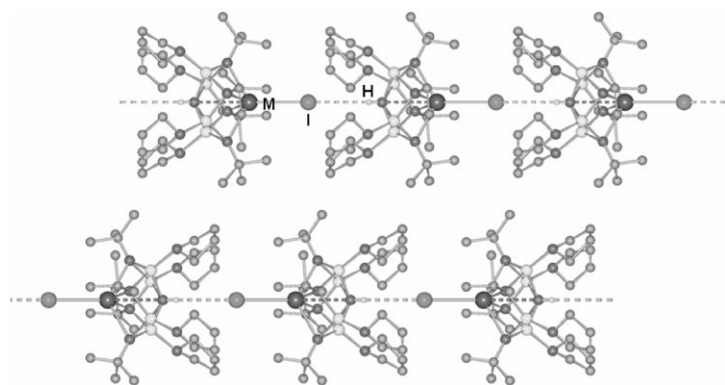


Figure 2. Typical stacking of  $[\text{IM}(\text{OtBu})_4\{\text{Li}(\text{thf})_4(\text{OH})\}]$  **1–4**, by hydrogen bonding between I and HO in the solid state; H atoms have been omitted for clarity.

The reaction of  $[\text{EuI}_2(\text{thf})_5]^{[7b]}$  with five equivalents of a 1 M solution of  $\text{LiOtBu}$  in THF in the presence of  $\text{LiOH}$  leads to the isolation of  $[\text{IEu}(\text{OtBu})_4\{\text{Li}(\text{thf})_4(\text{OH})\}] \cdot \text{THF}$  (**4**). Complex **4** crystallizes from the mother liquor at  $-25^\circ\text{C}$  after several months in a very low yield in form of colorless cubic crystals with tetragonal space group  $P4/nmm$  (No. 129) and with two molecules per unit cell. Unfortunately, attempts to reproduce the mixed-metal cluster **4** failed, and full characterization of this complex could not be achieved. Nevertheless, one single-crystal was used for the collection of the X-ray diffraction data to obtain the crystal structure of **4**. The structure of **4** is isostructural with those of general formula  $[\text{IM}(\text{OtBu})_4\{\text{Li}(\text{thf})_4(\text{OH})\}]$  ( $\text{M} = \text{Ca}$  **1**,  $\text{Sr}$  **2**,<sup>[3a]</sup>  $\text{Ba}$  **3**,<sup>[3a,15]</sup> The rare earth metal ion  $\text{Eu}^{2+}$  is position on the crystallographic  $4mm$  site ( $1/4, 1/4, z$  ( $c$ )) as are the halide I and the O1-hydroxy group. The Li ion is found on a crystallographic mirror plane  $m$  ( $x, 1/4, z$  ( $i$ )) together with the attached C1 atom and one of the three methyl groups C2. The neutral clusters are arranged along the fourfold axis with rather short  $\text{I}\cdots\text{O1(H)}$  hydrogen bonds of 3.286(1) Å (Figure 2). Only few compounds of di- and trivalent lanthanides (Sm, Eu, Yb) in combination with the  $\text{OtBu}$  anion, for instance with the europium cation, are known. The  $\text{Eu}-\text{O}(\text{OtBu})$  distances in **4** are 2.485(4) Å, and are slightly shorter

than the  $\text{Eu}-\text{O}(\text{OtBu})$  bond lengths observed in  $[\text{Eu}^{\text{II}}\text{Ge}_2(\mu\text{-OtBu})_6]$  (average 2.496 Å),<sup>[12]</sup> in which the  $\text{OtBu}$  groups act as  $\mu$ -bridging ligands. From the literature, this is to our knowledge the only compound with  $\text{Eu}^{2+}-\text{OtBu}$  bonds. Surprisingly, with the more commonly used  $\text{Eu}^{3+}$  ion, only two compounds with  $\text{Eu}^{3+}-\text{OtBu}$  bonds are known, namely  $[\text{EuNa}_8(\text{OtBu})_{10}\text{Cl}]^{[17]}$  and  $[\{(\text{C}_5\text{Me}_5)\text{Eu}^{\text{III}}(\text{OtBu})(\mu\text{-OtBu})_2\}]_2$ .<sup>[16]</sup> The first compound possesses terminal and  $\mu_3$ -bridging  $\text{OtBu}$  groups, the second compound terminal and  $\mu$ -bridging  $\text{OtBu}$ -anions. The corresponding  $\text{Eu}^{3+}-\text{OtBu}$  distances, as expected, in both cases are shorter than those observed in **4**. While there is no direct bond between the europium cation and the hydroxy group, the  $\text{Eu}\cdots\text{O}(\text{OH})$  distance in **4** is relatively short with 2.974(7) Å, and the  $\text{Li}\cdots\text{Li}$  contacts at 2.673(1) Å are shorter than in **1**.

Structures containing a similar square arrangement of four alkali metals as observed for  $[\text{IM}(\text{OtBu})_4\{\text{Li}(\text{thf})_4(\text{OH})\}]$  ( $\text{M} = \text{Ca}$  **1**,  $\text{Sr}$  **2**,<sup>[3a]</sup>  $\text{Ba}$  **3**,<sup>[3a,15]</sup>  $\text{Eu}$  **4**), are:  $[(\text{OR})_8\text{Cr}_2\text{Na}_4(\text{thf})_4]$  ( $\text{R} = i\text{Pr}, \text{Ph}$ ),<sup>[18]</sup>  $[\{\text{Ph}_2\text{P}(\text{NSiMe}_3)_2\}_2\text{CLi}_2]$ ,<sup>[14]</sup>  $[\text{Li}_4\text{Na}_4(\text{OtBu})_4\{\text{PhN}(\text{H})\}_4(\text{NaOH})(4\text{-Me-py})_4]$ ,<sup>[19]</sup>  $[\text{Li}_4\text{K}_4(\text{OtBu})_4(\text{C}_6\text{H}_{11}\text{O})_4(\text{KOH})(\text{thf})_5]$ ,<sup>[20]</sup>  $\text{Na}_4[\{\text{P}\{\text{Si}(\text{F})\text{R}_2\}(\text{Si}i\text{Pr}_3)_2\}]_2$  ( $\text{R} = 2,4,6\text{-}i\text{Pr}_3\text{-C}_6\text{H}_2$ ),<sup>[21]</sup>  $[(\text{LiOtBu})_{10}(\text{LiOH})_6]$ ,<sup>[22]</sup>  $[\text{Me}_2\text{C}(\text{CH}_2)_3\text{CMe}_2\text{NLi}]_4$ ,<sup>[23]</sup>  $[\{\text{Li}(\text{N}t\text{Bu})_3\text{S}\}_2]$ ,<sup>[24]</sup>  $[(\text{Li}_4\text{L})\{(\text{LiOH})(\text{hmpa})_4\}]$  ( $\text{H}_4\text{L} = \text{tert-butylcalix}[4]\text{arene}$ ;  $\text{HMPA} = \text{OP}(\text{NMe}_2)_3$ ),<sup>[25]</sup> and  $[(t\text{BuO})_8\text{Li}_4\text{K}_4]$ .<sup>[26]</sup> In the structures of  $[(\text{LiOtBu})_{10}(\text{LiOH})_6]$ ,  $[\text{Li}_4\text{Na}_4(\text{OtBu})_4\{\text{PhN}(\text{H})\}_4(\text{NaOH})(4\text{-Me-py})_4]$ , and  $[\text{Li}_4\text{K}_4(\text{OtBu})_4(\text{C}_6\text{H}_{11}\text{O})_4(\text{KOH})(\text{thf})_5]$ , the square  $\text{Li}_4\text{O}_4$  antiprism can be found and is capped on one side by an  $\text{HO}^-$  ligand. These fragments show similar  $\text{Li}-\text{OtBu}$  and  $\text{Li}-\text{OH}$  bond lengths as **1** and **4**.

With the series of compounds **1–4**, the most important structural differences can be discussed. The most relevant bond lengths and angles are given in Table 1, together with literature data on the molecular precursors for these cluster compounds,  $[\text{MI}_2(\text{thf})_n]$ ,  $\text{M} = \text{Ca}, \text{Sr}, \text{Ba}, \text{Eu}$  and  $n = 4$  (for Ca) or 5. The  $\text{M}^{2+}-\text{I}$  distances get shorter when passing from the monomer to the cluster compounds, decreasing from 3.106(2) Å in  $[\text{CaI}_2(\text{thf})_4]$  (and 3.137(9) Å for  $[\text{CaI}_2(\text{dme})_2(\text{thf})]$ ) to 3.072(2) Å on average in **1**, from 3.235 Å in  $[\text{EuI}_2(\text{thf})_5]^{[7b]}$  to 3.210(2) Å in **4** and from 3.228(8) and 3.378(8) Å in  $[\text{MI}_2(\text{thf})_5]$  for Sr and Ba, respectively to 3.223(2) and 3.344(2) Å in the corresponding compounds **2** and **3**. This can be explained by the lower coordination number of europium and strontium (respectively barium) with six (respectively five) in **2–4** compared to seven in  $[\text{MI}_2(\text{thf})_5]$  ( $\text{M} = \text{Sr}, \text{Ba}, \text{Eu}$ ) due to steric protection by the *tert*-butyl groups of the cluster. The  $\text{Ca}-\text{OH}$ ,  $\text{Sr}\cdots\text{OH}$ , and  $\text{Eu}\cdots\text{OH}$  bonds in **1**, **2**, and **4**, respectively, are shorter than the  $\text{Ca}/\text{Sr}/\text{Eu}\cdots\text{Li}$  distances, whereas in compound **3**, the  $\text{Ba}-\text{OH}$  bond is longer than the intermetallic  $\text{Ba}\cdots\text{Li}$  distance. This can be explained by the higher charge concentration on  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ , and  $\text{Eu}^{2+}$  compared to  $\text{Ba}^{2+}$ , leading to a stronger attraction of the  $\text{OH}^-$  ion and a stronger repulsion of the  $\text{Li}^+$  ions for Ca, Sr, and Eu. Also, bond valence sums for the  $\text{M}^{2+}$  ions in **1–4** reveal that for  $\text{Ca}^{2+}$  and  $\text{Sr}^{2+}$ , the  $\text{M}-\text{OH}$  has to be taken into account in order to compensate

Table 1. Principal bond lengths and angles on the molecular precursors  $[MI_2(\text{thf})_n]$ ,  $M = \text{Ca}, \text{Sr}, \text{Ba}, \text{Eu}$  and  $n = 4$  (for Ca) or 5 and the corresponding cluster compounds  $[IM(\text{OrBu})_4\{\text{Li}(\text{thf})\}_4(\text{OH})]$ .

	$[\text{CaI}_2(\text{thf})_4]$	$[\text{CaI}_2(\text{dme})_2(\text{thf})]$	<b>1</b>	$[\text{EuI}_2(\text{thf})_5]$	<b>4</b>	$[\text{SrI}_2(\text{thf})_5]$	<b>2</b>	$[\text{BaI}_2(\text{thf})_5]$	<b>3</b>
CN <sup>[a]</sup>	6	7	6	7	5	7	6	7	5
$M^{2+}-\text{I}$	3.106	3.137	3.072	3.235	3.210	3.228	3.223	3.378	3.344
$M^{2+}-\text{O}(\text{thf})$	2.34	2.391	–	2.587	–	2.586	–	2.728	–
$M^{2+}-\text{OrBu}$	–	–	2.352	–	2.485	–	2.482	–	2.597
$M^{2+}-\text{OH}$	–	–	2.696	–	2.974	–	2.935	–	3.115
$\text{I}-M^{2+}-\text{I}$	180	178.60	–	178.00	–	176.34	–	178.61	–
$\text{I}\cdots\text{O}-\text{H}$	–	–	3.612	–	3.286	–	3.241	–	3.935
$M^{2+}\cdots M^{2+}$	–	–	2.822	–	3.005	–	2.972	–	3.108

[a] CN = coordination number.

the positive charge on the cation, whereas for **3** and **4**, the bond valence sum is reached with the five closest contacts,  $M-\text{I}$  and  $M-\text{OrBu}$  (Table 2).

Table 2. Bond valence sums for the  $M^{2+}$  and  $\text{Li}^+$  metal cations in the clusters compounds  $[IM(\text{OrBu})_4\{\text{Li}(\text{thf})\}_4(\text{OH})]$  **1–4**.

	<b>1</b>	<b>4</b>	<b>2</b>	<b>3</b>
$V_{\text{Li}^+}$	1.12	1.12	1.1	1
$V_{M^{2+}}$ <sup>[a]</sup>	1.98 (6)	2.00 (5)	2.11 (6)	1.80 (5)
	1.96 (6)	2.30 (5)		

[a] Coordination number given in parentheses.

To corroborate these experimental results and provide further insight into the observed differences between the complexes, electronic structure calculations were carried by the use of density functional theory. The calculations were carried out by using the Gaussian03 suite of programs<sup>[61]</sup> with the B3LYP functional and the LANL2DZ basis set for I, Ba, Sr, Ca; the 6–31G\* basis set for O, Li, and H; and the 3–21G\* basis set C. Starting from the X-ray geometry, the  $\text{I}-\text{M}$ ,  $\text{M}-\text{O}$ ,  $\text{O}-\text{H}$ , and  $\text{Li}-\text{O}$  distances were allowed to relax. The remaining internal coordinates were fixed at the crystallographic values. The  $\text{M}-\text{O}$  bond lengths varied between 2.80 and 3.23 Å, while the  $\text{I}-\text{M}$  distances were between 3.30 and 3.60 Å. The diameter of the  $\text{Li}_4$  ring increases from 3.79 Å for **1** to 3.85 Å for **3**. It is also of interest to compare the nuclear charges on the most relevant atoms. While the charge on the M atom increases from 1.81 for Ca to 1.90 for Ba, the charge on the I atom partially counteracts this: it changes from  $-0.88$  to  $-0.92$ . The fact that the  $\text{Ba}-\text{OH}$  bond length increases so much relative to the real value seems indeed to confirm that the barium cation does not “see” the OH group, its charge being compensated by the other anions. One can therefore approve of the coordination number of five to the barium cation, whereas the  $\text{M}-\text{OH}$  bond has to be considered in the other compounds of this series.

We have shown so far that with LiOH and LiOrBu, 50% of the iodide of the starting material  $\text{MI}_2$  can be eliminated and replaced by OH or OrBu to obtain different cluster compounds. NaOrBu, which is a stronger base than the corresponding lithium compound, allows the elimination of 75% of the iodide in the initial alkaline earth metal iodide. This leads to the so far largest known  $\text{Sr}_{12}$  cluster  $[\text{Li}(\text{thf})_4]-$

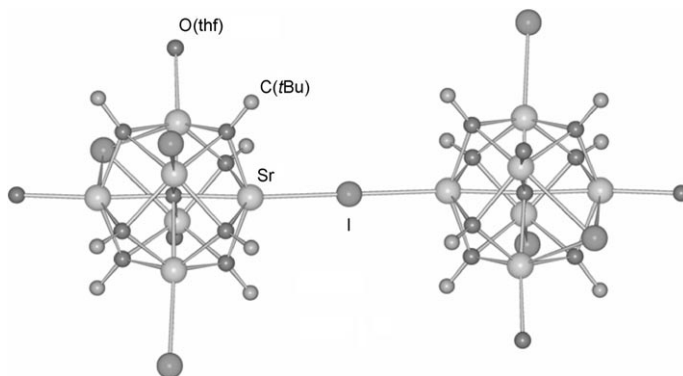


Figure 3. 75% Iodide elimination from  $\text{SrI}_2$  leads to a  $\text{Sr}_{12}$  aggregate; methyl groups of the OrBu ligands and H atoms have been omitted for clarity.

$[\{\text{Sr}_6(\text{O})(\text{OrBu})_7(\mu_3-\text{I})(\text{I})_2(\text{thf})_3\}_2(\mu-\text{I})]$  (Figure 3).<sup>[3c]</sup> Its structure has been described elsewhere<sup>[3c]</sup> and will therefore not be discussed in detail here. It is cited, however, to show the step-wise increase of iodide elimination and the great and fascinating structural variety of such aggregates.

**The  $[\text{MM}'_6(\text{OPh})_8(\text{thf})_6]$ -type clusters:** In the following, we describe reactions of  $\text{MI}_2$  ( $M = \text{Ca}, \text{Sr}, \text{Ba}, \text{Sm}, \text{Eu}$ ) with LiOPh, in which total substitution of iodide can be achieved, leading to mixed-metal clusters.

The heterometallic  $[\text{CaLi}_6(\text{OPh})_8(\text{thf})_6]$  cluster (**5**) was obtained from three different reactions.

- 1) The reaction of  $\text{CaI}_2$  in THF via  $[\text{CaI}_2(\text{thf})_4]$  with an excess of a 1 M solution of LiOPh in THF, under dry and inert conditions at room temperature, yields small crystals of **5** within one week after recrystallization in a THF/hexane mixture, as described previously.<sup>[3b]</sup>
- 2) Replacing  $[\text{CaI}_2(\text{thf})_4]$  by  $[\text{CaI}_2(\text{dme})_2(\text{thf})]$ , the same reaction affords also crystals of **5** in a similar yield.
- 3) Larger crystals of **5** can also be obtained quickly (one night) by the use of a microwave-assisted reaction (500 W for two minutes).

Compound **5** crystallizes in the monoclinic space group  $P2_1/n$  (No. 14) with two molecules in the unit cell. The structure is based on two  $\text{CaLi}_3$  tetrahedra linked through the Ca vertex (Figure 4), and bridged by OPh anions. The structure

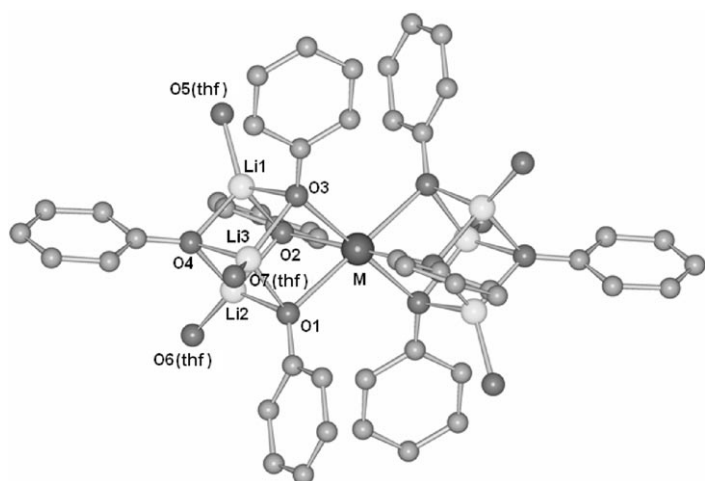


Figure 4. Molecular structure of  $[MLi_6(OPh)_8(thf)_6]$ ,  $M = Ca$  (5),  $Sr$  (6),  $Ba$  (7),  $Sm$  (8),  $Eu$  (9); H atoms have been omitted for clarity.

can alternatively be described as two vertex-sharing  $CaLi_3O_4$  heterocubanes. This heterocubane motif has already been described in some homometallic alkaline earth clusters, that is, with calcium,<sup>[3a,13]</sup> but it is more frequently found with transition metals such as zinc.<sup>[27]</sup> It can also be observed in heterometallic clusters, with mixed transition metals<sup>[28]</sup> and with mixed alkali/transition metals.<sup>[4a]</sup> Only a few references are reported in the literature combining calcium ions and aryloxides (with phenolate<sup>−</sup>,<sup>[29]</sup> 2,6-Me<sub>2</sub>-(C<sub>6</sub>H<sub>3</sub>O)<sup>−</sup>,<sup>[30]</sup> 2,6-*i*Pr<sub>2</sub>-(C<sub>6</sub>H<sub>3</sub>O)<sup>−</sup><sup>[31]</sup> and 2,6-Ph<sub>2</sub>-(C<sub>6</sub>H<sub>3</sub>O)<sup>−</sup> anions<sup>[32]</sup>).

Working under the same three possible reaction conditions as for the synthesis of 5, the reactions of SrI<sub>2</sub> with an excess of LiOPh in THF yield crystals of  $[SrLi_6(OPh)_8(thf)_6]$  (6). Compound 6 crystallizes like 5 in the monoclinic space group  $P2_1/n$  (No. 14). The structure is isostructural to the one described for 5, the calcium cation being formally replaced by a strontium cation, the average Sr-μ<sub>3</sub>-OPh distance being 2.516(2) Å. This average distance is shorter than the Sr-μ<sub>3</sub>-OPh bond lengths in  $[Sr_4(OPh)_8(PhOH)_2(thf)_6]$ <sup>[33]</sup> and  $[Sr_3(OPh)_6\{hmpa\}_3]$ ,<sup>[29]</sup> but longer than Sr-μ-OPh distances in the same references. The reaction of BaI<sub>2</sub> in THF (but not the microwave-assisted reaction) with an excess of a 1 M solution of LiOPh in THF under inert atmosphere yields crystals of  $[BaLi_6(OPh)_8(thf)_6]$  (7). Compound 7 crystallizes in the triclinic space group  $P\bar{1}$  (No. 2) with one molecule in the unit cell. The structure is again similar to 5 and 6. An inversion center is situated at the position of the barium cation which is on the crystallographic position (1/2, 0, 1/2) (*f*). The barium cation reaches a coordination number

of six with a mean value of Ba-μ<sub>3</sub>-OPh distance at 2.718(9) Å. They compare well with those found in  $[Ba_6(OPh)_{12}(tmeda)_4]$ <sup>[29]</sup> (average 2.730(2) Å; tmeda = *N,N,N',N'*-tetramethyl 1,2-ethanediamine), and are slightly longer than those in  $[HBA_5(O)(OPh)_9(thf)_8]$ <sup>[34]</sup> (average 2.686 Å), but slightly shorter than the average Ba-μ<sub>3</sub>-OPh distances in  $[H_2Ba_8(\mu_3-O)_2(OPh)_{14}(hmpa)_6]$ <sup>[35]</sup> (average 2.762 Å) and much more shorter than the Ba-μ<sub>3</sub>-OPh bond lengths in  $[BaTi(OC_6H_5)_6(dmf)_2]_2$  (average 2.815 Å; dmf = *N,N*-dimethylformamide).<sup>[36]</sup>

The heterometallic  $[SmLi_6(OPh)_8(thf)_6]$  cluster (8) can be prepared by two different synthetic routes.

- 1) The reaction of  $[SmI_2(thf)_5]$ <sup>[7c]</sup> with an excess of LiOPh in THF. This reaction was performed under dry and inert atmosphere in a glovebox at room temperature. After recrystallization in a THF/hexane mixture, single-crystals of 8 grown within one week at −25 °C.
- 2) Cluster 8 can also be obtained more quickly (two days) by a microwave-assisted reaction (500 W for two minutes).

Compound 8 crystallizes in the monoclinic space group  $P2_1/n$  (No. 14) with two molecules in the unit cell. As for 5–7, the structure of 8 consists of two  $SmLi_3$  tetrahedra linked through the Sm vertex. The samarium cation is situated on an inversion center at the crystallographic position (1, 0, 1) (*a*) and reaches a coordination number of six with an average Sm-μ<sub>3</sub>-OPh distance of 2.530(2) Å, much longer relative to the terminal Sm-OPh bond length found in  $[Sm(Cp^*)_2(OPh)(thf)]$  (Cp\* = C<sub>5</sub>Me<sub>5</sub>)<sup>[37]</sup> (Sm-OPh = 2.1645(14) Å). The Li-O(OPh) bond lengths (average 1.970(7) Å) are slightly longer than those observed in the literature.<sup>[4a,38]</sup> Very weak intermolecular hydrogen bonds can be found between THF molecules of neighboring clusters in 8 with a O5⋯H25A distance at 2.962(4) Å (Figure 5). This leads to the formation of infinite polymeric chains of cluster 8. This structural detail was not observed for the alkaline earth metal analogues.

The reaction of EuI<sub>2</sub> in THF via  $[EuI_2(thf)_5]$ <sup>[7b]</sup> with an excess of LiOPh in THF was carried out under a dry and

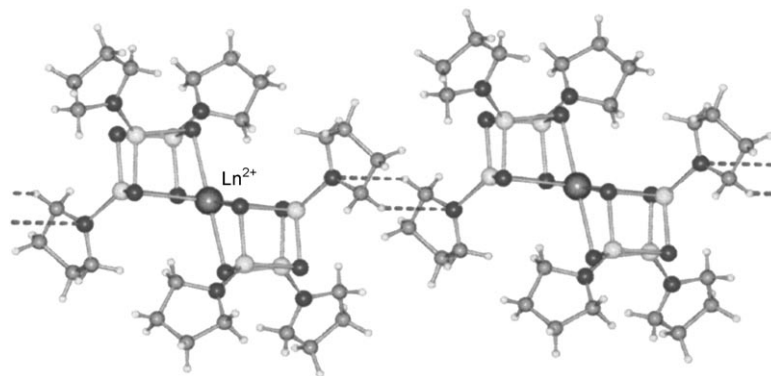


Figure 5. Hydrogen bonding between cluster units in  $[MLi_6(OPh)_8(thf)_6]$ ,  $M = Sm$  (8),  $Eu$  (9); phenyl rings have been omitted for clarity.

inert atmosphere. After recrystallization in a hexane/THF mixture solution within one week at low temperature ( $-25^{\circ}\text{C}$ ) crystals of  $[\text{EuLi}_6(\text{OPh})_8(\text{thf})_6]$  (**9**) formed in a low yield (24%). Compound **9** crystallizes in the monoclinic space group  $P2_1/n$  (No. 14) with two molecules in the unit cell. The structure is in principle isostructural to compounds **5–8**.

It consists of two  $\text{EuLi}_3\text{O}_4$  cubanes linked through a vertex, that is, the  $\text{Eu}^{2+}$  ion. Only few compounds of divalent lanthanides with aryloxides are described in the literature, and none with the sterically unhindered phenoxide. However,  $\text{Sr}^{2+}$ ,  $\text{Eu}^{2+}$ , and  $\text{Sm}^{2+}$  ions have approximately the same ionic radii (for a coordination number of six:  $r_{\text{Sr}^{2+}} = 1.18 \text{ \AA}$ ,  $r_{\text{Eu}^{2+}} = 1.17 \text{ \AA}$ , for a coordination number of 7:  $r_{\text{Sm}^{2+}} = 1.22 \text{ \AA}$ ); hence the  $\text{Ln}^{2+}-\text{OPh}$  bonds should be of the same order as the  $\text{Sr}^{2+}-\text{OPh}$  distances. The europium cation is situated on an inversion center at the crystallographic position  $(0, \frac{1}{2}, 0)$  (c) and reaches a coordination number of six with an average  $\text{Eu}-\mu_3\text{-OPh}$  distance of  $2.540(7) \text{ \AA}$ . These bonds are slightly longer than the  $\text{Sr}-\mu_3\text{-OPh}$  distances in **6**, and are also longer (on average) than  $\text{Eu}-\mu\text{-OAr}$  bond lengths in other aryloxide compounds, for instance  $[\text{Eu}_4(\mu\text{-OC}_6\text{H}_3\text{-}i\text{Pr}_2\text{-}2,6)_4(\text{OC}_6\text{H}_3\text{-}i\text{Pr}_2\text{-}2,6)_2(\mu_3\text{-OH})_2(\text{NCMe})_6]$  ( $2.403\text{--}2.543 \text{ \AA}$ ),<sup>[39]</sup>  $[\text{Eu}_2(\mu\text{-OC}_6\text{H}_3\text{-}i\text{Pr}_2\text{-}2,6)_4(\text{NCMe})_5]$  ( $2.438(6)\text{--}2.494(6) \text{ \AA}$ ),<sup>[40]</sup> or  $[\text{Eu}(\mu\text{-OC}_6\text{H}_3\text{-Me}_2\text{-}2,6)_2(\text{thf})_2]_3]$  ( $2.444(13)\text{--}2.581(12) \text{ \AA}$ ).<sup>[41]</sup> As expected, the  $\text{Eu}-\mu_3\text{-OPh}$  distances in **9** are longer than the terminal  $\text{Eu}-\text{OAr}$  bonds in divalent europium aryloxide adducts:  $[\text{Eu}(\text{OC}_6\text{H}_3\text{-Me}_2\text{-}2,6)_2(\text{thf})_3] \cdot 0.75 \text{ THF}$  ( $2.309(14)\text{--}2.313(12) \text{ \AA}$ ),<sup>[42]</sup>  $[\text{Eu}_4(\mu\text{-OC}_6\text{H}_3\text{-}i\text{Pr}_2\text{-}2,6)_4(\text{OC}_6\text{H}_3\text{-}i\text{Pr}_2\text{-}2,6)_2(\mu_3\text{-OH})_2(\text{NCMe})_6]$  ( $2.284(6)\text{--}2.299(6) \text{ \AA}$ ) and  $[\text{Eu}(\text{OC}_6\text{H}_3\text{-}t\text{Bu}_2\text{-}2,6)_2(\text{NCMe})_4]$  ( $2.313(12)\text{--}2.35(2) \text{ \AA}$ ).<sup>[39]</sup> As in **8**, weak intermolecular hydrogen bonds can be found between the THF molecules of neighboring  $[\text{EuLi}_6(\text{OPh})_8(\text{thf})_6]$  clusters with a  $\text{O6}\cdots\text{H32B}$  distance at  $2.993(3) \text{ \AA}$ . This leads to the formation of infinite polymeric chains of molecules of **9** along the  $c$  axis, similar to **8** (Figure 5).

Thus, a total of five compounds of the type  $[\text{MLi}_6(\text{OPh})_8(\text{thf})_6]$  with all heavier alkaline earth metal as well as divalent lanthanide ions have been synthesized and will now be compared. The most relevant bond lengths and angles of the series of compounds **5–9** are given in Table 3, together with literature data on the starting materials, the cluster compounds  $[\{\text{Li}(\text{OPh})(\text{thf})\}_6]$ <sup>[43a]</sup> and  $[\{\text{Li}(\text{OPh})(\text{thf})\}_4]$ .<sup>[43b]</sup> Each lithium cation in the structures **5–9** completes its usual tetrahedral coordination sphere with a terminally bonded THF ligand. The  $\text{Li}-\text{O}(\text{thf})$  bond lengths in all compounds are common and correspond well with those described in litera-

ture compounds.<sup>[4a,15,38f,43]</sup> The only difference between the alkaline earth metal compounds and the lanthanide analogues can be found in the intermolecular weak, but still remarkable, contacts between the THF molecules. We cannot however prove if this effect is due to the lanthanide ions, or to differences in packing of the molecules.

Whereas exchanging  $\text{LiOtBu}$  by  $\text{NaOtBu}$  leads to different reaction products, the reactions of  $\text{MI}_2$  with  $\text{NaOPh}$  instead of  $\text{LiOPh}$  lead to the homologous  $[\text{MNa}_6(\text{OPh})_8(\text{thf})_6]$  cluster compounds ( $\text{M} = \text{Ca}$  **10**,  $\text{Sr}$  **11**,  $\text{Ba}$  **12**; Figure 6).

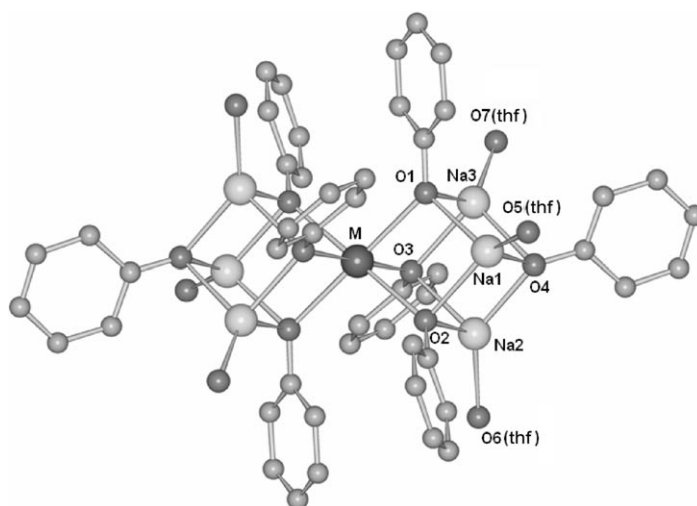


Figure 6. Molecular structure of  $[\text{MNa}_6(\text{OPh})_8(\text{thf})_6]$ ,  $\text{M} = \text{Ca}$  (**10**),  $\text{Sr}$  (**11**),  $\text{Ba}$  (**12**); carbon atoms of the THF molecules and H atoms have been omitted for clarity.

The reaction of  $\text{CaI}_2$  with an excess of  $\text{NaOPh}$  in THF, under dry and inert atmosphere at room temperature, yields crystals of **10** within one week at  $-25^{\circ}\text{C}$ , after recrystallization from a THF/hexane mixture. Compound **10** crystallizes in the monoclinic space group  $P2_1/n$  (No. 14) with two molecules in the unit cell. The structure of **10** is very similar to that of compound **5**, except that the lithium atoms are formally replaced by sodium cations, resulting in an unusually low coordination number for the latter. The calcium cation is situated on an inversion center on the crystallographic position  $(0, \frac{1}{2}, \frac{1}{2})$  ( $d$ ). The  $\text{Na}-\text{O}(\text{OPh})$  bond lengths (average  $2.295(1) \text{ \AA}$ ) are slightly shorter than those observed in the starting material  $[\{\text{Na}(\text{OPh})(\text{thf})\}_6]$  (average  $2.327(2) \text{ \AA}$ )<sup>[44]</sup> and in  $[\{\text{Na}(\text{OPh})(\text{dme})\}_4]$  (average  $2.326(7) \text{ \AA}$ ),<sup>[45]</sup> but they are shorter than those in other literature described species such as  $[(\text{PhO})_8\text{Cr}_2\{\text{Na}(\text{thf})\}_4]$ .<sup>[46]</sup> Each sodium cation pos-

Table 3. Principal bond lengths in **5–9** and the lithium phenoxide compounds reported.

	$[\{\text{Li}(\text{OPh})(\text{thf})\}_6]$ <sup>[43a]</sup>	$[\{\text{Li}(\text{OPh})(\text{thf})\}_4]$ <sup>[43b]</sup>	<b>5</b>	<b>9</b>	<b>6</b>	<b>8</b>	<b>7</b>
$r_{\text{M}^{2+}}$	–	–	1	1.17	1.18	1.22(CN7)	1.35
$\text{M}-\text{OPh}$	–	–	2.375(9)	2.540(7)	2.516(1)	2.530(2)	2.718(9)
$\text{Li}-\text{OPh}$	1.957	1.93	1.973(2)	1.97(3)	1.937(5)	1.927(7)	1.964(6)
$\text{Li}\cdots\text{Li}$	2.619	2.62	2.613(3)	2.563(3)	2.605(6)	2.611(8)	2.577(8)
$\text{Li}-\text{O}(\text{thf})$	1.978	1.92	1.935(3)	1.956(7)	1.935(3)	1.935(3)	1.935(3)



sesses a tetrahedral coordination sphere completed with a terminally bonded THF ligand. The Na–O(thf) bond lengths of **10** (average Na–O(thf) = 2.270(3) Å) are slightly shorter than those observed in compounds in the literature data,<sup>[44,47]</sup> but slightly longer than in the compound [(PhO)<sub>8</sub>Cr<sub>2</sub>{Na(thf)}<sub>4</sub>].<sup>[46]</sup> Similar isostructural homologous series by exchange of alkali ions have been observed for [(*t*BuO)<sub>8</sub>Li<sub>4</sub>M<sub>4</sub>], in which M is Na, K, Rb or Cs.<sup>[26b]</sup> We have, however, not yet realized structures with higher homologues than sodium so far; this research being pursued currently in our laboratories.

The reaction under the same conditions of SrI<sub>2</sub> or BaI<sub>2</sub> with an excess of NaOPh in THF, under dry and inert atmosphere at room temperature, yields crystals of [SrNa<sub>6</sub>(OPh)<sub>8</sub>(thf)<sub>6</sub>] (**11**) or [BaNa<sub>6</sub>(OPh)<sub>8</sub>(thf)<sub>6</sub>] (**12**) within one week. Compounds **11** and **12** crystallize in the monoclinic space group *P*2<sub>1</sub>/*n* (No. 14). They are isostructural with the calcium analogue **10** and possess a very similar structures to those of compounds **6** and **7**, respectively, with the lithium cations formally replaced by sodium cations. An inversion center is situated at the position of the strontium cation in **11** which lies on the crystallographic position (0, 1/2, 0 (*c*)), whereas for **12**, the barium cation lies on the crystallographic position (1/2, 1/2, 1/2 (*a*)).

All the compounds **10–12** have been prepared using the same reaction pathway and present the same general formula as well as structural features. Surprisingly, the three clusters **10–12** adopt the same motif observed with the lithium analogues **5–7**. The use of a larger alkali metal did not influence at all the general structure of the clusters and the orientation of the anions in the coordination sphere of the alkaline earth metal ions. Moreover, the sodium cations are satisfied with a distorted tetrahedral coordination sphere, while they usually prefer the higher coordination number five. From the solid-state structure of the sodium starting compound [[Na(OPh)(thf)]<sub>6</sub>],<sup>[44]</sup> the formation of this motif cannot be easily interpreted. However, in solution, no data are available concerning the structure or at least the degree of aggregation of the “Na(OPh)” reagent. It is thus possible that those cubane-like aggregates of NaOPh exist in solution, and that the alkaline earth metal ions can easily act as fusion points between such two heterocubane units by substitution of two Na ions by one M<sup>2+</sup> ion (M = Ca, Sr, Ba). The most relevant bond lengths of the series of compounds **10–12** are given in Table 4, together with literature data on the known cluster compound [[Na(OPh)(thf)]<sub>6</sub>].<sup>[44]</sup> The M–OPh bond lengths vary as expected when going from the smaller calcium to the larger barium cation. All distances in both cubanes (Na–OPh, Na···Na, and Na–O(thf)) of the

Table 4. Principal bond lengths in **10–12** and [[Na(OPh)(thf)]<sub>6</sub>].

	[[Na(OPh)(thf)] <sub>6</sub> ] <sup>[47]</sup>	<b>10</b>	<b>11</b>	<b>12</b>
M–OPh	–	2.365(7)	2.525(7)	2.698(7)
Na–OPh	2.312(2)	2.295(1)	2.303(2)	2.284(7)
Na···Na	3.275(4)	3.211(5)	3.231(1)	3.205(1)
Na–O(thf)	2.293(1)	2.270(3)	2.281(2)	2.279(8)

heterometallic compounds **10–12** are slightly shorter than those observed in [[Na(OPh)(thf)]<sub>6</sub>]. This is probably due to the introduction of a larger cation in the core of the compound [[Na(OPh)(thf)]<sub>6</sub>], the loss of the electron density available for sodium cations involves a contraction of the cubane subunits. This was also observed with clusters **5–7** involving LiOPh.

The reaction of CaI<sub>2</sub> with an equal amount of LiOPh and Li*t*Bu in THF, affords single crystals of [CaLi<sub>6</sub>(OPh)<sub>6</sub>(*Or*Bu)<sub>2</sub>(thf)<sub>6</sub>] (**13**) (Figure 7). Compound **13** crystallizes in

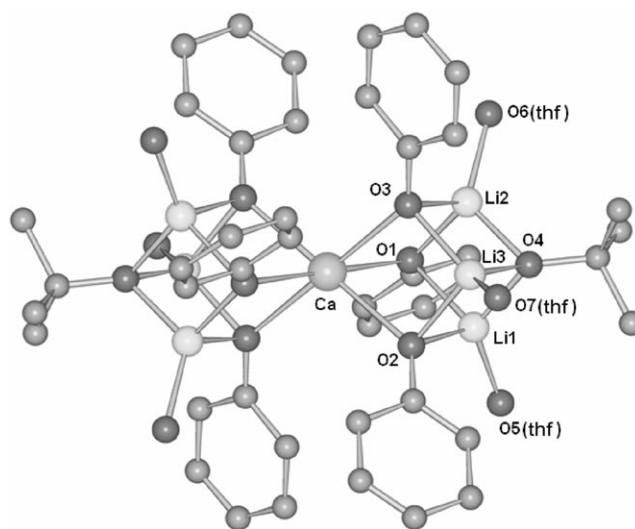


Figure 7. The mixed-ligand cluster [CaLi<sub>6</sub>(OPh)<sub>6</sub>(*Or*Bu)<sub>2</sub>(thf)<sub>6</sub>] (**13**); H atoms have been omitted for clarity.

the triclinic space group *P*1̄ (No. 2) with one molecule per unit cell. Similar to compounds **5–9**, the structure consists of two CaLi<sub>3</sub> tetrahedra linked through the Ca vertex due to a crystallographic inversion center on which the calcium cation is found (1, 1/2, 1/2 (*g*)). The four triangular faces of these two equivalent tetrahedra are μ<sub>3</sub>-bridged by alcoholate anions: three phenolates and one *tert*-butanolate group. Although different symmetry operations might be expected analyzing the crystal structure of **13**, such as a C<sub>3</sub> axis, no correlation matrix was found indicating a higher symmetry. Further careful analysis of the X-ray data gave no hints for the presence of a higher symmetry. In a previous article, Gagné et al.<sup>[48a]</sup> described the synthesis of a mixed sodium alkoxide/phenoxide catalyst, namely [Na<sub>4</sub>(OPh)<sub>3</sub>(*Or*Bu)], obtained by simple mixing of the Na*Or*Bu and NaOPh in THF. It is possible to expect that the formation of an analogue heteroleptic alkali cluster is also possible with lithium resulting in [Li<sub>*x*</sub>(OPh)<sub>*y*</sub>(*Or*Bu)<sub>*z*</sub>] (maybe [Li<sub>4</sub>(OPh)<sub>3</sub>(*Or*Bu)] considering the structure of **13**).<sup>[48b–d]</sup>

**The [Ca<sub>2</sub>(dme)<sub>2</sub>(OPh)<sub>6</sub>{M'(dme)}<sub>2</sub>]-type clusters and other DME derivatives of [MLi<sub>6</sub>(OPh)<sub>8</sub>(thf)<sub>6</sub>]:** To consider if the use of different Lewis coordinating solvents can have an important impact on the structure or even lead to a total rearrangement of the structure, some attempts of recrystalliza-

tion of the THF-adducts with DME, a polydentate ligand, were undertaken. The reaction of an excess of LiOPh in THF with  $\text{CaI}_2$  forms a deep brown solution that was evaporated to dryness. At room temperature, the solid residue was recrystallized from DME, affording  $[\text{Ca}_2(\text{dme})_2(\text{OPh})_6\{\text{Li}(\text{dme})\}_2]$  (**14**) overnight (Figure 8).<sup>[3b]</sup> This mole-

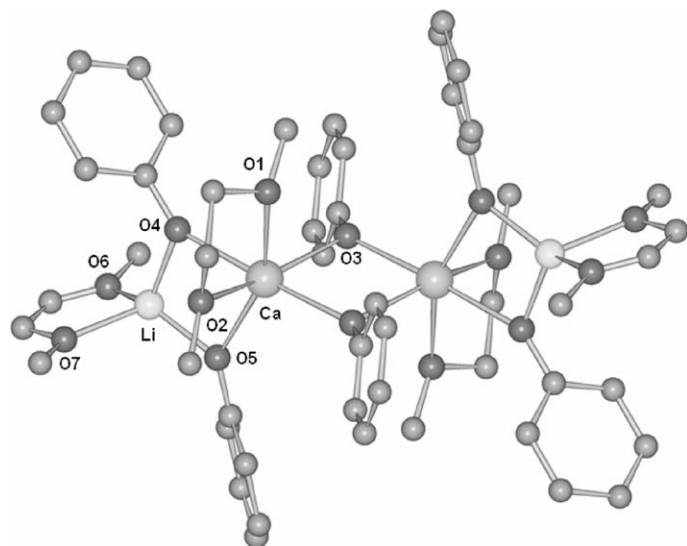


Figure 8. The DME derivative  $[\text{Ca}_2(\text{dme})_2(\text{OPh})_6\{\text{Li}(\text{dme})\}_2]$  (**14**); H atoms have been omitted for clarity.

cule consists of a bent chain arrangement of Li-Ca-Ca-Li in which the metal ions are bridged pairwise by two phenolate groups each and symmetric Li-Ca-Ca angles of  $141.83(6)^\circ$ . The structure of **14** can therefore also be described as a chain of two  $\text{LiCaO}_2$  rhombi linked to a  $\text{Ca}_2\text{O}_2$  rhombus through a calcium cation. Each cation is furthermore coordinated by a terminal DME ligand, so that the calcium cation reaches a distorted octahedral coordination sphere, whereas lithium is surrounded by four oxygen atoms in the form of a distorted tetrahedron. This linear motif has already been observed in different compounds with lithium,<sup>[4,49]</sup> sodium,<sup>[46]</sup> and even potassium<sup>[50]</sup> as external metals, and alkaline earth or transition metals as the central metals.

The values of the Ca-O distances formed by the four bridging aryloxide groups (average  $\text{Ca-O}(\text{OPh}) = 2.281(1) \text{ \AA}$ ) compare well with the ones observed in the literature, and the Li-O bond lengths (average  $\text{Li-O}(\text{OPh}) = 1.864(3) \text{ \AA}$ ) are slightly shorter than literature data.<sup>[29,38]</sup> The Ca-O distances to the DME ligands (average  $\text{Ca-O}(\text{dme}) = 2.440(2) \text{ \AA}$ ) are slightly longer than those observed in  $[\text{Ca}(\text{dme})_3]\text{I}$  (average  $\text{Ca-O}(\text{dme}) = 2.423 \text{ \AA}$ <sup>[51]</sup>), but correspond well with others observed in the literature.<sup>[30,52]</sup> The Li-O bond lengths to the DME groups (average  $\text{Li-O}(\text{dme}) = 1.986(3) \text{ \AA}$ ) compare well with those observed in the literature.<sup>[53]</sup> We have shown previously by <sup>7</sup>Li NMR studies, that compounds **5** and **14** are related insofar, as single crystals of **5** transform into the THF-derivative of **14**, namely  $[\text{Ca}_2(\text{thf})_n(\text{OPh})_6\{\text{Li}(\text{thf})\}_m]$ , when dissolved in THF, and yield

compound **14** and LiOPh upon recrystallisation from DME.<sup>[3b]</sup>

A different derivative of the clusters  $[\text{MNa}_6(\text{OPh})_8(\text{thf})_6]$  is obtained when they are treated with the bidentate ligand DME. Thus, the reaction of an excess of NaOPh in THF with  $\text{CaI}_2$  forms a light brown solution, which was evaporated to dryness. At room temperature, the solid residue was recrystallized from DME, and afforded single crystals of  $[\{\text{Ca}(\text{dme})_2(\text{OPh})_6\}\{\text{Na}(\text{dme})\}_2]$  (**15**). Compound **15** crystallizes in the monoclinic space group  $P2_1/n$  (No. 14) with two molecules per unit cell. The structure of **15** (Figure 9) is

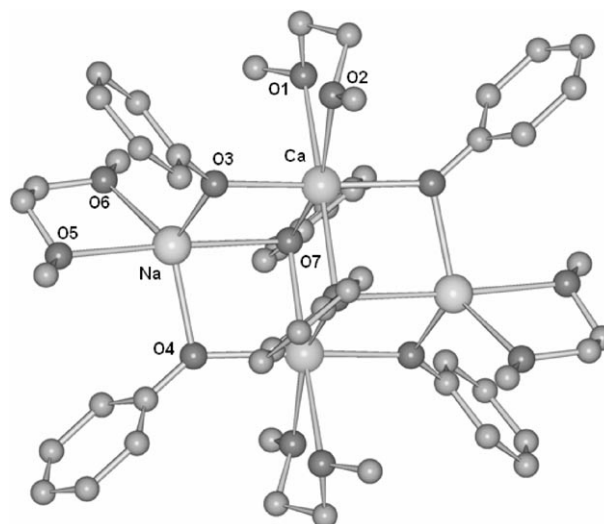


Figure 9. DME derivative  $[\{\text{Ca}(\text{dme})_2(\text{OPh})_6\}\{\text{Na}(\text{dme})\}_2]$  (**15**); H atoms have been omitted for clarity.

common for 1:1 heterometallic  $\text{M}, \text{M}'$ -alkoxides,<sup>[54]</sup>  $\text{M}, \text{M}'$ -aryloxides<sup>[55]</sup> and other compounds<sup>[56]</sup> (this is also true for  $\text{M}' = \text{M}$ ). With metal ions of a higher oxidation state, usually with transition metals, the Lewis coordinating molecules are formally replaced by other anionic ligands in order to neutralize the clusters. This motif can be described as a two connected face-sharing cubes, each with one vertex missing. The structure of **15** consists of a distorted square of metal cations with calcium and sodium in opposite vertices. The metal ions, calcium and sodium, are linked by one  $\mu$ -OPh group and both calcium cations are linked to each sodium cation with one  $\mu_3$ -OPh group. The metal cations are coplanar due to an inversion center found in the geometrical middle of the rhombi  $\text{Ca}_2(\text{O}7)_2$ . Each cation is furthermore coordinated by a terminal DME ligand, so that the calcium cations reach a coordination number of six (distorted octahedral), whereas the sodium cations have a common coordination number of five (distorted trigonal bipyramid). The Na- $\mu_3$ -OPh distances in **15** (average  $2.506(1) \text{ \AA}$ ) are longer than the distances found in the compounds **10-12** as well as those cited above, probably due to different binding partners and the higher coordination number. The phenyl rings of the OPh groups bridging the two calcium and sodium cations



are parallel, as are the phenyl rings of the OPh groups of opposite vertices due to symmetry. Two intramolecular C–H... $\pi$  interactions due to symmetry exist between the phenyl rings of  $\mu$ -OPh and  $\mu_3$ -OPh phenolate groups in a T-shape conformation. Moreover, one very weak intermolecular hydrogen bond can be found between molecules through one phenyl ring and one DME molecule with a H3...O1 distance of 3.011(1) Å, leading to the formation of sheets.

Although compounds **14** and **15** are structurally very different, they do possess the same general formula  $[\text{Ca}_2(\text{dme})_2(\text{OPh})_6\{\text{M}'(\text{dme})_2\}]$  ( $\text{M}' = \text{Li}$  **14**, Na **15**), whereas the cluster compounds  $[\text{CaM}'_6(\text{OPh})_8(\text{thf})_6]$  ( $\text{M}' = \text{Li}$  **5**, Na **10**), obtained from THF, possess the same general formula but also the same general structural motif. The only difference between **5**, **14** and **10**, **15** is the nature of the alkali metal ion. Thus, we can expect that the packing of the phenyl rings of the phenolate anions in the compounds **5** and **10** forces the sodium cations in compound **10** to only allow a low coordination number four, with one terminal THF molecule, whereas smaller lithium cations in compound **5** are well satisfied with this situation. However, in the presence of DME, the structures of **14** and **15** are presumably less compact than their “THF analogues” **5** and **10**, respectively, meaning a less strong packing of phenolate ligands around the metal cations. This can be reflected by the coordination of one DME molecule to each metal cation in **14** and **15**, whereas in **5** and **10** the alkali cations accept one THF molecule to complete their coordination sphere. In **14** and **15**, both alkali cations adopt their usual coordination geometry, a distorted tetrahedral for lithium atoms in **14** and a trigonal bipyramidal arrangement for the sodium cations in **15**.

After results obtained with calcium clusters, we were interested in studying the influence of the Lewis coordinating DME solvent on clusters  $[\text{MLi}_6(\text{OPh})_8(\text{thf})_6]$  ( $\text{M} = \text{Sr}$  **6**, Ba **7**). Indeed, does the size of the alkaline earth metal also have an influence on the structure after addition of DME? Previous results show that strontium and barium are similar to each other with the preparation of clusters with the same composition **6**, **7**, **11**, and **12**, and also as far as the formation of  $[\text{MI}_2(\text{dme})_3]$  ( $\text{M} = \text{Sr}$ , Ba) is concerned.<sup>[51]</sup> These last compounds differ from the Ca compound, namely  $[\text{Ca}(\text{dme})_3\text{I}]$ , in which one iodide is lost in the direct coordination sphere of the calcium cation.

Unfortunately, attempts to recrystallize **7** from DME were not successful. Nevertheless, the same procedure for the cluster **6** leads to the crystallization of two new compounds. The first one was obtained after two weeks treatment of **6** with DME, leading to single crystals of  $[(\mu\text{-dme})\{\text{SrLi}_6(\text{OPh})_8(\text{thf})_4\}]$  (**16**; Figure 10). The quality of the single crystals was not very good; however, the structure could be solved to give satisfactory unambiguous positions for the heavy atoms. To obtain a better quality data and a lower  $R_1$  factor for **16**, which is also due to high disorder in one terminal coordinating THF molecule, another single crystal was measured three months later, revealing yet another new crystal structure  $[(\mu\text{-dme})\{\text{SrLi}_6(\text{OPh})_8(\text{thf})_2(\text{dme})_2\}]$  (**17**; Figure 11). Compounds **16** and **17** crystallize in the mono-

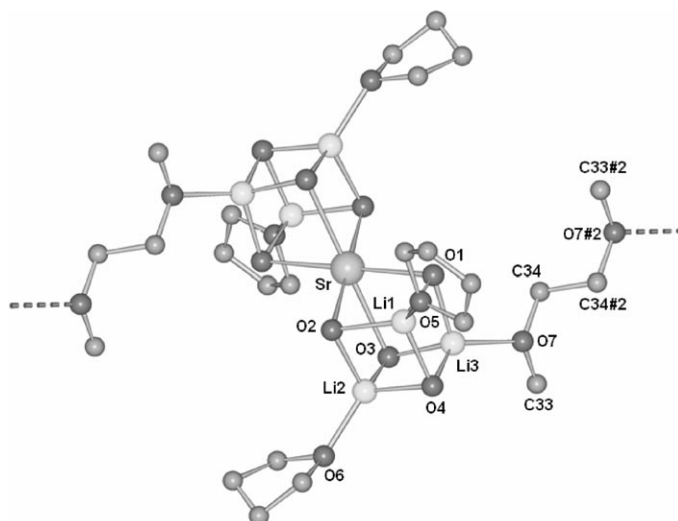


Figure 10. DME-derivative  $[(\mu\text{-dme})\{\text{SrLi}_6(\text{OPh})_8(\text{thf})_4\}]$  **16**; phenyl rings and H atoms have been omitted for clarity.

clinic space group  $P2_1/n$  (No. 14) with two units per unit cell.

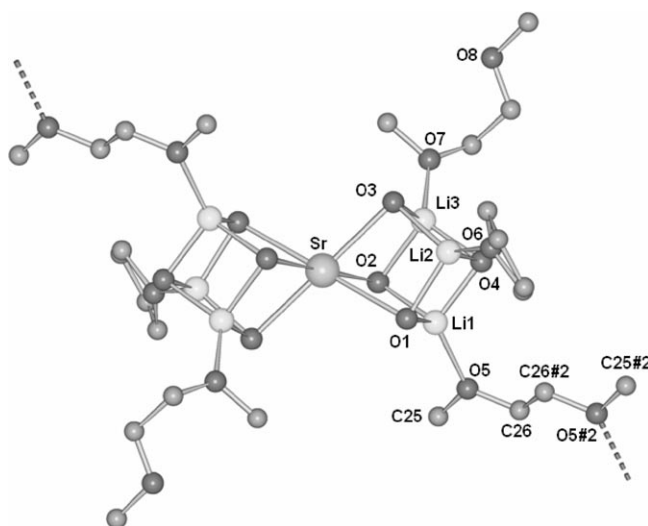


Figure 11. Another DME derivative  $[(\mu\text{-dme})\{\text{SrLi}_6(\text{OPh})_8(\text{thf})_2(\text{dme})_2\}]$  **17**; phenyl rings and H atoms have been omitted for clarity.

These two compounds **16** and **17** have very similar structures, and also resemble that of the initial compound **11**. Indeed the  $\{\text{SrLi}_6(\text{OPh})_8\}$  core of the structure remains in all compounds the same. In **16**, one terminally THF molecule binding to a lithium cation in each asymmetric unit of **11** has been replaced by one DME molecule, which now acts as a  $\mu$ -bridge between two neighboring cluster units, leading to a one-dimensional chain of  $\text{SrLi}_6$  clusters. The two other lithium cations still carry their terminally bonded THF molecule. In **17**, the bridge between the cluster units through the DME ligand is still present as in **16**, but in addition another DME molecule has formally replaced one terminally

coordinating THF molecule per asymmetric unit, and acts now as a terminal DME ligand, binding with only one oxygen atom. This is a rare coordination mode for the DME molecule. In both compounds **16** and **17**, DME acts as a monodentate ligand to a cation, one behaves as a bridging ligand through the oxygen atoms giving rise to an infinite polymer, whereas the other one, in **17**, acts as a terminal monodentate DME ligand. In both structures, a crystallographic center of inversion is located between the two methylene carbon atoms of the bridging DME ligand and relates cluster units forming a one-dimensional polymeric chain.

The complete substitution of THF by DME was not observed so far. As a third DME ligand would probably also act as monodentate terminal ligand, disorder can increase due to the dangling part of the monodentate ligands. It might be that compound **17** is an intermediate to another linked system in which the clusters are connected by DME ligands in all three directions. They would then, however, have to come very close to each other; this might be hindered by the phenolate ligands.

Compared to **10**, compound **11** does not spontaneously dissociate into an analogue Sr compound to give **14**. Instead, simple substitution of THF by DME takes place as a very slow process. How can this be accounted for? The calcium cation is relatively small and has to carry six large OPh anions at a distance of 2.375(9) Å. The Sr cation is 0.18 Å larger in ionic radius, but the Sr–OPh distances are only 0.14 Å longer than the Ca–OPh contacts in **10**. This could be representative of a more “comfortable” placement of the ligands around the Sr ions with respect to the Ca ion, meaning also less tension in the alkaline earth metal ion environment.

## Conclusion

For Group 2 metal clusters, a series of cluster compounds were isolated and characterized:

- $[\text{IM}(\text{O}t\text{Bu})_4\{\text{Li}(\text{thf})_4(\text{OH})\}]$  ( $M = \text{Ca}, \text{Sr}, \text{Ba}, \text{Eu}$ )
- $[\text{Li}(\text{thf})_4][\{\text{Sr}_6(\text{O}t\text{Bu})_7(\mu_3\text{-I})(\text{I})_2(\text{thf})_3\}_2(\mu\text{-I})]$
- $[\text{MLi}_6(\text{OPh})_8(\text{thf})_6]$  ( $M = \text{Ca}, \text{Sr}, \text{Ba}, \text{Sm}, \text{Eu}$ )
- $[\text{MNa}_6(\text{OPh})_8(\text{thf})_6]$  ( $M = \text{Ca}, \text{Sr}, \text{Ba}$ )
- $[\text{CaLi}_6(\text{OPh})_6(\text{O}t\text{Bu})_2(\text{thf})_6]$
- $[\{\text{Ca}(\text{dme})_2(\text{OPh})_6\{\text{M}'(\text{dme})_2\}]$  ( $M' = \text{Li}, \text{Na}$ )
- $[(\mu\text{-dme})\{\text{SrLi}_6(\text{OPh})_8(\text{thf})_{4-n}(\text{dme})_n\}]$  ( $n = 0$  or  $2$ )

Several conclusions can be drawn from these series of results:

- 1) We were able to show that substitution reactions and coordination chemistry similar to transition metals are possible. Depending of different major factors, such as the bulk of the R group of the alkoxide or aryloxy reagents associated with the nature of the alkali metal and the resulting basicity, 50, 75, or even 100% of iodide present in the initial starting materials can be eliminated.

- 2) Alkaline earth metal ions present similar if not the same cluster types as divalent lanthanide ions. No significant changes of the structures are observed upon formal substitution of the  $M^{2+}$  metal ion.
- 3) Introducing a mix of alkyl and aryl oxide anions does not influence the structure type for  $[\text{CaLi}_6(\text{OPh})_6(\text{O}t\text{Bu})_2(\text{thf})_6]$ . Different ratios of the ligands are currently being investigated.
- 4) The formal substitution of the smaller lithium ion by the larger sodium ion has no influence with the terminal monodentate ligand THF for the compounds  $[\text{CaM}'_6(\text{OPh})_8(\text{thf})_6]$ , but influences strongly in the case of the bidentate ligand DME as shown in the set of compounds  $[\{\text{Ca}(\text{dme})_2(\text{OPh})_6\{\text{M}'(\text{dme})_2\}]$ .
- 5) The compounds  $[\text{MLi}_6(\text{OPh})_8(\text{thf})_6]$  show different strained structures, as shown by their behavior against the bidentate ligand DME. Whereas the comparatively small calcium ions relaxes easily into the new structure  $[\{\text{Ca}(\text{dme})_2(\text{OPh})_6\{\text{Li}(\text{dme})_2\}]$ , the analogue strontium compound remains intact, with simple substitution of the outer THF ligands by DME in order to form one-dimensional chains.

These results show the huge variety of structures possible in the chemistry of alkaline earth metal ions and divalent f elements, reminiscent of transition-metal cluster chemistry. They also give hints on possible aggregates that might be formed as intermediates in organic synthesis during reactions with superbases for instance. The study of such cluster compounds in non-aqueous solvents is so promising for the discovery of new aggregate types that we will continue our efforts of research in this field.

## Experimental Section

**General:** All experiments were carried out under an inert nitrogen or argon atmosphere, using Schlenk techniques. The solvents THF and DME were dried over Na/benzophenone ketyl and distilled under nitrogen prior to use. The NMR spectra for **2** and **3** were recorded on a Varian Gemini 300 spectrometer and for other compounds were carried out on a Bruker DRX-400 MHz with dried deuterated solvents, the chemical shifts are relative to TMS as an internal standard.  $^7\text{Li}$  and  $^{23}\text{Na}$  NMR measurements for all compounds, except **2** and **3**, were performed on a Bruker Avance 600 MHz with 1 M LiCl or 0.1 M NaCl, respectively, in  $\text{D}_2\text{O}$  in sealed capillaries as external standard. The IR spectrum of **1** was acquired on a Shimadzu FTIR-8400S spectrometer equipped with a golden Gate ATR (attenuated total reflection) system. The IR spectra of **2** and **3** were registered on a Perkin–Elmer Spectrum One FT-IR spectrometer on CsI plates in Nujol. Further elemental analyses or investigations other than single-crystal structure analysis were usually difficult due to air and water sensitivity of the compounds when taken from the mother solution. Compounds **1–4** contain OH groups that were not deliberately added to the reaction solution, but were present in the starting material of commercial (Aldrich) 1 M solution of LiO*t*Bu in THF, as could be shown with Gilman titrations of LiOH. Typically, a freshly opened 1 M solution of LiO*t*Bu in THF contained up to 0.22 M LiOH (and 0.83 M LiO*t*Bu) in addition to an insoluble white deposit of additional LiOH. Such deposits were not observed for the solutions of MOPh, for which no MOH could be detected.

**[Ca(O<sup>t</sup>Bu)<sub>4</sub>(Li(thf))<sub>4</sub>(OH)]·THF (1)**

**Method A:** CaI<sub>2</sub> (0.294 g, 1.00 mmol) was dried for 30 min under vacuum at 300 °C and was dissolved in freshly dried and distilled THF (20 mL) under magnetic stirring; the resulting solution was then heated to reflux for 15 min. At room temperature, a 1 M solution of LiO<sup>t</sup>Bu in THF (10 equiv, 10.0 mL) was added dropwise under nitrogen. The solution was left at room temperature under magnetic stirring for two days. Afterwards the solution was filtered. The yellow brown solution was cooled to -25 °C to give colorless single crystals of **1** with a small amount of white precipitate within one week in a yield of 45% with respect to CaI<sub>2</sub>.

**Method B:** CaI<sub>2</sub> (0.302 g, 1.03 mmol) was dried for 30 min under vacuum at 300 °C and then dissolved in a 1:1 mixture of freshly dried and distilled THF/DME (30 mL), heating to reflux under magnetic stirring to give the starting material [CaI<sub>2</sub>(dme)<sub>2</sub>(thf)]. At room temperature, a 1 M solution of LiO<sup>t</sup>Bu in THF (4 equiv, 4.1 mL) was added dropwise under nitrogen, followed by the same workup as in method A (yield of 70% with respect to CaI<sub>2</sub>). Elemental analysis calcd (%) for C<sub>36</sub>H<sub>77</sub>Li<sub>4</sub>CaIO<sub>10</sub> (864.72 g mol<sup>-1</sup>): C 50.00, H 8.97; found: C 44.71, H 8.07% (large discrepancies due to solvent loss during preparation of the sample); IR:  $\tilde{\nu}$  = 2885 (w), 1462 (w), 1357 (m), 1200 (s), 1036 (m), 957 (s), 902 (m), 758 (w), 655 (w), 594 cm<sup>-1</sup> (m); <sup>7</sup>Li NMR data (233.23 MHz, [D<sub>8</sub>]THF):  $\delta$  = 0.953 ppm; <sup>13</sup>C NMR data (CD<sub>3</sub>CN):  $\delta$  = 26.16 (m, CH<sub>2</sub>), 31.33 (s, CH<sub>3</sub>), 68.21 ppm (m, CH<sub>2</sub>O); <sup>1</sup>H NMR data (CD<sub>3</sub>CN):  $\delta$  = 1.17 (s, CH<sub>3</sub>), 1.80 (m, CH<sub>2</sub>), 3.64 ppm (m, CH<sub>2</sub>O).

**[Sr(O<sup>t</sup>Bu)<sub>4</sub>(Li(thf))<sub>4</sub>(OH)] (2):** A 1 M solution of LiO<sup>t</sup>Bu containing LiOH (15%) in THF (5 mmol, 5 mL) was added to a white suspension of SrI<sub>2</sub> (0.39 g, 1.1 mmol) in THF (25 mL), to yield a yellow turbid solution after 2 h of stirring at room temperature. After filtration of the precipitate, the yellow solution was allowed to stand at room temperature. Colorless single crystals of **2** (in a yield of 50% referred to SrI<sub>2</sub>) suitable for X-ray analysis grew from the solution in a few days. IR (CsI, Nujol):  $\tilde{\nu}$  = 3676 (w), 3545 (m), 2993 (s), 2923 (Nujol), 2818 (s), 1769 (w), 1595 (m), 1476 (s), 1459 (Nujol), 1427 (s), 1376 (Nujol), 1360 (m), 1083 (w), 857 (s), 722 (Nujol), 502 cm<sup>-1</sup> (s); MS/EI (low-resolution mass data (centroid)): *m/z* (%): 45 (9), 55 (54), 56 (13), 57 (100), 59 (38) [(CH<sub>2</sub>)<sub>2</sub>COH]<sup>+</sup>, 67 (14), 69 (35), 70 (6), 71 (24), 81 (20), 83 (22), 85 (11), 95 (20), 97 (17), 109 (11), 111 (7), 128 (5); <sup>7</sup>Li NMR (116 MHz, [D<sub>8</sub>]THF):  $\delta$  = 0.29 ppm; <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  = 1.05 (s, CH<sub>3</sub>), 1.41 (m, CH<sub>2</sub>), 3.57 ppm (m, CH<sub>2</sub>O); <sup>1</sup>H NMR ([D<sub>8</sub>]THF):  $\delta$  = 1.14 (s, CH<sub>3</sub>), 1.78 (m, CH<sub>2</sub>), 3.62 ppm (m, CH<sub>2</sub>O).

**[Ba(O<sup>t</sup>Bu)<sub>4</sub>(Li(thf))<sub>4</sub>(OH)] (3):** BaI<sub>2</sub> was dried under vacuum at 200 °C and the reaction carried out under nitrogen atmosphere. A 0.2 M solution of LiO<sup>t</sup>Bu (4 mmol) in THF (20 mL) was added to BaI<sub>2</sub> (0.391 g, 1 mmol) and LiOH (0.024 g, 1 mmol) dissolved in freshly dried and distilled THF (20 mL) to yield a milky white solution after 30 min of stirring. The solution was cooled to -20 °C to give colorless crystals of **3** in a yield of 65% with respect to BaI<sub>2</sub>. IR (CsI, Nujol):  $\tilde{\nu}$  = 3584 (s), 3050 (vs, Nujol), 1596 (s, Nujol), 1440 (s, Nujol), 1374 (s, Nujol), 1260 (m), 1100 (w), 1020 (w), 802 (m), 497 (s, br), 275 (s), 238 (w); MS/EI (low-resolution): *m/z* (%): 889 (6) [M]<sup>+</sup>, 815 (8) [M-tBuOH]<sup>+</sup>, 741 (7) [M-2tBuOH]<sup>+</sup>, plus degradation compounds at 355 (10), 281 (56), 207 (100), 133 (16), 73 (38), 59 (3); <sup>7</sup>Li NMR (116 MHz, [D<sub>8</sub>]THF):  $\delta$  = 0.84 ppm; <sup>13</sup>C NMR ([D<sub>8</sub>]THF):  $\delta$  = 31.78 ppm (CH<sub>3</sub>); <sup>1</sup>H NMR ([D<sub>8</sub>]THF):  $\delta$  = 1.147 (s, CH<sub>3</sub>), 1.78 (m, CH<sub>2</sub>), 3.62 (m, CH<sub>2</sub>O), 4.5 ppm (s, OH).

**[Eu(O<sup>t</sup>Bu)<sub>4</sub>(Li(thf))<sub>4</sub>(OH)]·THF (4):** In a Labmaster glovebox under an inert atmosphere of nitrogen, a 1 M solution of LiO<sup>t</sup>Bu in THF (5 equiv, 4.3 mL) was added dropwise to solid EuI<sub>2</sub> (0.350 g, 0.86 mmol). The solution was left at room temperature under magnetic stirring for two days. Afterwards the solution was filtered. The red-brown solution was cooled to -25 °C to give small colorless single crystals of **4** with a small amount of green precipitate within six months in a very low yield which could not be estimated. Elemental analysis and NMR studies were unfortunately impossible to perform on this compound.

**[CaLi<sub>6</sub>(OPh)<sub>8</sub>(thf)<sub>6</sub>] (5):** CaI<sub>2</sub> (0.301 g, 1.02 mmol) was dried for 30 min under vacuum at 300 °C and was dissolved in freshly dried and distilled THF (20 mL) under magnetic stirring; the resulting solution was then heated to reflux for 15 min. At room temperature, a 1 M solution of

LiO<sup>t</sup>Bu in THF (10 equiv, 10.2 mL) was added dropwise under nitrogen. The solution was left at room temperature under magnetic stirring for two days. Afterwards the solution was evaporated to dryness yielding a brown solid which was partially dissolved in a 1:10 THF/hexane mixture (15 mL). The mixture was left at room temperature under magnetic stirring for one night and then filtered. Colorless single crystals of **5** suitable for X-ray analysis grew in a yield of 72% with respect to CaI<sub>2</sub> at room temperature within three days. Elemental analysis calcd (%) for C<sub>72</sub>H<sub>88</sub>CaLi<sub>6</sub>O<sub>14</sub> (1259.14): C 68.68, H 7.04, O 17.79; found: C 67.85, H 6.99, O 17.56; <sup>7</sup>Li NMR (233.23 MHz, [D<sub>8</sub>]THF):  $\delta$  = 0.79, 1.07 ppm; <sup>13</sup>C NMR ([D<sub>8</sub>]THF):  $\delta$  = 26.46 (m, CH<sub>2</sub>), 68.31 (m, CH<sub>2</sub>O), 114.24 (s, *para*), 118.95 (s, *ortho*), 129.63 ppm (s, *meta*); <sup>13</sup>C NMR data (CD<sub>3</sub>CN):  $\delta$  = 26.15 (s, CH<sub>2</sub>), 68.28 (s, CH<sub>2</sub>O), 115.59 (s, *para*), 120.71 (s, *ortho*), 129.49 (s, *meta*), 166.58 ppm (s, basal Ph); <sup>1</sup>H NMR ([D<sub>8</sub>]THF):  $\delta$  = 1.77 (m, CH<sub>2</sub>), 3.62 (m, CH<sub>2</sub>O), 6.38 (brd, CH *ortho*), 6.71 (brd, CH *meta*), 6.94 ppm (brt, CH *para*).

**[SrLi<sub>6</sub>(OPh)<sub>8</sub>(thf)<sub>6</sub>] (6):** SrI<sub>2</sub> (0.351 g, 1.03 mmol) was dried for 30 min under vacuum at 300 °C and was dissolved in freshly dried and distilled THF (25 mL) under magnetic stirring; the resulting solution was then heated to reflux for 15 min. At room temperature, a 1 M solution of LiO<sup>t</sup>Bu in THF (10 equiv, 10.3 mL) was added dropwise under nitrogen. The solution was left at room temperature under magnetic stirring for two days. Afterwards the solution was evaporated to dryness yielding a brown solid which was partially dissolved in a 1:10 THF/hexane mixture (15 mL). The mixture was left at room temperature under magnetic stirring for one night and then filtered. Colorless single crystals of **6** suitable for X-ray analysis grew in a yield of 56% with respect to SrI<sub>2</sub> at -25 °C within three days. Elemental analysis calcd (%) for C<sub>72</sub>H<sub>88</sub>SrLi<sub>6</sub>O<sub>14</sub> (1306.68): C 66.18, H 6.79; found: C 64.03, H 6.67; <sup>7</sup>Li NMR (233.23 MHz, [D<sub>8</sub>]THF):  $\delta$  = 0.975, 0.825 ppm (hydrolysis of the solution is envisaged); <sup>13</sup>C NMR ([D<sub>8</sub>]THF):  $\delta$  = 26.37 (m, CH<sub>2</sub>), 68.21 (m, CH<sub>2</sub>O), 114.79 (s, *para*), 119.41 (s, *ortho*), 129.62 ppm (s, *meta*); <sup>1</sup>H NMR ([D<sub>8</sub>]THF):  $\delta$  = 1.78 (m, CH<sub>2</sub>), 3.62 (m, CH<sub>2</sub>O), 6.39 (t, *J* = 7.2 Hz), 6.60 (d, *J* = 7.6 Hz), 6.95 ppm (t, *J* = 7.7 Hz).

**[BaLi<sub>6</sub>(OPh)<sub>8</sub>(thf)<sub>6</sub>] (7):** BaI<sub>2</sub> (0.402 g, 1.03 mmol) was dried for 30 min under vacuum at 300 °C and was dissolved in freshly dried and distilled THF (25 mL) under magnetic stirring; the resulting solution was then heated to reflux for 15 min. The mixture was allowed to cool to room temperature and a 1 M solution of LiO<sup>t</sup>Bu in THF (10 equiv, 10.3 mL) was added dropwise under nitrogen. The solution was left at room temperature under magnetic stirring for two days. Afterwards the solution was evaporated to dryness yielding a brown solid which was partially dissolved in a 1:10 THF/hexane mixture (15 mL). The mixture was left at room temperature under magnetic stirring for one night and then filtered. Colorless single crystals of **7** suitable for X-ray analysis grew in a yield of 68% with respect to BaI<sub>2</sub> at -25 °C within three days. elemental analysis calcd (%) for C<sub>72</sub>H<sub>88</sub>BaLi<sub>6</sub>O<sub>14</sub> (1356.45): C 63.75, H 6.54; found: C 60.51, H 6.07; <sup>7</sup>Li NMR (233.23 MHz, [D<sub>8</sub>]THF):  $\delta$  = 0.821 ppm; <sup>13</sup>C NMR ([D<sub>8</sub>]THF): 26.36 (m, CH<sub>2</sub>), 68.21 (m, CH<sub>2</sub>O), 114.38 (s, *para*), 119.82 (s, *ortho*), 129.59 (s, *meta*), 167.92 ppm (s, basal Ph); <sup>1</sup>H NMR ([D<sub>8</sub>]THF):  $\delta$  = 1.78 (m, CH<sub>2</sub>), 3.62 (m, CH<sub>2</sub>O), 6.36 (t, *J* = 7.1 Hz), 6.59 (d, *J* = 7.8 Hz), 6.95 (t, *J* = 7.4 Hz).

**[SmLi<sub>6</sub>(OPh)<sub>8</sub>(thf)<sub>6</sub>] (8):** In the labmaster glovebox, a 1 M solution of LiO<sup>t</sup>Bu in THF (10 equiv, 10 mL) was added dropwise under nitrogen to a 0.1 M solution of SmI<sub>2</sub> in THF (10 mL, 1.0 mmol). The blue-purple solution was left at room temperature under magnetic stirring for two days. Afterwards the solution was evaporated to dryness yielding a blue solid, which was partially dissolved in a 1:10 THF/hexane mixture (15 mL). The mixture was left at room temperature under magnetic stirring for one night and then filtered. Colorless single crystals of **8** suitable for X-ray analysis grew in a yield of 45% with respect to SmI<sub>2</sub> at -25 °C within two weeks at low temperature (-25 °C); <sup>13</sup>C NMR ([D<sub>8</sub>]THF):  $\delta$  = 26.31 (m, CH<sub>2</sub>), 68.18 (m, CH<sub>2</sub>O), 115.33, 118.78, 129.53 ppm (m, Ph); <sup>1</sup>H NMR ([D<sub>8</sub>]THF):  $\delta$  = 1.63 (m, CH<sub>2</sub>), 3.47 (m, CH<sub>2</sub>O), 6.28 (t, *J* = 7.0 Hz), 6.45 (d, *J* = 7.8 Hz), 6.82 ppm (t, *J* = 7.5 Hz).

**[EuLi<sub>6</sub>(OPh)<sub>8</sub>(thf)<sub>6</sub>] (9):** In the labmaster glovebox, a 1 M solution of LiO<sup>t</sup>Bu in THF (10 equiv, 10.1 mL) was added dropwise under nitrogen to EuI<sub>2</sub> (0.410 g, 1.01 mmol). The colorless solution was left at room tem-

perature under magnetic stirring for two days. Afterwards the solution was evaporated to dryness yielding a light green-blue solid, which was partially dissolved in a 1:10 THF/hexane mixture (15 mL). The mixture was left at room temperature under magnetic stirring for one night and then filtered. Colorless single crystals of **9** suitable for X-ray analysis grew in a yield of 24% with respect to  $\text{EuI}_2$  within two weeks at  $-25^\circ\text{C}$ . Unfortunately, crystals of **9** are very sensitive to air and moisture and the crystals melt within two minutes of the mother liquor being removed, even though working under argon. Elemental analysis and NMR studies were unfortunately impossible to perform on these samples or gave inconsistent results.

**[CaNa<sub>6</sub>(OPh)<sub>8</sub>(thf)<sub>6</sub>] (10)**: In a schlenk tube,  $\text{CaI}_2$  (0.301 g, 1.02 mmol) was dried for 30 min under vacuum at  $300^\circ\text{C}$  and then dissolved in freshly dried and distilled THF (15 mL) under magnetic stirring; the resulting solution was then heated to reflux for 15 min. In another schlenk,  $\text{NaOPh}\cdot 3\text{H}_2\text{O}$  (10 equiv, 1.742 g) was dried for 30 min under vacuum at  $300^\circ\text{C}$  and then dissolved in freshly dried and distilled THF (20 mL). At room temperature, both solutions are mixed together under nitrogen. The resulting solution was left at room temperature under magnetic stirring for two days. Afterwards the solution was evaporated to dryness yielding a light brown solid, which was partially dissolved in a 1:10 THF/hexane mixture (15 mL). The mixture was left at room temperature under magnetic stirring for one night and then filtered. Colorless single crystals of **10** suitable for X-ray analysis grew in a yield of 65% with respect to  $\text{CaI}_2$  within three days at  $-25^\circ\text{C}$ . Elemental analysis calcd (%) for  $\text{C}_{72}\text{H}_{88}\text{CaNa}_6\text{O}_{14}$  (1355.44): C 63.80, H 6.54; found: C 57.70, H 5.46 (due to fast loss of solvent molecules);  $^{23}\text{Na}$  NMR ( $[\text{D}_8]\text{THF}$ ):  $\delta = 1.23$  ppm (br);  $^{13}\text{C}$  NMR ( $[\text{D}_8]\text{THF}$ ):  $\delta = 26.36$  (m,  $\text{CH}_2$ ), 68.21 (m,  $\text{CH}_2\text{O}$ ), 114.59 (s, *para*), 119.68 (s, *ortho*), 129.62 (s, *meta*), 167.14 ppm (s, basal Ph);  $^1\text{H}$  NMR ( $[\text{D}_8]\text{THF}$ ):  $\delta = 1.78$  (m,  $\text{CH}_2$ ), 3.62 (m,  $\text{CH}_2\text{O}$ ), 6.35 (t,  $J = 7.1$  Hz), 6.68 (d,  $J = 7.6$  Hz), 6.92 ppm (t,  $J = 7.7$  Hz).

**[SrNa<sub>6</sub>(OPh)<sub>8</sub>(thf)<sub>6</sub>] (11)**: In a schlenk tube,  $\text{SrI}_2$  (0.362 g, 1.06 mmol) was dried for 30 min under vacuum at  $300^\circ\text{C}$  and was dissolved in freshly dried and distilled THF (15 mL) under magnetic stirring; the resulting solution was then heated to reflux for 15 min. In another schlenk,  $\text{NaOPh}\cdot 3\text{H}_2\text{O}$  (10 equiv, 1.804 g) was dried for 30 min under vacuum at  $300^\circ\text{C}$  and then dissolved in freshly dried and distilled THF (20 mL). At room temperature, both solutions are mixed together under nitrogen. The resulting solution was left at room temperature under magnetic stirring for two days. Afterwards the solution was evaporated to dryness yielding a light brown solid, which was partially dissolved in a 1:10 THF/hexane mixture (15 mL). The mixture was left at room temperature under magnetic stirring for one night and then filtered. Colorless single crystals of **11** suitable for X-ray analysis grew in a yield of 63% with respect to  $\text{SrI}_2$  at  $-25^\circ\text{C}$  within three days at low temperature ( $-25^\circ\text{C}$ ). Elemental analysis calcd (%) for  $\text{C}_{72}\text{H}_{88}\text{SrNa}_6\text{O}_{14}$  (1402.98): C 61.62, H 6.31; found: C 59.83, H 5.95.

**[BaNa<sub>6</sub>(OPh)<sub>8</sub>(thf)<sub>6</sub>] (12)**: In a schlenk tube,  $\text{BaI}_2$  (0.405 g, 1.03 mmol) was dried for 30 min under vacuum at  $300^\circ\text{C}$  and was dissolved in freshly dried and distilled THF (15 mL) under magnetic stirring; the resulting solution was then heated to reflux for 15 min. In another schlenk,  $\text{NaOPh}\cdot 3\text{H}_2\text{O}$  (10 equiv, 1.762 g) was dried for 30 min under vacuum at  $300^\circ\text{C}$  and then dissolved in freshly dried and distilled THF (20 mL). At room temperature, both solutions are mixed together under nitrogen. The solution was left at room temperature under magnetic stirring for two days. Afterwards the solution was evaporated to dryness yielding a light brown solid, which was partially dissolved in a 1:10 THF/hexane mixture (15 mL). The mixture was left at room temperature under magnetic stirring for one night and then filtered. Colorless single crystals of **12** suitable for X-ray analysis grew in a yield of 65% with respect to  $\text{BaI}_2$  at  $-25^\circ\text{C}$  within three days at low temperature ( $-25^\circ\text{C}$ ). Elemental analysis calcd (%) for  $\text{C}_{72}\text{H}_{88}\text{BaNa}_6\text{O}_{14}$  (1452.70): C 59.51, H 6.11; found: C 56.63, H 6.02;  $^{23}\text{Na}$  NMR ( $[\text{D}_8]\text{THF}$ ):  $\delta = 2.58$  ppm (br);  $^{13}\text{C}$  NMR ( $[\text{D}_8]\text{THF}$ ):  $\delta = 26.36$  (m,  $\text{CH}_2$ ), 68.21 (m,  $\text{CH}_2\text{O}$ ), 112.66 (s, *para*), 119.54 (s, *ortho*), 129.69 (s, *meta*), 169.95 ppm (s, basal Ph);  $^1\text{H}$  NMR ( $[\text{D}_8]\text{THF}$ ):  $\delta = 1.77$  (m,  $\text{CH}_2$ ), 3.61 (m,  $\text{CH}_2\text{O}$ ), 6.22 (d,  $J = 7.1$  Hz), 6.49 (d,  $J = 8.0$  Hz), 6.86 ppm (t,  $J = 7.7$  Hz).

**[CaLi<sub>6</sub>(OPh)<sub>6</sub>(*o*-Bu)<sub>2</sub>(thf)<sub>6</sub>] (13)**:  $\text{CaI}_2$  (0.298 g, 1.01 mmol) was dried for 30 min under vacuum at  $300^\circ\text{C}$  and was dissolved in freshly dried and distilled THF (25 mL) under magnetic stirring; the resulting solution was then heated to reflux for 15 min. At room temperature, a 1 M solution of  $\text{LiOPh}$  in THF (5 equiv, 5.1 mL) and a 1 M solution of  $\text{LiO}i\text{Bu}$  in THF (5 equiv, 5.1 mL) was added dropwise under nitrogen. The solution was left at room temperature under magnetic stirring for two days. Afterwards the solution was evaporated to dryness yielding a brown solid, which was partially dissolved in a 1:10 THF/hexane mixture (15 mL). The mixture was left at room temperature under magnetic stirring for one night and then filtered. Colorless single crystals of **13** suitable for X-ray analysis grew in a yield of 53% with respect to  $\text{CaI}_2$  at  $-25^\circ\text{C}$  within three days. elemental analysis calcd (%) for  $\text{C}_{68}\text{H}_{96}\text{CaLi}_6\text{O}_{14}$  (1219.17): C 66.99, H 7.94; found: C 60.95, H 6.46 (fast loss of solvent);  $^{13}\text{C}$  NMR ( $\text{CD}_3\text{CN}$ ):  $\delta = 26.79$  (m,  $\text{CH}_2$ ), 32.03 (s,  $\text{CH}_3$ ), 68.9 (m,  $\text{CH}_2\text{O}$ ), 116.26 (s, *para*), 121.31 (s, *ortho*), 130.35 (s, *meta*), 167.04 ppm (s, basal Ph).

**[Ca(dme)<sub>2</sub>(OPh)<sub>6</sub>{Li(dme)}<sub>2</sub>] (14)**:  $\text{CaI}_2$  (0.2696 g, 0.92 mmol) was dried for 30 min under vacuum at  $300^\circ\text{C}$  and was dissolved in freshly dried and distilled THF (20 mL) under magnetic stirring; the resulting solution was then heated to reflux for 15 min. At room temperature, a 1 M solution of  $\text{LiOPh}$  in THF (6 equiv, 5.5 mL) was added dropwise under nitrogen. The solution was left at room temperature under magnetic stirring for two days. Afterwards the solution was evaporated to dryness yielding a brown solid, which was partially dissolved in DME (10 mL). The mixture was left at room temperature under magnetic stirring for one night and then filtered. During the night at room temperature, colorless single-crystals of **14** suitable for X-ray analysis grew in a yield of 64% with respect to  $\text{CaI}_2$  at room temperature. elemental analysis calcd (%) for  $\text{C}_{52}\text{H}_{70}\text{Ca}_2\text{Li}_2\text{O}_{14}$  (1013.12): C 61.65, H 6.96, O 22.11; found: C 59.47, H 6.87, O 21.79;  $^7\text{Li}$  NMR (233.23 MHz,  $[\text{D}_{10}]\text{DME}$ ):  $\delta = 1.01$  ppm;  $^{13}\text{C}$  NMR ( $\text{CD}_3\text{CN}$ ):  $\delta = 58.80$  (s,  $\text{CH}_3$ ), 72.04 (s,  $\text{CH}_2\text{O}$ ), 115.63 (s, *para*), 120.92 (s, *ortho*), 129.20 (s, *meta*), 166.23 ppm (s, basal Ph);  $^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ ):  $\delta = 3.27$  (s,  $\text{CH}_3$ ), 3.44 (m,  $\text{CH}_2$ ), 6.42 (br d, CH *ortho*), 6.71 (m, CH *meta*); 6.86 ppm (br t, CH *para*);  $^1\text{H}$  NMR data ( $[\text{D}_8]\text{THF}$ ):  $\delta = 3.27$  (br d,  $\text{CH}_3$ ), 3.43 (br d,  $\text{CH}_2$ ), 6.42 (br d, CH *ortho*), 6.73 (br d, CH *meta*), 6.95 ppm (m, CH *para*).

**[Ca(dme)<sub>2</sub>(OPh)<sub>6</sub>{Na(dme)}<sub>2</sub>] (15)**: In a schlenk tube,  $\text{CaI}_2$  (0.301 g, 1.02 mmol) was dried for 30 min under vacuum at  $300^\circ\text{C}$  and was dissolved in freshly dried and distilled THF (15 mL) under magnetic stirring; the resulting solution was then heated to reflux for 15 min. In another schlenk,  $\text{NaOPh}\cdot 3\text{H}_2\text{O}$  (10 equiv, 1.742 g) was dried for 30 min under vacuum at  $300^\circ\text{C}$  and then dissolved in freshly dried and distilled THF (20 mL). At room temperature, both solutions were mixed together under nitrogen. The solution was left at room temperature under magnetic stirring for two days. Afterwards the solution was evaporated to dryness yielding a brown solid, which was partially dissolved in DME (10 mL). The mixture was left at room temperature under magnetic stirring for one night and then filtered. Colorless single crystals of **15** suitable for X-ray analysis grew in a yield of 65% with respect to  $\text{CaI}_2$  within three days at  $-25^\circ\text{C}$ . elemental analysis calcd (%) for  $\text{C}_{52}\text{H}_{70}\text{Ca}_2\text{Na}_2\text{O}_{14}$  (1045.22): C 59.75, H 6.75; found: C 58.62, H 6.43;  $^{23}\text{Na}$  NMR ( $[\text{D}_8]\text{THF}$ ):  $\delta = 1.14$  ppm (br);  $^{13}\text{C}$  NMR ( $[\text{D}_8]\text{THF}$ ):  $\delta = 58.90$  (m,  $\text{CH}_3$ ), 72.72 (m,  $\text{CH}_2$ ), 112.58 (s, *para*), 119.45 (s, *ortho*), 129.75 (s, *meta*), 170.26 ppm (s, basal Ph);  $^1\text{H}$  NMR ( $[\text{D}_8]\text{THF}$ ):  $\delta = 3.27$  (m,  $\text{CH}_3$ ), 3.43 (m,  $\text{CH}_2$ ), 6.23 (t,  $J = 7.1$  Hz), 6.47 (d,  $J = 7.7$  Hz), 6.88 ppm (t,  $J = 7.7$  Hz).

**[(*n*-dme){SrLi<sub>6</sub>(OPh)<sub>8</sub>(thf)<sub>4</sub>] (16) and [(*n*-dme){SrLi<sub>6</sub>(OPh)<sub>8</sub>(thf)<sub>2</sub>(dme)<sub>2</sub>] (17)**:  $\text{SrI}_2$  (0.387 g, 1.13 mmol) was dried for 30 min under vacuum at  $300^\circ\text{C}$  and was dissolved in freshly dried and distilled THF (15 mL) under magnetic stirring; the resulting solution was then heated to reflux for 15 min. The  $\text{SrI}_2$  did not completely dissolve; at room temperature, a 1 M solution of  $\text{LiOPh}$  in THF (10 equiv, 10.3 mL) was added dropwise under nitrogen to the milky white solution. The solution was left at room temperature under magnetic stirring for two days. Afterwards the solution was evaporated to dryness yielding a brown solid, which was partially dissolved in DME (10 mL). The mixture was left at room temperature under magnetic stirring for one night and then filtered. Colorless single crystals of **16** suitable for X-ray analysis grew in a yield of ca. 22% with respect to  $\text{SrI}_2$  at  $-25^\circ\text{C}$  within one week. Three

months later, another single-crystal was picked, but melted rapidly due to its sensitivity to air and moisture even working under an atmosphere of argon. The yield was impossible to estimate. It was impossible to characterize spectroscopically and analytically the compounds **16** and **17**, except by X-ray diffraction.

**X-ray experiments:** Single crystals were mounted on a glass fiber and all geometric and intensity data were taken from this crystal. Data collection with  $\text{MoK}\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) was performed, at the University of Basel on a STOE IPDS-II diffractometer equipped with an Oxford Cryo-system open flow cryostat.<sup>[58]</sup> Absorption corrections were partially integrated in the data reduction procedure.<sup>[59]</sup> The structures were solved by direct methods (SHELXS) and refined using full-matrix least-squares on  $F^2$  (SHELXL-97<sup>[60]</sup>). All heavy atoms could be refined anisotropically, but were not refined for the final structure in case of heavy disorder of solvent molecules. Some  $R$  values therefore remained relatively high. Hydrogen atoms were introduced as fixed contributors when a residual electronic density was observed near their expected positions. CCDC-616797 (**1**), 616798 (**4**), 296413 (**5**), 616799 (**6**), 616800 (**7**), 616802 (**8**), 616801 (**9**), 616803 (**10**), 616804 (**11**), 616805 (**12**), 616807 (**13**), 296414 (**14**), 616806 (**15**), 644607 (**16**) and 644608 (**17**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif). For the other compounds, data have been submitted previously.

**[Ca(OtBu)<sub>4</sub>[Li(thf)<sub>4</sub>(OH)]·THF (1):**  $\text{C}_{36}\text{H}_{77}\text{Li}_4\text{CaO}_{10}$ ,  $M_r = 864.72 \text{ g mol}^{-1}$ , tetragonal,  $P4/nmm$  (No. 129),  $a = 15.5962(14)$ ,  $c = 9.9953(9) \text{ \AA}$ ,  $V = 2431.3(4) \text{ \AA}^3$ ,  $Z = 2$ ,  $\rho_{\text{calcd}} = 1.181 \text{ Mg m}^{-3}$ ,  $F(000) = 916$ ,  $T = 203 \text{ K}$ ,  $\mu(\text{MoK}\alpha) = 0.807 \text{ mm}^{-1}$ ,  $1.80 < \theta < 27.20^\circ$ , 1525 reflections of which 1525 unique and 596 observed, 69 parameters refined, GOOF (on  $F^2$ ) = 0.987,  $R1 = \Sigma |F_o - F_c| / \Sigma F_o = 0.1061$ ,  $wR2 = 0.3143$  for  $I > 2\sigma(I)$  and  $R1 = 0.1624$ ,  $wR2 = 0.3476$  for all data. All heavy atoms were refined anisotropically, except for the methyl groups of disordered *t*Bu units and some disordered THF molecules. Several batches of crystals were measured, trying to improve the crystal quality and the data, but without success so far. However, the structure of the cluster could be attributed without any doubt. The disorder observed for *t*Bu groups and THF, leads to the high  $R1$  value. The highest peak in remaining electron density of 0.72 is found near iodide ions. The positions of the hydrogen atoms could not be calculated due to the heavy disorder, but were included in the determination of the molar mass.

**[Eu(OtBu)<sub>4</sub>[Li(thf)<sub>4</sub>(OH)]·THF (4):**  $\text{C}_{36}\text{H}_{77}\text{Li}_4\text{EuO}_{10}$ ,  $M_r = 976.60 \text{ g mol}^{-1}$ , tetragonal,  $P4/nmm$  (No. 129),  $a = 15.4602(8)$ ,  $c = 12.800(1) \text{ \AA}$ ,  $V = 2437.4(2) \text{ \AA}^3$ ,  $Z = 2$ ,  $\rho_{\text{calcd}} = 1.331 \text{ Mg m}^{-3}$ ,  $F(000) = 1002$ ,  $T = 203 \text{ K}$ ,  $\mu(\text{MoK}\alpha) = 1.963 \text{ mm}^{-1}$ ,  $1.86 < \theta < 27.15^\circ$ , 18914 reflections of which 1524 unique and 1339 observed, 68 parameters refined, GOOF (on  $F^2$ ) = 1.731,  $R1 = \Sigma |F_o - F_c| / \Sigma F_o = 0.0770$ ,  $wR2 = 0.2022$  for  $I > 2\sigma(I)$  and  $R1 = 0.0918$ ,  $wR2 = 0.2141$  for all data. All heavy atoms were refined anisotropically, except for the methyl groups of disordered *t*Bu units and some disordered THF molecules. However, the structure of the cluster **4** could be attributed without any doubt. The disorder observed for *t*Bu groups and THF, leads to the reasonable  $R1$  value. The highest peak in remaining electron density of 1.32 is found near the iodide ions. The positions of the hydrogen atoms could not be calculated due to the heavy disorder, but were included in the determination of the molar mass.

**[CaLi<sub>6</sub>(OPh)<sub>8</sub>(thf)<sub>6</sub> (5):**  $\text{C}_{72}\text{H}_{88}\text{O}_{14}\text{Li}_6\text{Ca}$ ,  $M_r = 1259.14 \text{ g mol}^{-1}$ , monoclinic,  $P2_1/n$  (No. 14),  $a = 12.6187(9)$ ,  $b = 21.0709(10)$ ,  $c = 13.3065(10) \text{ \AA}$ ,  $\beta = 92.039(6)^\circ$ ,  $V = 3535.8(4) \text{ \AA}^3$ ,  $Z = 2$ ,  $\rho_{\text{calcd}} = 1.183 \text{ Mg m}^{-3}$ ,  $F(000) = 1340$ ,  $T = 203 \text{ K}$ ,  $\mu(\text{MoK}\alpha) = 0.149 \text{ mm}^{-1}$ ,  $1.81 < \theta < 27.20^\circ$ , 28126 reflections of which 7438 unique and 4715 observed, 422 parameters refined, GOOF (on  $F^2$ ) = 1.025,  $R1 = \Sigma |F_o - F_c| / \Sigma F_o = 0.0719$ ,  $wR2 = 0.1856$  for  $I > 2\sigma(I)$  and  $R1 = 0.1119$ ,  $wR2 = 0.2137$  for all data.

**[SrLi<sub>6</sub>(OPh)<sub>8</sub>(thf)<sub>6</sub> (6):**  $\text{C}_{72}\text{H}_{88}\text{Li}_6\text{SrO}_{14}$ ,  $M_r = 1306.68 \text{ g mol}^{-1}$ , monoclinic,  $P2_1/n$  (No. 14),  $a = 12.5866(6)$ ,  $b = 21.3721(12)$ ,  $c = 13.2208(6) \text{ \AA}$ ,  $\beta = 92.415(4)^\circ$ ,  $V = 3553.3(3) \text{ \AA}^3$ ,  $Z = 2$ ,  $\rho_{\text{calcd}} = 1.221 \text{ Mg m}^{-3}$ ,  $F(000) = 1376$ ,  $T = 203 \text{ K}$ ,  $\mu(\text{MoK}\alpha) = 0.819 \text{ mm}^{-1}$ ,  $2.28 < \theta < 27.12^\circ$ , 27501 reflections of which 7217 unique and 6059 observed, 422 parameters refined, GOOF (on  $F^2$ ) = 0.842,  $R1 = \Sigma |F_o - F_c| / \Sigma F_o = 0.0518$ ,  $wR2 = 0.1465$  for  $I > 2\sigma(I)$  and  $R1 = 0.0627$ ,  $wR2 = 0.1606$  for all data.

**[BaLi<sub>6</sub>(OPh)<sub>8</sub>(thf)<sub>6</sub> (7):**  $\text{C}_{72}\text{H}_{88}\text{Li}_6\text{BaO}_{14}$ ,  $M_r = 1356.40 \text{ g mol}^{-1}$ , triclinic,  $P\bar{1}$  (No. 2),  $a = 12.644(3)$ ,  $b = 13.113(3)$ ,  $c = 13.418(3) \text{ \AA}$ ,  $\alpha = 62.51(3)$ ,  $\beta = 66.20(3)$ ,  $\gamma = 87.96(3)^\circ$ ,  $V = 1774.3(7) \text{ \AA}^3$ ,  $Z = 1$ ,  $\rho_{\text{calcd}} = 1.269 \text{ Mg m}^{-3}$ ,  $F(000) = 706$ ,  $T = 203 \text{ K}$ ,  $\mu(\text{MoK}\alpha) = 0.620 \text{ mm}^{-1}$ ,  $1.79 < \theta < 29.15^\circ$ , 2615 reflections unique and observed, 421 parameters refined, GOOF (on  $F^2$ ) = 1.202,  $R1 = \Sigma |F_o - F_c| / \Sigma F_o = 0.1083$ ,  $wR2 = 0.2545$  for  $I > 2\sigma(I)$  and  $R1 = 0.1083$ ,  $wR2 = 0.2545$  for all data.

**[EuLi<sub>6</sub>(OPh)<sub>8</sub>(thf)<sub>6</sub> (8):**  $\text{C}_{72}\text{H}_{88}\text{Li}_6\text{EuO}_{14}$ ,  $M_r = 1371.02 \text{ g mol}^{-1}$ , monoclinic,  $P2_1/n$  (No. 14),  $a = 12.6257(13)$ ,  $b = 21.4887(18)$ ,  $c = 13.1836(13) \text{ \AA}$ ,  $\beta = 92.611(8)^\circ$ ,  $V = 3572.9(6) \text{ \AA}^3$ ,  $Z = 2$ ,  $\rho_{\text{calcd}} = 1.274 \text{ Mg m}^{-3}$ ,  $F(000) = 1426$ ,  $T = 203 \text{ K}$ ,  $\mu(\text{MoK}\alpha) = 0.938 \text{ mm}^{-1}$ ,  $1.81 < \theta < 26.97^\circ$ , 19472 reflections of which 7372 unique and 3467 observed, 374 parameters refined, GOOF (on  $F^2$ ) = 1.234,  $R1 = \Sigma |F_o - F_c| / \Sigma F_o = 0.1634$ ,  $wR2 = 0.2930$  for  $I > 2\sigma(I)$  and  $R1 = 0.2939$ ,  $wR2 = 0.3550$  for all data.

**[SmLi<sub>6</sub>(OPh)<sub>8</sub>(thf)<sub>6</sub> (9):**  $\text{C}_{72}\text{H}_{88}\text{Li}_6\text{SmO}_{14}$ ,  $M_r = 1369.41 \text{ g mol}^{-1}$ , monoclinic,  $P2_1/n$  (No. 14),  $a = 12.5617(11)$ ,  $b = 21.439(2)$ ,  $c = 13.1273(13) \text{ \AA}$ ,  $\beta = 92.769(7)^\circ$ ,  $V = 3531.2(6) \text{ \AA}^3$ ,  $Z = 2$ ,  $\rho_{\text{calcd}} = 1.288 \text{ Mg m}^{-3}$ ,  $F(000) = 1424$ ,  $T = 203 \text{ K}$ ,  $\mu(\text{MoK}\alpha) = 0.892 \text{ mm}^{-1}$ ,  $2.45 < \theta < 27.16^\circ$ , 5946 reflections of which 5072 unique and 3959 observed, 422 parameters refined, GOOF (on  $F^2$ ) = 1.047,  $R1 = \Sigma |F_o - F_c| / \Sigma F_o = 0.0523$ ,  $wR2 = 0.1333$  for  $I > 2\sigma(I)$  and  $R1 = 0.0668$ ,  $wR2 = 0.1460$  for all data.

**[CaNa<sub>6</sub>(OPh)<sub>8</sub>(thf)<sub>6</sub> (10):**  $\text{C}_{72}\text{H}_{88}\text{Li}_6\text{CaO}_{14}$ ,  $M_r = 1355.44 \text{ g mol}^{-1}$ , monoclinic,  $P2_1/n$  (No. 14),  $a = 13.398(3)$ ,  $b = 19.727(4)$ ,  $c = 13.885(3) \text{ \AA}$ ,  $\beta = 96.78(3)^\circ$ ,  $V = 3644.2(13) \text{ \AA}^3$ ,  $Z = 2$ ,  $\rho_{\text{calcd}} = 1.235 \text{ Mg m}^{-3}$ ,  $F(000) = 1436$ ,  $T = 203 \text{ K}$ ,  $\mu(\text{MoK}\alpha) = 0.182 \text{ mm}^{-1}$ ,  $1.80 < \theta < 27.38^\circ$ , 26472 reflections of which 7596 unique and 2621 observed, 422 parameters refined, GOOF (on  $F^2$ ) = 0.951,  $R1 = \Sigma |F_o - F_c| / \Sigma F_o = 0.0939$ ,  $wR2 = 0.2114$  for  $I > 2\sigma(I)$  and  $R1 = 0.2211$ ,  $wR2 = 0.2785$  for all data.

**[SrNa<sub>6</sub>(OPh)<sub>8</sub>(thf)<sub>6</sub> (11):**  $\text{C}_{72}\text{H}_{88}\text{Li}_6\text{SrO}_{14}$ ,  $M_r = 1402.98 \text{ g mol}^{-1}$ , monoclinic,  $P2_1/n$  (No. 14),  $a = 13.1422(12)$ ,  $b = 21.5560(3)$ ,  $c = 13.3541(11) \text{ \AA}$ ,  $\beta = 100.512(7)^\circ$ ,  $V = 3719.6(5) \text{ \AA}^3$ ,  $Z = 2$ ,  $\rho_{\text{calcd}} = 1.253 \text{ Mg m}^{-3}$ ,  $F(000) = 1472$ ,  $T = 203 \text{ K}$ ,  $\mu(\text{MoK}\alpha) = 0.819 \text{ mm}^{-1}$ ,  $2.21 < \theta < 27.18^\circ$ , 12490 reflections of which 6585 unique and 4459 observed, 422 parameters refined, GOOF (on  $F^2$ ) = 1.119,  $R1 = \Sigma |F_o - F_c| / \Sigma F_o = 0.0719$ ,  $wR2 = 0.1889$  for  $I > 2\sigma(I)$  and  $R1 = 0.1106$ ,  $wR2 = 0.2112$  for all data.

**[BaNa<sub>6</sub>(OPh)<sub>8</sub>(thf)<sub>6</sub> (12):**  $\text{C}_{72}\text{H}_{88}\text{Li}_6\text{BaO}_{14}$ ,  $M_r = 1452.70 \text{ g mol}^{-1}$ , monoclinic,  $P2_1/n$  (No. 14),  $a = 13.0582(6)$ ,  $b = 21.4307(12)$ ,  $c = 13.3046(7) \text{ \AA}$ ,  $\beta = 101.749(4)^\circ$ ,  $V = 3645.2(3) \text{ \AA}^3$ ,  $Z = 2$ ,  $\rho_{\text{calcd}} = 1.324 \text{ Mg m}^{-3}$ ,  $F(000) = 1508$ ,  $T = 203 \text{ K}$ ,  $\mu(\text{MoK}\alpha) = 0.641 \text{ mm}^{-1}$ ,  $1.85 < \theta < 27.18^\circ$ , 25544 reflections of which 7974 unique and 6526 observed, 422 parameters refined, GOOF (on  $F^2$ ) = 1.032,  $R1 = \Sigma |F_o - F_c| / \Sigma F_o = 0.0377$ ,  $wR2 = 0.0875$  for  $I > 2\sigma(I)$  and  $R1 = 0.0495$ ,  $wR2 = 0.0943$  for all data.

**[CaLi<sub>6</sub>(OPh)<sub>8</sub>(OtBu)<sub>2</sub>(thf)<sub>6</sub> (13):**  $\text{C}_{68}\text{H}_{96}\text{Li}_6\text{CaO}_{14}$ ,  $M_r = 1219.17 \text{ g mol}^{-1}$ , triclinic,  $P\bar{1}$  (No. 2),  $a = 12.489(3)$ ,  $b = 13.199(3)$ ,  $c = 13.824(3) \text{ \AA}$ ,  $\alpha = 101.50(3)$ ,  $\beta = 110.16(3)$ ,  $\gamma = 114.79(3)^\circ$ ,  $V = 1776.9(7) \text{ \AA}^3$ ,  $Z = 1$ ,  $\rho_{\text{calcd}} = 1.139 \text{ Mg m}^{-3}$ ,  $F(000) = 654$ ,  $T = 203 \text{ K}$ ,  $\mu(\text{MoK}\alpha) = 0.146 \text{ mm}^{-1}$ ,  $1.72 < \theta < 27.21^\circ$ , 14290 reflections of which 7296 unique and 2478 observed, 407 parameters refined, GOOF (on  $F^2$ ) = 0.956,  $R1 = \Sigma |F_o - F_c| / \Sigma F_o = 0.1031$ ,  $wR2 = 0.2143$  for  $I > 2\sigma(I)$  and  $R1 = 0.2481$ ,  $wR2 = 0.2843$  for all data.

**[[Ca(dme)]<sub>2</sub>(OPh)<sub>6</sub>[Li(dme)]<sub>2</sub> (14):**  $\text{C}_{52}\text{H}_{70}\text{Li}_2\text{Ca}_2\text{O}_{14}$ ,  $M_r = 1013.12 \text{ g mol}^{-1}$ , triclinic,  $P\bar{1}$  (No. 2),  $a = 10.9810(14)$ ,  $b = 11.1620(16)$ ,  $c = 14.197(2) \text{ \AA}$ ,  $\alpha = 103.438(11)$ ,  $\beta = 99.261(11)$ ,  $\gamma = 117.736(9)^\circ$ ,  $V = 1423.0(3) \text{ \AA}^3$ ,  $Z = 1$ ,  $\rho_{\text{calcd}} = 1.182 \text{ Mg m}^{-3}$ ,  $F(000) = 540$ ,  $T = 203 \text{ K}$ ,  $\mu(\text{MoK}\alpha) = 0.259 \text{ mm}^{-1}$ ,  $1.55 < \theta < 27.17^\circ$ , 11354 reflections of which 5814 unique and 2164 observed, 321 parameters refined, GOOF (on  $F^2$ ) = 0.922,  $R1 = \Sigma |F_o - F_c| / \Sigma F_o = 0.0750$ ,  $wR2 = 0.1659$  for  $I > 2\sigma(I)$  and  $R1 = 0.1885$ ,  $wR2 = 0.2241$  for all data.

**[[Ca(dme)]<sub>2</sub>(OPh)<sub>6</sub>[Na(dme)]<sub>2</sub> (15):**  $\text{C}_{52}\text{H}_{70}\text{Na}_2\text{Ca}_2\text{O}_{14}$ ,  $M_r = 1045.22 \text{ g mol}^{-1}$ , monoclinic,  $P2_1/n$  (No. 14),  $a = 11.8532(6)$ ,  $b = 14.7474(6)$ ,  $c = 16.7570(9) \text{ \AA}$ ,  $\beta = 103.158(4)^\circ$ ,  $V = 2852.3(2) \text{ \AA}^3$ ,  $Z = 2$ ,  $\rho_{\text{calcd}} = 1.217 \text{ Mg m}^{-3}$ ,  $F(000) = 1112$ ,  $T = 203 \text{ K}$ ,  $\mu(\text{MoK}\alpha) = 0.274 \text{ mm}^{-1}$ ,  $2.36 < \theta < 27.16^\circ$ , 21471 reflections of which 5991 unique and 5518 observed, 321 parameters refined, GOOF (on  $F^2$ ) = 1.047,  $R1 = \Sigma |F_o - F_c| / \Sigma F_o = 0.0389$ ,  $wR2 = 0.1058$  for  $I > 2\sigma(I)$  and  $R1 = 0.0421$ ,  $wR2 = 0.1086$  for all data.

**[(u-dme)[SrLi<sub>6</sub>(OPh)<sub>8</sub>(thf)<sub>4</sub>] (16):**  $\text{C}_{68}\text{H}_{82}\text{Li}_6\text{SrO}_{14}$ ,  $M_r = 1252.60 \text{ g mol}^{-1}$ , monoclinic,  $P2_1/n$  (No. 12),  $a = 11.4549(18)$ ,  $b = 22.739(4)$ ,  $c = 13.396(2) \text{ \AA}$ ,  $\beta = 101.438(12)^\circ$ ,  $V = 3419.9(9) \text{ \AA}^3$ ,  $Z = 2$ ,  $\rho_{\text{calcd}} = 1.216 \text{ Mg m}^{-3}$ ,  $F(000) =$

1316,  $T=203$  K,  $\mu(\text{Mo}_{\text{K}\alpha})=0.848$  mm<sup>-1</sup>,  $2.02 < \theta < 27.29^\circ$ , 19599 reflections of which 7001 unique and 2596 observed, 405 parameters refined, GOOF (on  $F^2$ ) = 1.245,  $R1 = \sum |F_o - F_c| / \sum F_o = 0.1381$ ,  $wR2 = 0.2776$  for  $I > 2\sigma(I)$  and  $R1 = 0.2977$ ,  $wR2 = 0.3483$  for all data. All heavy atoms were refined anisotropically. The positions of the hydrogen atoms could be calculated using riding models for all carbon atoms but high disorder was observed on two THF ligands.

**[(*u*-dme)(SrLi<sub>6</sub>(OPh)<sub>8</sub>(thf)<sub>2</sub>(dme)<sub>2</sub>)] (17):** C<sub>68</sub>H<sub>80</sub>Li<sub>6</sub>SrO<sub>16</sub>,  $M_r = 1288.63$  g mol<sup>-1</sup>, monoclinic,  $P2_1/n$  (No. 14),  $a = 12.8075(11)$ ,  $b = 19.2227(18)$ ,  $c = 14.3397(15)$  Å,  $\beta = 94.950(8)^\circ$ ,  $V = 3517.2(6)$  Å<sup>3</sup>,  $Z = 2$ ,  $\rho_{\text{calc}} = 1.217$  Mg m<sup>-3</sup>,  $F(000) = 1356$ ,  $T = 203$  K,  $\mu(\text{Mo}_{\text{K}\alpha}) = 0.828$  mm<sup>-1</sup>,  $1.78 < \theta < 26.93^\circ$ , 24964 reflections of which 7061 unique and 4632 observed, 415 parameters refined, GOOF (on  $F^2$ ) = 1.116,  $R1 = \sum |F_o - F_c| / \sum F_o = 0.1233$ ,  $wR2 = 0.3088$  for  $I > 2\sigma(I)$  and  $R1 = 0.1684$ ,  $wR2 = 0.3440$  for all data.

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