Organic heterobimetallic complexes of the alkaline earth metals (Ae = Ca, Sr, Ba) with tetrahedral metallate anions of three-valent metals (M = B, Al, Ga, and V)†‡§

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Heterobimetallic compounds with complex cations of the very electropositive alkaline earth metals (Ae) and organic tetrahedral anions of trivalent elements (M) form solvent-separated ions. Depending on the metals, they can be prepared by addition of carbanions or amides to MR_3, *via* reduction of $VMes_4$ with the alkaline earth metals and by transmetallation of $VMes_3$. For comparison reasons selected alkali metal derivatives are also included in this study. Average structural parameters of the boranates $[Ca(thf)_6][BPh_4]_2$ (**1**) and $[CaI(thf)_5][BPh_4]$ (**2**), the alanates $[Li(thf)_2(tmeda)][AlPh_3(tmp)]$ (**3**), $[(thf)_2K(N\text{-carbazolyl})_2AlMes_2]$ (**4**), and $[Sr(thf)_7][AlPh_4]_2$ (**5**), of the gallate $[Ca(dme)_4][GaEt_3(N\text{-carbazolyl})]_2$ (**6**), and of the vanadates $[Li(thf)_4][VMes_4]$ (**7**), $[CaI(thf)_5][VMes_4]$ (**8**), $[Ca(thf)_6][VMes_4]_2$ (**9**), and $[Sr(thf)_6][VMes_4]_2$ (**10**), are discussed. All these complexes contain complex cations of the type $[(L)_nM]^+$, and tetrahedral anions of the type $[ER_4]^-$. Only **4** crystallizes as a contact ion pair because the soft K^+ cation shows no preference for hard bases such as ethers or for soft arene π-systems.

Introduction

The chemistry of heterobimetallic compounds represents a vastly growing field because these compounds exhibit strongly different properties and reactivity than their homoleptic congeners. Therefore, metal metallates represent a substance class with a long history.[1] If the electronegativity of the involved metals differs significantly the formation of "ate" complexes is observed and solvent-separated or contact ion pairs are found. Often the s-block metals (alkali (A) and alkaline earth metals (Ae))[2,3] form the cation which can be coordinated by neutral Lewis bases such as ethers or amines, whereas the complex "ate" anions contain the nobler and more electronegative metal. In the case of rather similar electronegativities of the metals, the heterobimetallic complexes often prefer the formation of molecular cage or ring compounds. Despite the fact that the organometallic "ate" chemistry of the heavy alkaline earth metals, calcium, strontium, and barium, has a long tradition and that early reviews have already discussed their alanates,[4] boranates and zincates,[5–7] the development of an organometallic chemistry of the heavy alkaline earth metals has been revived in this area.[8–16] In contrast to the nearly uninvestigated organometallic "ate" chemistry of calcium and its heavier congeners, first structural investigations of a magnesium alanate, $Mg(AlMe_4)_2$, were published more than 40 years ago.[17] The first structural investigations of heterobimetallic organocalcium derivatives were performed on $[(Cp^*)_2Ca\{\mu\text{-}Me_3Al(thf)\}]$.[18] Recent reinvestigations of calcium alkylalanates [19] showed their similarity to the ytterbium derivatives (contact ions in $[(phen)Ca(AlMe_4)_2]$ and polymeric $[Ca(AlEt_4)_2]_\infty$) and their tendency to degrade tetrahydrofuran leading to solvent-separated $\{[(thf)_4Ca(\mu\text{-}O\text{-}CH{=}CH_2)]\ [AlMe_4]\}_2$. Mixed alkyl/aryl alanates show redistribution reactions leading to solvent-separated $[Ca(thf)_6][AlMe_{4-x}Ph_x]_2$.[20] Boranates with the BH_4^- anion of the heavier alkaline earth metals are well-known.[21] A partial substitution of the hydrogen atoms by organyl groups leads to very reactive boranates such as *e.g.* $[CaCp'(HBEt_3)(thf)_2]$.[22] Recent reinvestigations on calcium tetraphenylboranates showed that these $[BPh_4]^-$ units are weakly coordinating anions which support the formation of solvent-separated ions.[23]

Alkaline earth metal metallates of transition metals also gained attention in the last few years. However, the late transition metals copper and zinc form cuprates(I) and zincates(II) with the anions, $[CuR_2]^-$ with linear C–Cu–C units[24,25] and $[ZnR_3]^-$ with zinc atoms, in distorted trigonal planar environments,[2,3,26] respectively. A contact ion pair with a distorted tetrahedrally coordinated transition metal was reported for a calcium manganate(II).[27] Metallates with tetrahedrally coordinated metal centers are also known for vanadium(III).[28–30] These investigations showed that bulky mesityl groups have to be employed in order to stabilize the coordination number of four at vanadium. The smaller phenyl

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substituents allow the synthesis of vanadates(II) with octahedrally coordinated metal centers in $[\{Li(Et_2O)\}_4VPh_6]$.[31,32] In order to isolate vanadates(III) with tetra-coordinate metal atoms, larger aryl groups have to be bound at the V(III) center. Thus, larger groups such as mesityl[29,33] or 2,6-dimethoxyphenyl[34] are suitable substituents. Heteroleptic distorted tetrahedral vanadates with lithoxy,[35–37] siloxy groups[38] and others[39] are also feasible if the bulkiness of the substituents enforces a coordination number of four. Tetrahedral vanadates(III) were isolated too, from the metathesis reaction of $[VCl_3(thf)_3]$ with LiC_6Cl_5, yielding $[V(C_6Cl_5)_4]^-$ anions,[40] whereas the smaller pentafluorophenyl groups form penta-coordinate vanadates(III) of the metal center in a trigonal bipyramidal environment.[41] Reduction of $[V(Mes)_3(thf)]$ by sodium or potassium in the presence of nitrogen led to the formation of $[(diglyme)_2Na][Na(Mes)_3V–N_2–V(Mes)_3]$ and $[(diglyme)_2K][(Mes)_3V–N_2–V(Mes)_3]$, respectively.[42,43]

In order to explore heterobimetallic complexes of the heavy alkaline earth metals with tetrahedrally coordinated metallate anions we have chosen the lighter elements of the boron group as well as vanadium. The Allred–Rochow electronegativity values of these elements (B: 2.01, Al: 1.47, Ga: 1.82, and V: 1.45) are significantly larger than the values of the heavier alkaline earth metals (Ca: 1.04, Sr: 0.99, and Ba: 0.97); therefore, solvent-separated alkaline earth metal metallates can be expected for tetraarylmetallates of these elements.

Recent developments in the field of heavy Grignard reagents, in particular of aryl alkaline earth metal halides, paved the way for the synthesis of heterobimetallic organylalanates, zincates, and cuprates of the heavy alkaline earth metals. Extending these previous investigations, we herein extend this interesting chemistry to other trivalent metallates of boron, gallium, and vanadium.

Results and discussion

Synthesis and characterization

Due to the higher stability of the BPh_4^- anion in comparison to the corresponding alanate, alkaline earth metal tetraphenylboranates are easier to handle than their higher homologues. Different synthetic procedures have been developed to synthesize derivatives of Ca, Sr and Ba. Harder *et al.* reported the preparation of $[\{CaBr(thf)_4\}_2][BPh_4]_2$ by metathesis reaction of $[CaBr_2(thf)_4]$ and $NaBPh_4$.[44] Recently, Ruhlandt-Senge and co-workers developed an alternative approach *via* a transamination reaction between $M[N(SiMe_3)_2]_2$ and $[HNR_3][BPh_4]$.[23] Several tetraphenylboranates of Ca, Sr and Ba were prepared in this manner in the presence of additional neutral donors.

Inspired by recent advances in the synthesis of calcium organocuprates *via* transmetallation reactions, where the reduction of organocopper compounds by metallic calcium is the initial step,[24,25] an alternative route to alkaline earth metal boranates by reduction of $Ag[BPh_4]$ was envisioned. Although the reaction of the activated metal powders of Ca, Sr and especially Ba took place smoothly and silver was deposited, we were not able to isolate well defined alkaline earth metal boranates from these reaction solutions in THF. However, an alternative reaction of $Ag[BPh_4]$ and $[CaI(Tolyl)(thf)_4]$ at 0 °C results in immediate precipitation of $[Ca(thf)_6][BPh_4]_2$ (**1**) besides minor amounts of silver. Stepwise cooling of the mother liquor to −40 °C led to further crops of **1**. A silver-containing product of the reaction could not be isolated, precipitation of AgI did not occur. When the mother liquor of the reaction was further concentrated at low temperatures, a yellow-orange oil was obtained which did not crystallize even at −78 °C. It can be assumed that this residue contains organometallic silver complexes. Slow warm-up of this residue to room temperature led to decolorization and subsequent precipitation of metallic silver in agreement with the thermal lability of such organometallic silver compounds. Additionally, colorless crystals of $[CaI(thf)_5][BPh_4]$ (**2**) were deposited during this process. The analytical data obtained for **2** are in good agreement with related derivatives and therefore need no further discussion (see experimental section).

In the case of the higher homologue aluminium, the use of silver salts is not promising for the preparation of organometallic alkaline earth metal alanates, since the higher arylating power of organometallic aluminium compounds, in comparison with their borane analogs, would probably lead to labile argentates instead. However, other redox reactions like that of alanes and alkaline earth metals offer a suitable access to heterobimetallic alanates like $Ca(AlEt_4)_2$.[45,46] Tetraaryl-substituted derivatives can be prepared by reaction of $Al(aryl)_3$ and the corresponding arylalkaline earth metal derivatives as reported for calcium.[20]

Following our previous investigation,[47] the synthesis of further amido-substituted organoalanates was attempted. Besides group transfer reactions from calcium amides to alanes, the metathesis reaction of calcium halides and alkali metal alanates might offer a suitable pathway to such compounds. The starting materials $[Li(thf)_2(tmeda)][AlPh_3(tmp)]$ (**3**) (tmp = tetramethypiperidide) and $[(thf)_2K(N\text{-carbazolyl})_2AlMes_2]$ (**4**) were prepared in good yields from $[(Et_2O)AlPh_3]$ or $[(Et_2O)AlCl(Mes)_2]$ and the corresponding alkali metal amides (see eqn (1) and (2)).

$$\mathrm{Li(tmp)} + \mathrm{(Et_2O)AlPh_3} \xrightarrow[\text{tmeda}]{\text{THF/toluene}} [\mathrm{(thf)_2(tmeda)Li}]^+[\mathrm{Ph_3Al(tmp)}]^- \tag{1}$$

$$2\mathrm{K}(N\text{-carbazolyl}) + \mathrm{(Et_2O)AlMes_2Cl} \xrightarrow[-\text{KCl}]{\text{THF/Et}_2\text{O}} [\mathrm{(thf)_2K}\text{-}\eta^6(N\text{-carbazolyl})_2\mathrm{AlMes_2}] \tag{2}$$

However, metathesis reaction of **3** with calcium iodide results in a complicated reaction mixture and no well defined reaction product was obtained. Similar results were obtained from the reaction of **4** and calcium iodide. Although precipitation of potassium iodide occurred, the isolation of a pure product failed. On the one hand, this behaviour is most likely associated to the well known redistribution reactions of substituents in alanates.[20] On the other hand, the multihapto coordination mode of potassium with the mesityl groups by π-arene–metal interactions in **4** additionally stabilizes the complex and hampers an effective metathesis reaction. Due to these unsatisfying results observed in the case of calcium, only the synthesis of homoleptic tetraaryl alanates *via* aryl group transfer was envisioned for the heavier alkaline earth metals strontium and barium.

Unfortunately, the organometallic chemistry of strontium and barium is still underdeveloped in comparison to the organocalcium chemistry. For instance, there are only a few structurally characterized aryl derivatives of strontium and barium known. The first were synthesized by Niemeyer and co-workers *via* aryl transfer from mercury to the heavier alkaline earth metals.[48]

Although a Grignard-type reaction of those metals and aryl halides (especially iodides) is possible too, an active Schlenk equilibrium in combination with an altered reactivity in solvent degradation reactions has prevented the isolation of simple aryl derivatives of strontium and barium thus far. However, the recent isolation of such solvent degradation products, which contained residual phenyl groups, underlined the initial formation of arylstrontium and arylbarium halides in these reactions.[49] The high alkalinity of the reaction solutions additionally indicates that the lack of aryl derivatives of strontium and barium is more related to problems of isolation but not formation of these derivatives.[50] Following this assumption, such solutions should be useful as synthetic equivalents for isolated organostrontium or organobarium derivatives.

Consequently, the reaction of a solution, obtained from activated strontium and iodobenzene in THF, and $AlPh_3$, resulted in formation of the expected strontium tetraphenylalanate (**5**) which was isolated in good yield (see eqn (3)).

$$\{(\mathrm{thf})_x\mathrm{SrPh_2}\} + 2(\mathrm{Et_2O})\mathrm{AlPh_3} \xrightarrow{\mathrm{THF}} [(\mathrm{thf})_7\mathrm{Sr}]^{2+}2[\mathrm{Ph_4Al}]^- \qquad (3)$$

The ^{27}Al-NMR experiment clearly shows the presence of the solvent-separated and highly symmetrical alanate species in the characteristic field range for tetracoordinated aluminium atoms (125–180 ppm). The tetrahedral environment is reflected in the ^{27}Al shift of 132.9 ppm and a small half-height width of 23 Hz ($[CaI(thf)_5][AlPh_4]_2$: 132.9 ppm).[20] The linewidth increases markedly with the bulkiness of the ligands and the resulting distortion of the geometry of the complex.[51] Compounds **3** and **4** show half-height widths of more than 4000 Hz for **3** and of 3848 Hz for **4**, and lie in the region for comparable systems such as $[AlEt_2(NEt_2)]$ (1220 Hz)[52] and $[AlPh_3(tmeda)]$ (3900 Hz).[53]

Attempts to isolate a corresponding barium alanate failed due to the extreme reactivity of the arylbarium species in ether, leading to degradation reactions, and the high solubility of organobarium species.[49]

Besides alanes, the corresponding gallanes were also included in this investigation. In order to obtain a similar geometry around the group 13 metal center, the mesityl derivative Mes_3Ga was chosen as a starting material instead of Ph_3Ga to compensate for the growing ionic radius from aluminium (53 pm) to gallium (61 pm). In contrast to their lighter homologues, no well defined gallanates of the heavier alkaline earth metals were isolated from the reaction of Mes_3Ga with [Ae(aryl)I] (aryl = Ph, Mes; M = Ca, Sr, Ba). Instead, depending on the reaction conditions employed, amorphous powders or oils containing several unidentified products were obtained. This unsatisfying finding is in agreement with the literature where the chemistry of the species of type $[Ga(Ar)_4]^-$ is nearly exclusively limited to the $[Ga(C_6F_5)_4]^-$ anion.[54–57] Mes_3Ga is an exceedingly weak Lewis acid and there are no stable adducts known with Lewis bases such as THF or Et_2O. In contrast to the aluminiumtriorganyls (which form Lewis acid–base adducts immediately), the considerably reduced Lewis acidity of $Ga(aryl)_3$ results in a nearly trigonal planar arrangement around the gallium center with the mesityl groups in a propeller-like arrangement.[58,59] In order to demonstrate that the group transfer from calcium to an organometallic gallium species represents a suitable procedure for the synthesis of calcium gallates, we varied the substituents at calcium as well as at gallium. Hence, the addition reaction of triethylgallane and $[Ca(dme)_2(NPh_2)_2]$ yielded the organometallic derivative of the formula $[Ca(dme)_4][GaEt_3(N\text{-carbazolyl})]_2$ (**6**) (eqn (4)). Compound **6** was formed during a period of two weeks by successive precipitation of a white solid, which was completely insoluble in common organic solvents. The diphenylamido group was dehydrogenated by oxidative C–H bond functionalization, resulting in cyclization and formation of the carbazolyl moiety. This type of reaction normally occurs by treatment of palladium acetate under reflux or microwave irradiation.[60] NMR spectroscopic investigations indicate the presence of *only* one species and there are no signs of ligand redistribution equilibria in contrast to the observations for alanate ions $[AlMe_{4-x}Ph_x]^-$ in solution. Interestingly, a similar reaction, which was carried out with triethylalane instead of triethylgallane, does not lead to a comparable ring closure in NMR experiments; instead, solely the expected addition reaction was observed.

$$2(\mathrm{dme})_2\mathrm{Ca}(\mathrm{NPh_2})_2 + 2\mathrm{GaEt_3} \xrightarrow[\substack{-''\mathrm{CaH_2}'' \\ -2''\mathrm{Ph_2NH}''}]{\mathrm{toluene}} [(\mathrm{dme})_4\mathrm{Ca}]^{2+}2[\mathrm{Et_3Ga}(N\text{-carbazolyl})]^- \qquad (4)$$

With vanadium, a transition metal is included, which resembles gallium with respect to its ion radius, while its electronegativity is more similar to aluminium (Al 1.47, V 1.45, Ga 1.82; Allred-Rochow). In contrast to gallium, tetramesityl vanadates are well known. A look at the alkali metal derivatives guides the way to the related chemistry of the alkaline earth metals. Besides the transmetallation reaction of LiMes and $[VMes_3(thf)]$, the reaction of alkali metals with $[VMes_3(thf)]$ is suitable to generate such alkali metal tetramesityl vanadates.[28] This chemistry has been well known for decades and $[Li(thf)_4][VMes_4]$ (**7**) was originally prepared from LiMes and $VMes_3$. Here we present the crystal structure of $[Li(thf)_4][VMes_4]$ (**7**).

The same strategy as used for the lithium compound allowed the preparation of the calcium derivative too. However, the reaction between $[CaI(Mes)(thf)_4]$ and $[VMes_3(thf)]$ is challenging because the high reactivity of the mesitylcalcium derivative promotes solvent degradation and rearrangement reactions.[61] These side reactions led to a product mixture from which pure $[CaI(thf)_5][VMes_4]$ (**8**) was obtained *via* fractional crystallization in low yield. The violet crystals are extremely air-sensitive and react upon exposure to air, as observed for the lithium derivative, to red $VMes_4$ as the major vanadium-containing species.[62] Alternatively, the reaction of metallic calcium and $[VMes_3(thf)]$ yields small amounts of

$[Ca(thf)_6][VMes_4]_2$ (**9**). The stabilization and isolation of low-valent vanadium species formed in the course of the reaction, as postulated for the related reaction of potassium and $[VMes_3(thf)]$,[28] was attempted by addition of cyclooctadiene, but failed. In light of the previous results, an alternative strategy to alkaline earth metal tetraarylvanadates seems highly desirable. The vanadium(IV) compound $[VMes_4]$ is a promising starting material. Therefore, the reversal of its formation by oxidation of tetramesityl vanadates was investigated. Highly divided metal powders of the heavier alkaline earth metals, calcium, strontium and barium, were employed as reducing agents in THF. While the reaction proceeded smoothly for barium, in the case of strontium much longer reaction times were necessary. Even after two days, only about one fifth of the starting material was consumed. However, the separation of the product and the educts is simple (see experimental section) and pure $\{[Sr(thf)_6][VMes_4]_2\}$ (**10**) was obtained. In the case of calcium no reaction at all was observed. These differences in reactivity seem to be not only related to their reducing power, but also to the affinity of those metals or their cations to aromatic π-systems. Probably, the side-on coordination of metal species to the mesityl group is an important step in the reduction of the highly shielded vanadium(IV) center in $V(aryl)_4$. Some additional evidence for this hypothesis is provided by the reaction of barium with $VMes_4$. While the reaction solution in THF showed the typical dark violet color of the $[VMes_4]^-$ anion, precipitation of the product with diethyl ether yielded a green solid. This color change might be related to a coordination of the barium cation to the mesityl groups under formation of a contact ion pair in the solid state. In addition, the reduction can also be performed in toluene, leading to a similar green product. If the compound is dissolved in donor solvents such as THF or 1,2-dimethoxyethane (DME), the dark violet color reappears and solvent-separated ions of $[Ba(dme)_5][VMes_4]_2 \cdot n$DME are formed.

Structural investigations

The compounds **1** to **10** are displayed in Fig. 1–10. In all these representations the ellipsoids show a probability level of 40% and the hydrogen atoms are neglected for clarity. Average values of selected structural parameters are listed in Table 1.

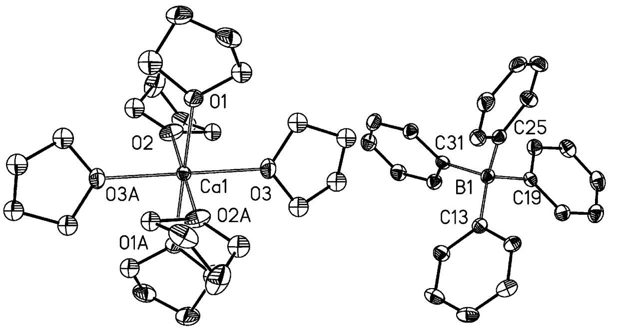

Fig. 1 Molecular structure and numbering scheme of $[Ca(thf)_6][BPh_4]_2$ (**1**). Symmetry-related atoms (−*x* + 1, −*y*, −*z* + 1) are marked with an "A"; the symmetry-related $[BPh_4^-]$ anion is omitted for clarity. Selected bond lengths (pm): Ca1–O1 234.2(3), Ca1–O2 232.5(3), Ca1–O3 234.1(3), B1–C13 164.7(6), B1–C19 165.9(6), B1–C25 165.2(6), B1–C31 164.1(6). Angles (deg.): C13–B1–C19 110.5(3), C13–B1–C25 107.7(3), C13–B1–C31 109.9(3), C19–B1–C25 109.8(3), C19–B1–C31 108.6(3), C25–B1–C31 110.3(3).

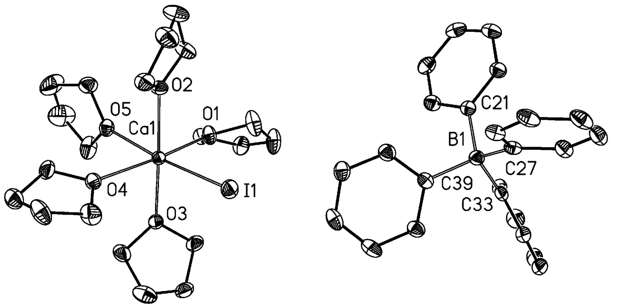

Fig. 2 Molecular structure and numbering scheme of $[CaI(thf)_5][BPh_4]$ (**2**). Selected bond lengths (pm): Ca1–I1 306.60(7), Ca1–O1 234.3(2), Ca1–O2 234.4(2), Ca1–O3 233.9(2), Ca1–O4 238.3(2), Ca1–O5 236.4(3), B1–C21 164.2(5), B1–C 27 164.2(5), B1–C33 164.8(5), B1–C39 165.0(5). Angles (deg.): C21–B1–C27 107.4(3), C21–B1–C33 109.2(3), C21–B1–C39 110.4(3), C27–B1–C33 110.4(3), C27–B1–C39 111.0(3), C33–B1–C39 108.4(3).

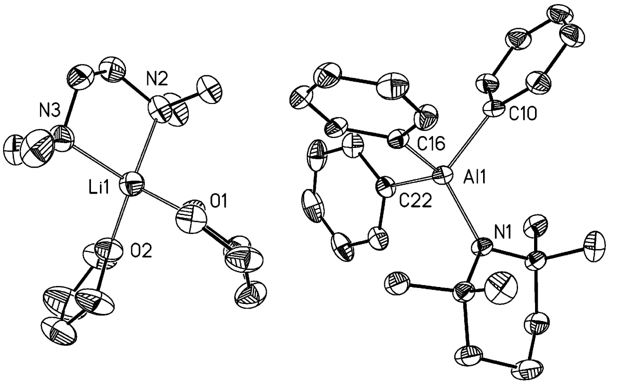

Fig. 3 Molecular structure and numbering scheme of $[Li(thf)_2(tmeda)]$-$[AlPh_3(tmp)]$ (**3**). Selected bond lengths (pm): Li1–O1 193.2(9), Li1–O2 194.0(9), Li1–N2 209.2(9), Li1–N3 208.0(9), Al1–N1 189.1(3), Al1–C10 203.4(4), Al1–C16 201.5(4), Al1–C22 202.0(4). Angles (deg.): N1–Al1–C10 115.4(2), N1–Al1–C16 116.7(2), N1–Al1–C22 108.4(2), C10–Al1–C16 100.7(2), C10–Al1–C22 108.1(2), C16–Al1–C22 106.8(2).

Most of these molecules consist of solvent-separated ions and have tetrahedral anions in common. Due to the fact that cations as well as anions can be considered as large soft ball-shaped ions, we do not expect to find short intermolecular distances. The contact ion pair $[(thf)_2K(N\text{-carbazolyl})_2AlMes_2]$ (**4**) represents the only exception. The hardness and softness of metal cations can be judged on the basis of the radius $r(M^{n+})$ of the cation and the charge *n*. The absolute hardness, based on ionization potential and electron affinity,[63–66] of the relevant alkali (Li^+ 35.12, Na^+ 21.08, K^+ 13.64) and alkaline earth metal cations (Ca^{2+} 19.52, Sr^{2+} 16.3, Ba^{2+} 12.8) increases with the charge, and decreases with the size. Hard Lewis acids favour the coordination of hard bases such as ethers and amines, whereas soft cations prefer soft bases such as aryl π-systems. The cations Ca^{2+} and Na^+ show a rather similar hardness, while the softer K^+ cation is comparable to Ba^{2+}. The latter also show rather similar radii (K^+: 152 pm, Ba^{2+}: 149 pm),[67] but due to a larger charge of the alkaline earth

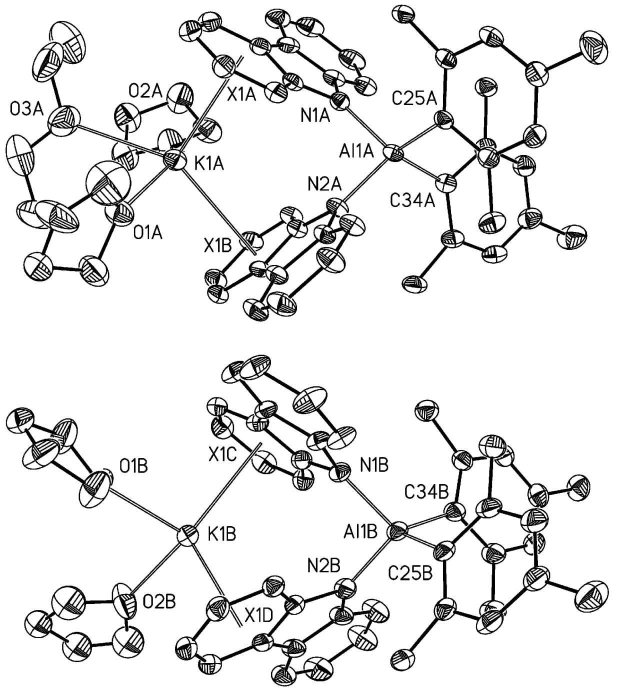

Fig. 4 Molecular structure and numbering scheme of (**4**). The asymmetric unit contains two molecules [$(Et_2O)(thf)_2K(N\text{-carbazolyl})_2AlMes_2$] (**4A**) and [$(thf)_2K(N\text{-carbazolyl})_2AlMes_2$] (**4B**). Selected bond lengths (pm): K1A–O1A 273.1(4), K1A–O2A 274.0(4), K1A–O3A 279.7(6), K1B–O1B 268.2(4), K1B–O2B 262.4(5), Al1A–N1A 192.0(4), Al1A–N2A 191.6(4), Al1A–C25A 202.7(4), Al1A–C 34A 201.9(4), Al1B–N1B 191.8(4), Al1B–N2B 193.0(5), Al1B–C 25B 202.4(5), Al1B–C34B 202.2(5). Angles (deg.): N1A–Al1A–N2A 95.7(2), N1B–Al1B–N2B 96.2(2).

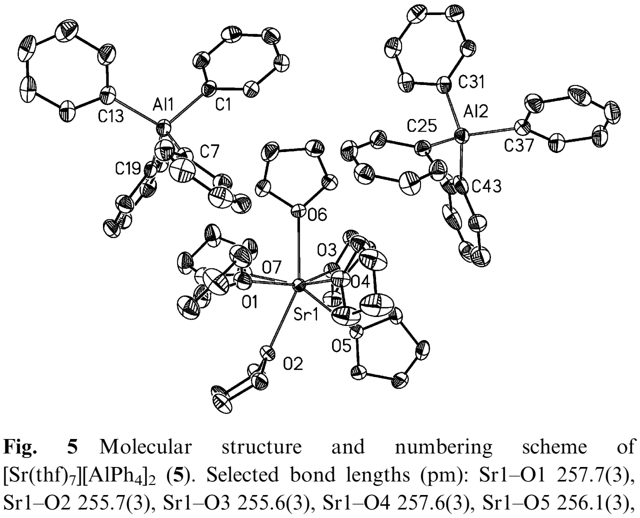

Fig. 5 Molecular structure and numbering scheme of [$Sr(thf)_7$][$AlPh_4$]$_2$ (**5**). Selected bond lengths (pm): Sr1–O1 257.7(3), Sr1–O2 255.7(3), Sr1–O3 255.6(3), Sr1–O4 257.6(3), Sr1–O5 256.1(3), Sr1–O6 254.8(3), Sr1–O7 258.4(3), Al1–C1 201.0(4), Al1–C7 200.3(4), Al1–C13 202.5(4), Al1–C19 199.8(4), Al2–C25 200.6(4), Al2–C31 199.8(5), Al2–C37 200.8(4), Al2–C43 201.3(5).

metal cation the preference of soft arene bases is less pronounced. The tetraphenylboranate (**1**, **2**) and tetraphenylalanate (**5**) anions show only small distortions of the tetrahedral geometry, whereas the substitution of one phenyl group by a bulky tetramethylpiperidino moiety in **3** enhances steric strain,

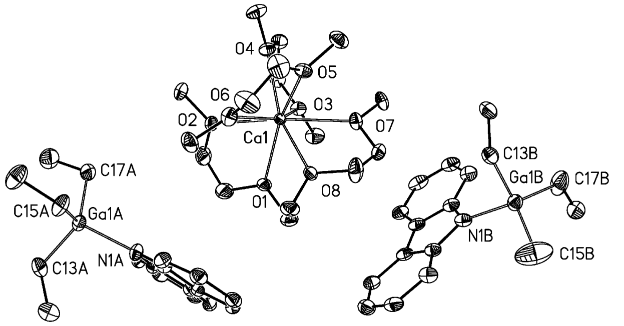

Fig. 6 Molecular structure and numbering scheme of [$Ca(dme)_4$][$GaEt_3(carbazolyl)$]$_2$ (**6**). The anions are distinguished by the letters "A" and "B". Selected bond lengths (pm): Ca1–O1 247.3(3), Ca1–O2 244.2(4), Ca1–O3 249.9(4), Ca1–O4 248.2(4), Ca1–O5 247.2(3), Ca1–O6 249.5(4), Ca1–O7 243.6(4), Ca1–O8 242.3(4), Ga1A–N1A 201.3(4), Ga1A-C13A 200.9(6), Ga1A-C15A 200.4(6), Ga1A-C17A 201.4(6), Ga1B-N1B 203.9(5), Ga1B-C13B 201.6(6), Ga1B-C15B 200.2(6), Ga1B-C17B 200.1(7).

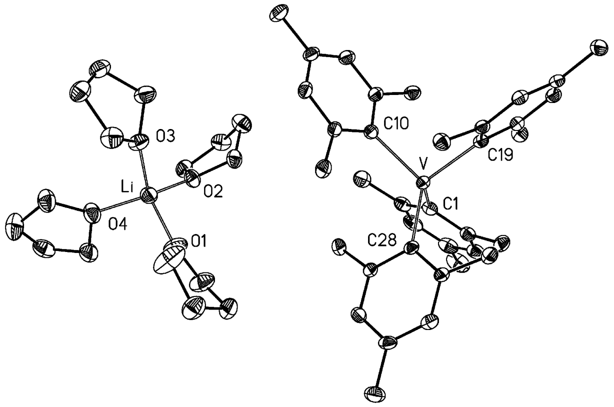

Fig. 7 Molecular structure and numbering scheme of [$Li(thf)_4$][$VMes_4$] (**7**). Selected bond lengths (pm): Li1–O1 191.5(6), Li1–O2 194.0(6), Li1–O3 192.9(6), Li1–O4 192.8(6), V–C1 214.5(3), V–C10 214.8(3), V–C19 215.2(3), V–C28 214.5(3). Angles (deg.): C1–V–C10 117.0(1), C1–V–C19 115.3(1), C1–V–C28 96.8(1), C10–V–C19 96.7(1), C10–V–C28 115.4(1), C19–V–C28 117.1(1).

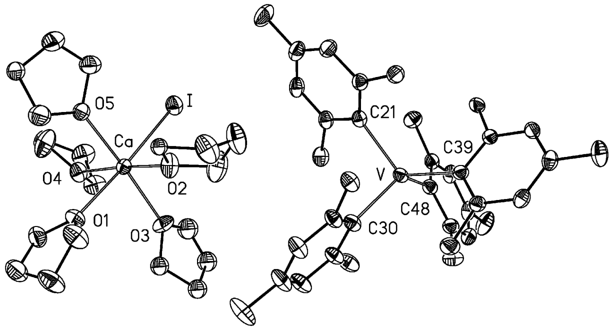

Fig. 8 Molecular structure and numbering scheme of [$CaI(thf)_5$][$VMes_4$] (**8**). Selected bond lengths (pm): Ca–I 302.86(9), Ca–O1 240.1(3), Ca–O2 233.7(3), Ca–O3 234.5(3), Ca–O4 235.3(3), Ca–O5 234.4(3), V–C21 215.4(4), V–C30 215.3(3), V–C39 215.2(3), V–C48 213.4(4). Angles (deg.): C21–V–C30 97.7(1), C21–V–C39 115.6(1), C21–V–C48 115.8(1), C30–V–C39 115.0(1), C30–V–C48 116.0(1), C39–V–C48 97.9(1).

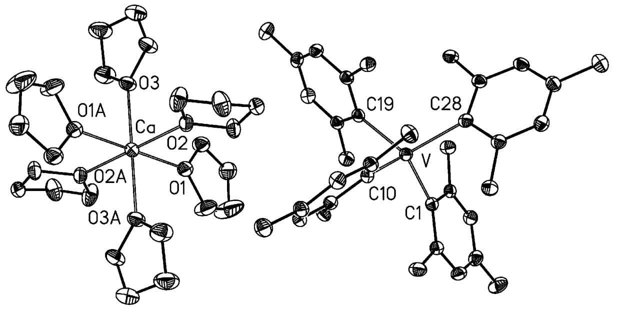

Fig. 9 Molecular structure and numbering scheme of $[Ca(thf)_6][VMes_4]_2$ (**9**). Symmetry-related atoms ($-x + 1, -y + 1, -z + 2$) are marked with an "A". The second symmetry-related anion is not shown for clarity. Selected bond lengths (pm): Ca–O1 234.4(2), Ca–O2 233.1(2), Ca–O3 237.7(2), V–C1 214.1(3), V–C10 215.3(3), V–C19 214.3(3), V–C28 214.2(3). Angles (deg.): C1–V–C10 114.8(1), C1–V–C19 118.2(1), C1–V–C28 97.3(1), C10–V–C19 97.0(1), C10–V–C28 117.7(1), C19–V–C28 113.2(1).

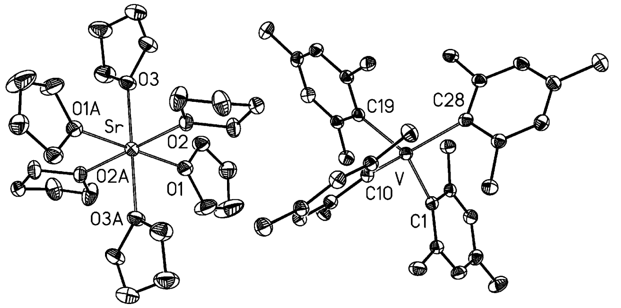

Fig. 10 Molecular structure and numbering scheme of $[Sr(thf)_6][VMes_4]_2$ (**10**). Symmetry-related atoms ($-x + 1, -y + 1, -z + 2$) are marked with an "A". The second symmetry-related anion is not shown for clarity. Selected bond lengths (pm): Sr–O1 249.3(4), Sr–O2 247.6(3), Sr–O3 252.8(4), V–C1 214.7(5), V–C10 214.8(5), V–C19 213.3(5), V–C28 215.9(5). Angles (deg.): C1–V–C10 115.2(2), C1–V–C19 118.2(2), C1–V–C28 96.9(2), C10–V–C19 97.0(2), C10–V–C28 117.6(2), C19–V–C28 113.5(2).

leading to a broader variation of the C–Al–C angles. Enhancement of steric pressure by substitution of the phenyl groups by mesityl substituents leads to severe distortions of the tetrahedral geometry. The difference between the two small and four large C–E–C angles is approx. 20° and is observed for the vanadates **8** to **11**. Such distortions are characteristic for tetrahedrons which are compressed along a C_2 axis. A direct comparison with the phenyl derivative is not possible because the smaller phenyl group leads to the formation of vanadate anions with larger coordination numbers (see above). In **4** the steric pressure is induced by the bulky mesityl groups, the amino units and the coordination of the carbazolyl π-systems to potassium, leading to a rather small N1–Al–N2 angle of approx. 96°. It is also noteworthy that the Al–C and Ga–C bond lengths show very similar values due to the d-block contraction of the radii, but the Ga–N distance to a carbazolyl group in **6** is approx 10 pm larger than the Al–N values in **3** and **4**. This fact can be attributed to the bulkiness of the attached organyl substituents (ethyl at Ga, less demanding phenyl at Al) and to their inductive effects (alkyl: $+I$, aryl: $-I$ effect). Despite a similar size of Al and Ga, the gallium atom contains many more electrons which should enhance the repulsion to anions. Therefore this effect strongly influences substituents with strongly electrovalent (ionic) bonds, whereas this effect is much smaller for covalently bound organyl groups.

The metal atoms are enwrapped by Lewis bases leading to sterically saturated cations. The coordination numbers strongly depend on the size of the metal and of the bulkiness of the Lewis bases. Tetra-coordinate lithium cations are very common[68,69] and are also found in **3**.

The heavy alkaline earth metal cations tend to enhance the coordination numbers as far as possible. Tetrahydrofuran molecules stabilize hexa-coordinate calcium cations leading to $[(thf)_6Ca]^{2+}$ as in **1** and **9** or to $[(thf)_5CaI]^+$ as in **2** and **8**. Slightly larger strontium cations allow both, hexa- and hepta-coordination as observed for $[(thf)_6Sr]^{2+}$ in **10** and for $[(thf)_7Sr]^{2+}$ in **5**. The compounds **9** and **10** show isomorphous solid state structures with the alkaline earth metals lying on inversion centers. The bidentate 1,2-dimethoxyethane molecules even enable an octa-coordinate calcium atom in $[(dme)_4Ca]^{2+}$ (**6**). In compound **4** potassium binds to two carbazolyl π-systems and to two THF molecules showing that hard and soft Lewis bases are accepted in nearly equal measure. The flexibility is even shown from the two different molecules **4A** and **4B** with an additional diethyl ether ligand in molecule A.

Table 1 Comparison of average structural parameters of solvent-separated $[Ca(thf)_6][BPh_4]_2$ (**1**), $[CaI(thf)_5][BPh_4]$ (**2**), $[Li(thf)_2(tmeda)][AlPh_3(tmp)]$ (**3**), $[(thf)_2K(N\text{-carbazolyl})_2AlMes_2]$ (**4**), $[Sr(thf)_7][AlPh_4]_2$ (**5**), $[Ca(dme)_4][GaEt_3(carbazolyl)]_2$ (**6**), $[Li(thf)_4][VMes_4]$ (**7**), $[CaI(thf)_5][VMes_4]$ (**8**), $[Ca(thf)_6][VMes_4]_2$ (**9**), and $[Sr(thf)_6][VMes_4]_2$ (**10**) with complex cations of the type $[(L)_nM]^+$ and tetrahedral anions of the type $[ER_4]^-$. [Bond lengths (pm) and angles (°)].

	1	2	3	4	5	6	7	8	9	10
M	Ca	Ca	Li	K	Sr	Ca	Li	Ca	Ca	Sr
C. No.[a]	6	6	4	4[b]	7	8	4	6	6	6
E	B	B	Al	Al	Al	Ga	V	V	V	V
M–O	233.6	235.5	193.6	275.6	256.6	246.5	192.8	235.6	235.1	249.9
M–N	—	—	208.6	—	—	—	—	—	—	—
M–I	—	306.6	—	0	—	—	—	302.9	—	—
E–C	165.0	164.6	202.3	202.3	200.9	200.8	214.8	214.8	214.5	214.7
E–N	—	—	189.1	191.8	—	202.6	—	—	—	—
C–E–C	109.5	109.5	109.4	109.5	109.5	109.4	109.7	109.7	109.7	109.7
C–E–C_{min}	107.7	107.4	100.7	95.7	107.3	102.5	96.7	97.7	97.0	96.9
C–E–C_{max}	110.5	111.0	116.7	114.3	112.2	116.1	117.1	116.0	118.2	118.2

[a] Coordination number of the metal atom M. [b] K binds to two THF molecules and side-on to two arene π-systems.

Experimental section

General

All manipulations were carried out in an argon atmosphere under anaerobic conditions. Prior to use, all solvents were thoroughly dried and distilled in an argon atmosphere. The reported compounds (except **1** and **2**) are extremely moisture- and air-sensitive. In many cases it was not possible to weigh out a definite amount because the weight of the substances changed permanently during handling and weighing. Therefore, the analysis is often limited to NMR and X-ray structure determinations. ^{1}H NMR and ^{13}C NMR spectra were recorded at [D_8]THF solutions at ambient temperature on a Bruker AC 200 MHz or a Bruker AC 400 MHz spectrometer. All spectra were referenced to deuterated THF as an internal standard. DEI-mass spectra were obtained on a Finnigan MAT SSQ 710 system (2,4-(dimethoxy)benzyl alcohol as matrix), IR measurements were carried out on a Perkin Elmer System 2000 FT-IR. Decomposition points were measured with a Reichert–Jung apparatus Type 302102. The aluminium contents were determined by complexometric titration (0.05 M EDTA, indicator Eriochrome Black T) of a hydrolysed aliquot after treatment with HNO_3. In the case of **5**, strontium was removed by precipitation as $SrSO_4$ before titration.

The starting materials [CaI(Ph)(thf)$_4$],[70] [$AlPh_3(Et_2O)$],[20] [$AlPh_3$(thf)],[20] $GaEt_3$,[71] [Ca(dme)$_2$(NPh_2)$_2$],[72] [AlCl(Et_2O)-Mes_2],[73] Li(tmp),[74] K(*N*-carbozolyl),[75] [$VMes_3$(thf)],[76] [Li(thf)$_4$][$VMes_4$][28] and $VMes_4$[62] were prepared according to known literature procedures. For activation the alkaline earth metals were dissolved in liquid ammonia and immediately thereafter the ammonia was removed in vacuo in order to avoid amide formation.[70]

Synthesis of [Ca(thf)$_6$][BPh_4]$_2$·2THF (1) and [CaI(thf)$_5$][BPh_4] (2)

Light was excluded by wrapping the apparatus in aluminium foil throughout preparation. Solid, freshly prepared $AgBPh_4$ (0.5 g, 1.17 mmol) was added to a rapidly stirred solution of [CaI(Tolyl)(thf)$_4$] in THF (14 mL, 0.075 M) at 0 °C. The reaction mixture was stirred for 1 h at 0 °C and formed a brownish solid, consistent with **1**, and a small amount of elemental silver was collected by filtration afterwards (290 mg). Further crystalline crops of **1** were obtained by stepwise cooling of the orange coloured mother liquor to −20 °C, and finally to −40 °C overnight. The supernatant solution was decanted and stored at −78 °C, but no further crystallization occurred at this temperature within one week. Therefore, the remaining reaction mixture was allowed to slowly warm to room temperature over a period of 24 h and kept at this temperature for another day. During this procedure the original yellow-orange colour of the solution faded and elemental silver formed in addition to colourless crystals of **2**. These crystals were isolated by decantation and dried in a vacuum. Yield: 230 mg (0.27 mmol, 26%) of **2** (slightly contaminated by elemental silver).

Physical data for 2. Anal. Calc. for $C_{44}H_{60}BCaIO_5$ (846.75 g mol^{-1}): C, 62.41; H, 7.14. Found: C, 60.69; H, 7.09.^{1}H NMR (400.25 MHz, 25 °C, [D_8]THF): δ 1.77 (20H, m, $C\mathit{H}_2$, THF), 3.62 (20H, m, $C\mathit{H}_2O$, THF), 6.72 (4H, t, $^3J_{H-H}$ = 7.2 Hz, *p*-H), 6.85 (8H, t, $^3J_{H-H}$ = 7.2 Hz, *m*-H), 7.26 (8H, m, *o*-H). ^{13}C{^{1}H} NMR (100.65 MHz, 25 °C, [D_8]THF): δ 26.3 (10C, $\mathit{C}H_2$, THF), 68.1 (10C, $\mathit{C}H_2O$, THF), 121.7 (8C, *m*-C), 125.6 (4C, *p*-C), 137.0 (8C, *o*-C), 165.1 (4C, q, $^1J_{C-B}$ = 49.3 Hz, *i*-C). MS (FAB-, *m*/*z*, [%]): 320 (BPh_4^- + 1) [100]. IR (Nujol, cm^{-1}) ν: 1946, m; 1882, m; 1823, m; 1765, w; 1625, m; 1579, s; 1345, s, 1295, s; 1247, s; 1178, s; 1134, s; 1018, s (br); 915, s; 864, s (br); 734, s; 708, s; 667, s; 610, s.

Suitable crystals of **1** and **2** were obtained directly from the reaction mixtures.

Synthesis of [Li(thf)$_2$(tmeda)][Ph_3Al(tmp)] (3)

A solution of Li(tmp) (14 mL, 2.98 mmol, 0.213 M) in toluene was dropped into a solution of (Et_2O)$AlPh_3$ (0.99 g, 2.98 mmol) in THF (5 mL) at −78 °C. After stirring for 2 h at room temperature a yellow solid had formed which was separated and redissolved in a mixture of THF (4 mL) and tmeda (2 mL). Reduction of one quarter of the volume, filtration and storage at −20 °C led to crystallization of colourless crystals. Separation and gently drying in vacuum gave 1.84 g (2.78 mmol, 93%) of **3**.

Physical data for 3. Decomposition above 32 °C. Anal. Calc. for $C_{41}H_{65}AlLiN_3O_2$ (665.92 g mol^{-1}): C, 73.89; H, 9.83; N, 6.31. Found: C, 73.53; H, 9.71; N, 6.40. ^{1}H NMR (200.25 MHz, 25 °C, [D_8]THF): δ 1.12 (12H, s, $C\mathit{H}_3$, tmp), 1.33 (4H, t, $C\mathit{H}_2$, tmp), 1.65 (2H, m, $C\mathit{H}_2$, tmp) 1.72 (8H, m, $C\mathit{H}_2$, THF), 2.28 (12H, s, $C\mathit{H}_3$, tmeda), 2.40 (4H, s, $C\mathit{H}_2$, tmeda), 3.65 (8H, m, $C\mathit{H}_2O$, THF), 7.22 (9H, m, *p*,*m*,*m*′-H), 7.78 (6H, *o*,*o*′-H). ^{13}C{^{1}H} NMR (50.32 MHz, 25 °C, [D_8]THF): δ 18.2 (1C, $\mathit{C}H_2$, tmp), 25.6 (4C, $\mathit{C}H_2$, THF), 31.5 (4C, $\mathit{C}H_3$, tmp), 38.6 (2C, $\mathit{C}H_2$, tmp), 18.2 (1C, $\mathit{C}H_2$, tmp), 45.0 (2C, $\mathit{C}H_3$, tmeda), 45.2 (2C, $\mathit{C}H_3$, tmeda), 49.0 (2C, $\mathit{C}(CH_3)_2$, tmp), 57.3 (2C, $\mathit{C}H_2$, tmeda), 67.9 (4C, $\mathit{C}H_2O$, THF), 124.5 (6C, *m*,*m*′-C), 126.9 (3C, *p*-C), 139.6 (6C, *o*,*o*′-C), 139.9 (3C, *i*-C). ^{27}Al NMR (104.28 MHz, 25 °C, [D_8]THF): very broad ($w_{1/2}$ > 4000 Hz). IR (Nujol, cm^{-1}) ν: 2371, m; 1878, w; 1846, w; 1803, w; 1763, w; 1735, w; 1696, m, 1686, m; 1664, m; 1648; m, 1593; m, 1593, s; 1571, m; 1303, s; 1165, s; 1074, m; 1033, m; 973, m; 917, m; 889, m; 674, m; 611, m.

Synthesis of [(thf)$_2$K(*N*-carbazolyl)$_2$$AlMes_2$] (4)

Solid (Et_2O)Mes_2AlCl (1.20 g, 3.10 mmol) was dissolved in diethyl ether (20 mL) and a solution of K(carbazolyl) (11.48 mL, 6.20 mmol, 0.54 M) in THF was added dropwise at −25 °C. The mixture was stirred at ambient temperature for 12 h. After filtration the pale yellow solution was stored at −20 °C to obtain colourless crystals. Filtration, washing with a few millilitres of cold n-pentane and drying in vacuum resulted in loss of coordinated diethyl ether and yielded **4** (2.15 g, 2.75 mmol, 88.7%).

Physical data for 4. Decomposition above 145 °C. Anal. Calc. for $C_{50}H_{54}AlK_2N_2O_2$ (781.06 g mol^{-1}): Al, 3.45 Found: Al, 3.36. ^{1}H NMR (400.25 MHz, 25 °C, [D_8]THF): δ 1.73 (8H, m, $C\mathit{H}_2$, THF), 2.13 (6H, s, *p*-$C\mathit{H}_3$, mes), 2.33 (12H, s, *o*,*o*′-$C\mathit{H}_3$, mes), 3.59 (8H, m, $C\mathit{H}_2O$, THF), 6.60 (4H, s, *m*,*m*′-$C\mathit{H}$, mes), 7.73 (4H, t, $^3J_{H-H}$ = 7.6 Hz, H_4, carbaz.), 7.12 (4H, t, $^3J_{H-H}$ = 7.2 Hz, H_5, carbaz.), 7.59 (4H, d, $^3J_{H-H}$ = 7.6 Hz, H_6, carbaz.), 8.00 (4H, d, $^3J_{H-H}$ = 7.2 Hz, H_3, carbaz.). $^{13}C\{^1H\}$ NMR (100.65 MHz, 25 °C, [D_8]THF): δ 21.3 (2C, *p*-CH_3, mes), 25.3 (4C, CH_2, THF), 26.4 (4C, *o,o′*-CH_3, mes), 67.6 (4C, CH_2O, THF), 115.1 (4C, C_6, carbaz.), 116.5 (4C, C_3, carbaz.), 118.9 (4C, C_4, carbaz.), 123.9 (4C, C_2, carbaz.), 125.2 (4C, C_5, carbaz.), 127.9 (4C, *m,m′*-*C*, mes), 137.7 (2C, *p*-*C*, mes), 141.2 (2C, *i*-*C*, mes), 146.5 (4C, *o,o′*-*C*, mes), 149.7 (4C, C_1, carbaz.). ^{27}Al NMR (25 °C, [D_8]THF): δ 199.6 ($w_{1/2}$ = 3848 Hz). IR (Nujol, cm^{-1}) ν: 2725, m; 2669, m; 1930, w; 1711, w; 1595, vs; 1508, vs; 1495, vs; 1417, s; 1388, s; 1310, vs; 1243, m; 1173, m; 1155, m; 1083, m; 1028, m; 995, w; 971, w; 934, w; 876, m; 745, vs; 690, s; 643, w.

Synthesis of $[Sr(thf)_7][AlPh_4]_2(THF)$ (5)

Solid $(Et_2O)AlPh_3$ (0.65 g, 1.96 mmol) was dissolved in THF (10 mL) and $\{(thf)_xSrPh_2\}$ (15.9 mL, 0.99 mmol, 0.062 M) in THF was added at −50 °C. After stirring for 1 h at this temperature the mixture was allowed to warm to room temperature and stirred for an additional 12 h. After filtration and storage of the mother liquor at −20 °C the formed colorless prisms of **5** were collected on a cooled frit and dried gently in vacuum. Yield: 0.96 g (0.76 mmol, 77%).

Physical data for 5. Decomposition above 83 °C. Anal. Calc. for $C_{76}H_{96}Al_2O_7Sr$ (1263.15 g mol^{-1}): C, 72.26; H, 7.66; Al, 4.27. Found: C, 71.98; H, 7.69; Al, 4.38. ^{1}H NMR (200.25 MHz, 25 °C, [D_8]THF): δ 1.77 (32H, m, CH_2, THF), 3.63 (32H, m, CH_2O, THF), 6.92 (8H, t, $^3J_{H-H}$ = 7.0 Hz, *p*-H), 7.09 (16H, t, $^3J_{H-H}$ = 7.2 Hz, *m*-H), 7.65 (16H, dd, $^3J_{H-H}$ = 7.4 Hz, *o*-H). $^{13}C\{^1H\}$ NMR (50.32 MHz, 25 °C, [D_8]THF): δ 26.3 (16C, CH_2, THF), 68.1 (16C, CH_2O, THF), 124.5 (16C, *m*-C), 126.9 (8C, *p*-C), 139.6 (16C, *o*-C), 139.9 (8C, *i*-C). ^{27}Al NMR (104.28 MHz, 25 °C, [D_8]THF): δ 132.9 ($w_{1/2}$ = 23 Hz). MS (Micro-ESI−, *m*/*z*, [%]): 335 (AlPh4-) [30]. IR (Nujol, cm^{-1}) ν: 2724, s; 1591, w; 1377, vs; 1305, m; 1247, w; 1154, w; 1085, m; 1041, m; 935, m; 889, m; 847, m; 674, m.

Synthesis of $[Ca(dme)_4][Ga(N\text{-carbazolyl})Et_3]_2\cdot PhMe$ (6)

Solid $(dme)_2Ca(NPh_2)_2$ (0.45 g, 0.816 mmol) was suspended in toluene (15 mL), and $GaEt_3$ (0.86 mL, 0.81 mmol, 0.94 M) in toluene was added at −10 °C. After stirring for 1 h at this temperature a clear solution was formed. The mixture was allowed to warm to room temperature and stirred for an additional 12 h. The resulting cloudy solution was filtered and the removed white solid (completely insoluble in common organic solvents) was discarded. The mother liquor was stored for 20 days at −20 °C and was repeatedly filtered during this time to remove newly formed portions of a fine precipitate. Afterwards, storage of the yellowish mother liquor at room temperature yielded colorless needles of **6** within 14 days which were collected on a Schlenk frit and dried gently in vacuum. Yield: 0.37 g (0.35 mmol, 86%).

Physical data for 6. Decomposition above 168 °C. Anal. Calc. for $C_{52}H_{86}CaGa_2N_2O_8\cdot C_7H_8$ (1138.91 g mol^{-1}): C, 62.22; H, 8.32. Found: C, 61.53; H, 8.12. ^{1}H NMR (400.15 MHz, 25 °C, [D_8]THF): δ 0.56 (12H, q, $^3J_{H-H}$ = 8.0 Hz, MeCH_2Ga), 1.31 (18H, t, $^3J_{H-H}$ = 7.0 Hz, *Me*CH2Ga), 2.16 (s, Ph*Me*), 3.02 (24H, s, OCH_3 (dme)), 3.21 (16H, s, CH_2O (dme)), 6.75-7.06 (m, *Ph*Me), 7.14 (46H, t, $^3J_{H-H}$ = 6.8 Hz, H4), 7.30 (4H, t, $^3J_{H-H}$ = 7.2 Hz, H5), 7.47 (4H, d, $^3J_{H-H}$ = 7.2 Hz, H6), 7.92 (4H, d, $^3J_{H-H}$ = 7.6 Hz, H3). $^{13}C\{^1H\}$ NMR (50.32 MHz, 25 °C, [D_8]THF): δ 5.2 (6C, MeCH_2Ga), 10.1 (6C, *Me*CH_2Ga), 21.4 (Ph*Me*), 58.9 (8C, OCH_3 (dme)), 72.7 (8C, CH_2O (dme)), 111.3 (4C, C6), 119.5 (4C, C2), 120.8 (4C, C3), 126.1 (4C, C4), 127.9, 128.4, 128.9 (*Ph*Me), 128.7 (4C, C5), 135.7 (*Ph*Me, *i*-C), 141.1 (4C, C1). IR (Nujol, cm^{-1}) ν: 2725, m; 2669, m; 2308, w; 1930, w; 1773, w; 1711, w; 1595, vs; 1508, vs; 1495, vs; 1417, s; 1338, s; 1310, s; 1261, m; 1243, m; 1173, m; 1115, m; 1063, m; 1074, m; 1028, m; 995, w; 971, w; 934, w; 876, m; 845, w; 819, m; 745, vs; 690, s; 643, m; 617,w; 568, m; 501, m.

Synthesis of $[(thf)_5CaI][VMes_4]\cdot 2THF$ (8)

A stirred solution of $[CaI(Mes)(thf)_4]$ (20 mL, 1.33 mmol, 0.0665 M) in THF was cooled to −40 °C and solid $[Mes_3V(thf)]$ (0.63 g, 1.31 mmol) was added. The resulting blue suspension was allowed to warm to 5 °C over a period of 3 h and a clear blue solution was formed. Storage at 5 °C overnight resulted in a color change to dark violet. Afterwards the solution was reduced to half of its original volume and stored at −20 °C. After six hours the formed dark violet crystals (380 mg) were collected on a Schlenk frit and dried in a vacuum. Further storage of the mother liquor at −20 °C resulted in crystallization of additional **7**, contaminated by $[CaI_2(thf)_4]$ (colorless crystals) and $[VMes_3(thf)]$ (blue crystals). Yield: 380 mg (0.32 mmol, 24%) violet crystals of $[CaI(thf)_5][Mes_4V]\cdot 2THF$.

Suitable crystals for X-ray diffraction experiments were obtained by cooling of a saturated solution in THF from room temperature to 5 °C.

Synthesis of $[(thf)_6Ca)][VMes_4]_2\cdot 4THF$ (9)

$[VMes_3(thf)]$ (1.95 g, 4.06 mmol) was added to a cooled suspension of activated calcium (0.38 g. 9.5 mmol) in THF (40 mL) and cyclooctadiene (2 mL) at 0 °C. The reaction mixture was shaken at this temperature until the blue color of the starting material had disappeared. The resulting yellow-brown suspension was filtered to remove the excess of calcium and the mother liquor was stored at −20 °C overnight. Afterwards the solution was reduced to half of the original volume in a vacuum and stored again at −20 °C. Dark violet crystals formed during one week. This solid was isolated by decantation, washed with a few millilitres of cold THF and dried in a vacuum. Yield: 210 mg (0.12 mmol, 6%).

Suitable crystals for X-ray diffraction experiments were obtained directly from the reaction mixture.

Synthesis of $[Sr(thf)_6][VMes_4]_2\cdot 4THF$ (10)

A solution of $VMes_4$ (1.32 g, 2.50 mmol) in THF (30 mL) was added to activated strontium at room temperature. The resulting red suspension was shaken for two days, filtered and the obtained solution was reduced to 5 mL in a vacuum afterwards. Thereafter, diethyl ether (20 mL) was added, resulting in a suspension which was stirred for 30 min at ambient temperature. The formed solid was isolated by filtration and extracted with boiling diethyl ether until the

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Table 2 Crystal data and refinement details for the X-ray structure determinations of compounds **1** to **10**

Compound	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
Formula	$C_{24}H_{48}CaO_6\cdot 2(C_{24}H_{20}B)\cdot 2(C_4H_8O)$	$C_{20}H_{40}CaIO_5\cdot C_{24}H_{20}B$	$C_{14}H_{32}LiNO_2\cdot C_{27}H_{33}AlN$	$C_{12}H_{26}KO_3\cdot C_8H_{16}KO_2\cdot 2(C_{42}H_{38}AlN_2)$	$C_{28}H_{56}O_7Sr\cdot 2(C_{24}H_{20}Al)\cdot C_4H_8O$	$C_{16}H_{40}CaO_8\cdot 2(C_{18}H_{23}GaN)\cdot 0.5\ C_7H_8$	$C_{16}H_{32}LiO_4\cdot C_{36}H_{44}V\cdot C_4H_8O$	$C_{20}H_{40}CaIO_5\cdot C_{36}H_{44}V\cdot 2(C_4H_8O)$	$C_{24}H_{48}CaO_6\cdot 2(C_{36}H_{44}V)\cdot 4(C_4H_8O)$	$C_{24}H_{48}O_6Sr\cdot 2(C_{36}H_{44}V)\cdot 4(C_4H_8O)$
FW (g mol^{-1})	1255.33	846.71	665.88	818.09	1335.21	1092.82	895.11	1199.36	1816.42	1863.96
T (K)	−90(2)	−90(2)	−90(2)	−90(2)	−90(2)	−90(2)	−90(2)	−90(2)	−90(2)	−90(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic	Orthorhombic	Monoclinic	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/n$	$P2_1/n$	$C2/c$	$P\bar{1}$	$P2_1/c$	$Pbca$	$P2_1/n$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
a (Å)	15.5626(4)	12.6919(3)	17.0743(5)	10.8940(4)	21.4995(4)	14.6288(2)	16.8019(5)	12.668(3)	13.5165(8)	13.5257(14)
b (Å)	14.6072(5)	15.3774(4)	16.2193(4)	12.2427(5)	18.2740(3)	21.8473(3)	17.3641(7)	34.081(7)	13.9755(6)	13.9195(12)
c (Å)	16.9537(5)	21.9023(5)	30.1905(9)	34.7637(13)	18.9071(4)	37.9734(6)	17.9993(6)	15.403(3)	14.9650(7)	15.1196(17)
α (°)	90	90	90	94.365(2)	90	90	90	90	76.564(3)	76.359(6)
β (°)	110.462(2)	93.797(1)	95.514(3)	91.070(2)	90.464(1)	90	95.473(2)	106.43(3)	71.192(3)	71.204(4)
γ (°)	90	90	90	104.162(2)	90	90	90	90	88.512(3)	88.437(7)
V (Å^3)	3610.8(2)	4265.25(18)	8322.1(4)	4479.2(3)	7428.0(2)	12136.3(3)	5227.4(3)	6378(2)	2599.0(2)	2615.1(5)
Z	2	4	8	4	4	8	4	4	1	1
ρ (g cm^{-3})	1.155	1.319	1.063	1.213	1.194	1.196	1.137	1.249	1.161	1.184
μ (mm^{-1})	1.41	9.13	0.83	1.82	8.03	10.21	2.34	7.68	2.85	7.39
Measured data	25235	29850	14979	19265	52349	71173	35187	44403	17683	16820
Data with $I > 2\sigma(I)$	6072	5951	3932	9481	10094	7444	6242	9859	6490	5655
Unique data (R_{int})	8234/0.0545	9736/0.0720	7658/0.0969	14916/0.0347	16953/0.0766	13866/0.1318	11904/0.0943	14552/0.0413	11543/0.0492	11235/0.0682
wR_2 (all data, on F^2)^a	0.2985	0.1203	0.2456	0.2594	0.2034	0.2589	0.1945	0.1818	0.1668	0.1926
R_1 ($I > 2\sigma(I)$)^a	0.1095	0.0502	0.0884	0.0910	0.0667	0.0824	0.0664	0.0593	0.0662	0.0777
S^b	1.088	1.009	1.023	1.050	1.029	1.039	1.013	1.019	1.011	1.019
Residual density (e Å^{-3})	0.828/−0.768	1.091/−0.822	0.270/−0.248	0.731/−0.433	1.056/−0.668	1.623/−0.484	0.430/−0.439	0.888/−1.042	0.363/−0.283	0.305/−0.467
Absorption method	None	None	None	None	None	None	None	None	None	None
CCDC No.	765641	765642	765643	765644	765645	765646	765647	765648	765649	765650

[a] Definition of the R indices: $R_1 = (\Sigma||F_o| - |F_c||)/\Sigma|F_o|$; $wR_2 = \Sigma[w(F_o{}^2 - F_c{}^2)^2]/\Sigma[w(F_o{}^2)^2]^{1/2}$ with $w^{-1} = \sigma^2(F_o{}^2) + (aP)^2 + bP$; $P = [2F_c{}^2 + \max(F_o{}^2)]/3$; [b] $s = \Sigma[w(F_o{}^2 - F_c{}^2)^2]/(N_o - N_p)^{1/2}$.

solvent was no longer colored. Yield: 450 mg (0.24 mmol, 19.3%) violet powder.

Suitable crystals for X-ray diffraction experiments can be obtained directly from the reaction mixture by cooling to −40 °C after removal of the excess of strontium.

Structure determinations

The intensity data for the compounds were collected on a Nonius KappaCCD diffractometer using graphite-monochromated Mo-Kα radiation. Data were corrected for Lorentz and polarization effects but not for absorption effects.[77,78]

The structures were solved by direct methods (SHELXS[79]) and refined by full-matrix least squares techniques against F_o^2 (SHELXL-97[80]). All hydrogen atoms were included at calculated positions with fixed thermal parameters. All non-disordered, non-hydrogen atoms were refined anisotropically with the exception of the THF molecules in **5**.[80] Crystallographic data as well as structure solution and refinement details are summarized in Table 2. XP (SIEMENS Analytical X-ray Instruments, Inc.) was used for structure representations.

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