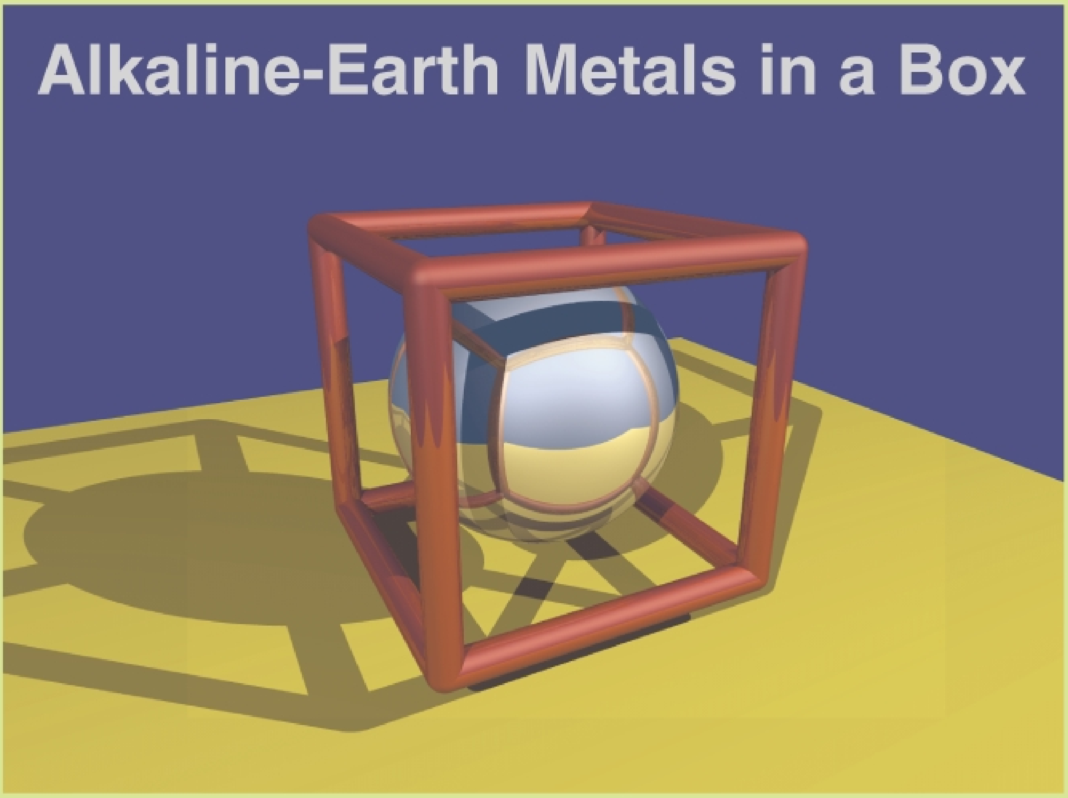

Completely solvated alkaline-earth cations, like [$Ca^{2+}(thf)_6$], crystallize in a box built of planar molecules. Numerous C-H···π interactions fixate the cation in the box.

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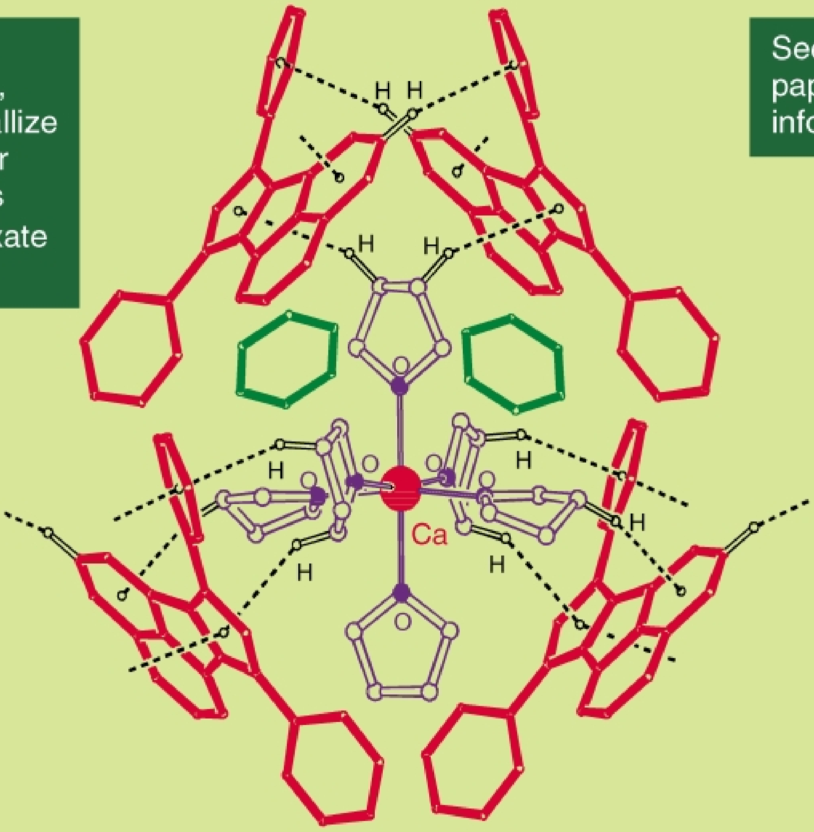

"Alkaline-Earth Metals in a Box": Structures of Solvent-Separated Ion Pairs

Sjoerd Harder,*[a] Florian Feil,[a] and Timo Repo[b]

Abstract: During our research on homoleptic organocalcium compounds, we found that fluorenylcalcium complexes show unusual solution behavior and precipitate from nonpolar solvents after addition of THF. Their solid-state structures reveal the unexpected rupture of both metal–carbanion bonds by the polar solvent THF. The crystal structures of five new Mg and Ca solvent-separated ion pairs are described. The compound $[Ca^{2+}(thf)_6][Me_3Si(fluorenyl^-)]_2$ is the first organometallic complex of a Group 2 element that crystallizes as a completely solvent-separated ion pair. The driving forces for its formation are: 1) the strong Ca–THF bond; 2) the stability of the free $[Me_3Si(fluorenyl)]^-$ ion; 3) encapsulation of $[Ca^{2+}(thf)_6]$ in a "box", the walls of which consist of anionic fluorenyl ligands and benzene molecules; and 4) the presence of numerous (THF)C–H$\cdots\pi$ interactions. The magnesium analogue $[Mg^{2+}(thf)_6][Me_3Si(fluorenyl^-)]_2$ is isostructural. Bis(7,9-diphenylcyclopenta[*a*]acenaphthadienyl)calcium also crystallizes as a completely solvent-separated ion pair and can likewise be described as a $[Ca^{2+}(thf)_6]$ species in a box of delocalized anions and benzene molecules. In addition, the structures of two Ph_4B^- complexes of Mg and Ca are described. $[Mg^{2+}(thf)_6][Ph_4B^-]_2$ crystallizes as a completely solvent-separated ion pair and also shows a solvated metal cation bonded via C–H$\cdots\pi$ interactions in a cavity formed by Ph_4B^- ions. $[(thf)_4CaBr^+][Ph_4B^-]$ has a structure in which one of the anionic ligands is still bonded to the Ca atom. Bridging bromide ligands result in the formation of the dimer $[(thf)_4CaBr^+]_2$.

Keywords: alkaline earth metals · cage compounds · hydrogen bonds · ion pairs

Introduction

Solvent-separated ion pairs (SSIPs) are well-established species in the organometallic chemistry of the alkali metals: many crystal structures are known[1] and extensive studies on SSIPs in solution have been published.[2] In contrast, SSIPs are much less common in the organometallic chemistry of the alkaline-earth metals. This is partly due to the limited structural data for alkaline-earth metal compounds in general (especially those of the heavier congeners Ca, Sr, and Ba), but may also be due to the much stronger electrostatic bonding between the doubly charged Group 2 cations and carbanions. This kinetic stabilization of the cation–anion bond prevents the bond cleavage needed for SSIP formation.

Bond cleavage in a contact ion pair can only occur if the resulting cation and anion are both effectively stabilized. Cations are stabilized by strongly polar solvents (high dielectric constant and dipole moment) and the presence of strong Lewis bases. Multidentate Lewis bases, which compensate for the loss in entropy, are especially effective cation stabilizers. Anion stabilization also requires highly polar solvents. In particular, protic solvents (e.g., alcohols) stabilize anions by encapsulating them in a network of strong hydrogen bonds. Protic solvents, however, cannot be used in highly basic systems, that is, compounds containing carbanions derived from acids with $pK_a > 16$. Other modes of anion stabilization involve the delocalization of negative charge (borates, extended π systems) and/or the use of sterically demanding substituents. Incorporation of the "free" anion in an organometallic aggregate also provides for stabilization. These forms of stabilization are observed in all the known Group 2 organometallic SSIPs listed below.

In the organoberyllium cation **1**,[3] the $ClBe^+$ ion is stabilized by three strongly electron-donating Arduengo carbenes. Several SSIP structures have been reported for organomagnesium compounds (**2**–**4**).[4] Reaction of diorganomagnesium compounds with multidentate ligands generally results in Mg–C bond cleavage. The strongly basic alkyl anions are stabilized by incorporation in large clusters (**2** and **3**), but the fluorenyl anion in **4**, in which the negative charge is largely delocalized, is "free". The first example of a monocationic organocalcium compound (**5**) was reported recent-

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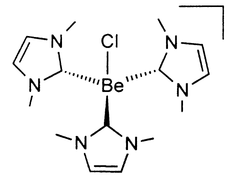
ly.[5] Reaction of Cp*CaI (Cp* = η^5-C_5Me_5) with the neutral but strongly polar $Ph_3P{=}O$ leads to complete dissociation of the Ca–I bond, but the Cp*–Ca bond remains intact. Finally, a monocationic organobarium compound is known (**6**).[6a] Although the Ph_4B^- ion can sandwich large metal cations (as in the polymeric structures of $Ph_4B^-K^+$ and $Ph_4B^-Rb^+$),[7] it shows noncoordinating behavior in **6**. Complete SSIPs were recently obtained by addition of crown ethers and the highly polar cosolvent hexamethylphosphoric triamide (HMPTA) to $(Ph_3C)_2Ba$ (**7**).[6b]

In our research on new polymerization catalysts,[8] we prepared several homoleptic organometallic Group 2 complexes. Some of these complexes show unusual solution behavior, and their solid-state structures reveal the unexpected rupture of both metal–carbanion bonds by common polar solvents such as THF.



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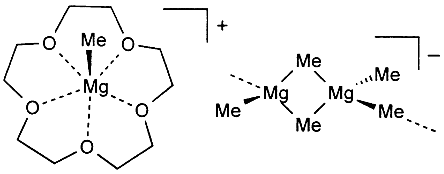

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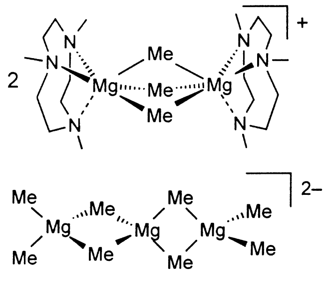

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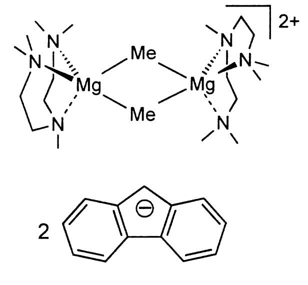

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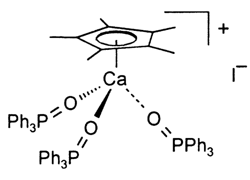

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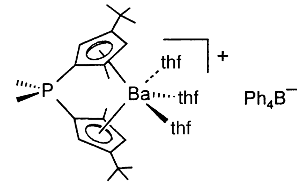

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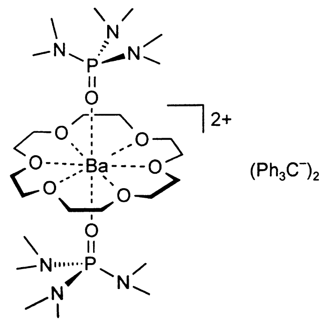
Results and Discussion

Bis(9-trimethylsilylfluorenyl)calcium (**8**) was prepared by a metathesis reaction between the corresponding potassium compound and CaI_2 in THF [Eq. (1); TMS = $SiMe_3$]. Isolation of the THF solution, evaporation of the solvent and drying under high vacuum (0.01 Torr, 80 °C, 2 h) yielded a red calcium compound with two residual THF ligands. The complex is soluble in benzene, but the addition of small amounts of THF results in the immediate formation of a precipitate. This is in striking contrast to the normal behavior of polar organometallic main group compounds.[9] Addition of more THF redissolves the orange precipitate. Large, bright orange crystals, obtained by slow vapor diffusion of THF into a solution of **8** in benzene, had the composition $[\mathbf{8}\cdot(thf)_6]\cdot C_6H_6$.



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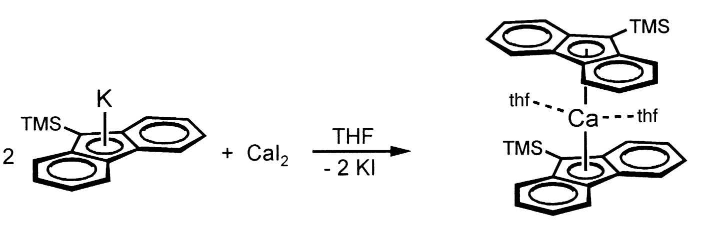


$[\mathbf{8}\bullet(thf)_2]$ (1)

A single-crystal structure determination revealed the presence of the ion pair $[Ca^{2+}(thf)_6][Me_3Si(fluorenyl^-)]_2$, which is formed by the scission of two fluorenyl–calcium bonds. The Ca^{2+} ion, which lies on a crystallographic center of

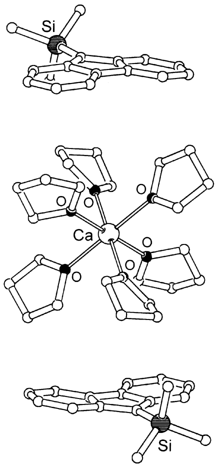


Figure 1. The "sandwich complex" $[Ca^{2+}(thf)_6][Me_3Si(fluorenyl^-)]_2$.

inversion, shows nearly perfect octahedral coordination by THF ligands: the Ca–O bond lengths are in the narrow range of 2.314(2) – 2.342(2) Å, and the bond angles between neighboring THF ligands deviate from 90° by at most 2.1°. The Ca^{2+} ion, which is completely coordinatively saturated by the THF ligands, is positioned between the perfectly parallel planes of the two large fluorenyl anions (Figure 1). This can be regarded as a sandwich complex with an unusually large cation. The shielding of the metal center by THF ligands inhibits any direct $Ca^{2+} \cdots$ anion contact and results in large distances between the fluorenyl anions and the Ca^{2+} ion (the $fluorenyl_{center} \cdots Ca^{2+}$ distance is 6.472 Å). Consequently, electrostatic bonding between the anions and the cation is weak (the electrostatic bonding energy between anion and Ca^{2+} ion is inversely proportional to the distance and is estimated to be approximately one-third of that in classical sandwich complexes).

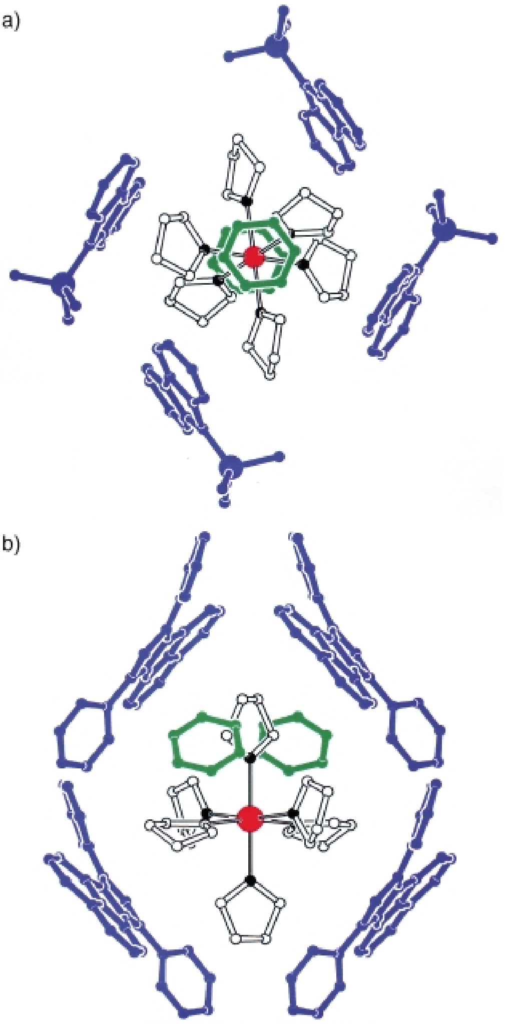


Figure 2. The "metal-in-a-box" model. The walls of the box are formed by four $[Me_3Si(fluorenyl)]^-$ ions (blue) and two benzene molecules (green). a) $[Ca^{2+}(thf)_6][Me_3Si(fluorenyl)^-]_2 \cdot C_6H_6$ and b) $[Ca^{2+}(thf)_6][ACp^-]_2 \cdot C_6H_6$ ($[\mathbf{10} \cdot (thf)_6] \cdot C_6H_6$).

The structure of $[\mathbf{8} \cdot (thf)_6]$ is quite unusual for an organometallic compound of the heavier alkaline-earth metals. Cyclopentadienyl complexes of Ca, Sr, and Ba always crystallize as contact ion pairs in which the two carbanions are directly bound to the metal atom.[10] Indenyl[11] and fluorenyl[12] complexes also form contact ion pairs. What are the driving forces for the formation of the SSIP $[Ca^{2+}(thf)_6][Me_3Si(fluorenyl^-)]_2$? First, the highly oxophilic nature of the Ca^{2+} ion is well known.[13] Six strong $O_{THF}–Ca^{2+}$ bonds compensate for the loss of electrostatic bonding energy between anion and cation. Second, the $[Me_3Si(fluorenyl)]^-$ ion is thermodynamically stable. The negative charge is not only delocalized over the fluorenyl ring but also over the Me_3Si group by negative hyperconjugation. Third, a more detailed investigation of the crystal packing shows that the sandwich complex interacts with two neighboring sandwiches and forms a two-dimensional coordination polymer (Figure 2 a). Therefore, $[\mathbf{8} \cdot (thf)_6]$ is more accurately described with a "metal in a box" model. The $[Ca^{2+}(thf)_6]$ species is enclosed in a box of which four walls are built from negatively charged fluorenyl rings. The structure also contains a perfectly ordered benzene molecule which, together with its symmetry-related partner, forms the bottom and the lid of the box. Thus, $[Ca^{2+}(thf)_6]$ is completely encapsulated by π systems, four of which are negatively charged. This box model only applies to a completely solvated Ca^{2+} cation (a naked Ca^{2+} would be too small for a snug fit), and certainly contributes to the stabilization of this SSIP. Finally, the above box model also implies another form of stabilization. The contact between the solvated cation and the walls of the box inevitably proceeds through the THF ligands, and this suggest the presence of nonclassical $C–H \cdots C$ hydrogen bonds. A search for short contacts between THF hydrogen atoms and the walls of the box shows that such interactions may indeed be important. Each THF ligand forms short $C–H \cdots C$ bonds to one of the walls (i.e., $H \cdots C$ contacts shorter than or close to the sum of the C and H van der Waals radii of 2.90 Å).[14] The shortest $H \cdots C$ contact is 2.615 Å. Such interactions are best described as $C–H \cdots \pi$ interactions (attraction between the $C^{\delta-}–H^{\delta+}$ dipole and the π-electron cloud).[15] The shortest $C–H \cdots ring_{center}$ interactions are shown in Figure 3. All the walls of the box show these interactions to both sides, and a three-dimensional network of hydrogen bonds is thus formed. Intuitively, one would expect the closest contacts to be between the outer β-hydrogen atoms and the walls, but the shortest wall ⋯ THF contacts are observed for the α-hydrogen atoms of the THF molecules. This is in good agreement with the concept of $C–H^{\delta+} \cdots C^{\delta-}$ hydrogen bonding: the most acidic protons are most likely to form the shortest and strongest bonds.[15g] The shortest contacts to a β-hydrogen atom of THF is, however, still quite short (2.765 Å) and these interactions also substantially contribute to the efficient binding of $[Ca^{2+}(thf)_6]$ in its cavity.

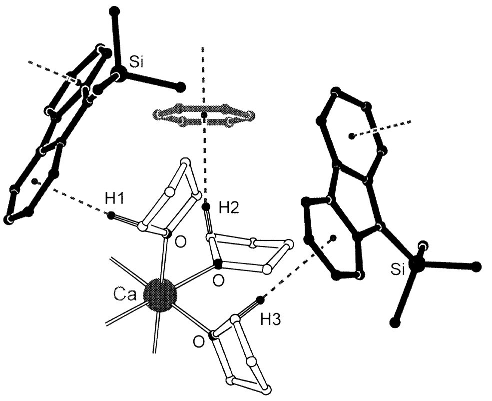
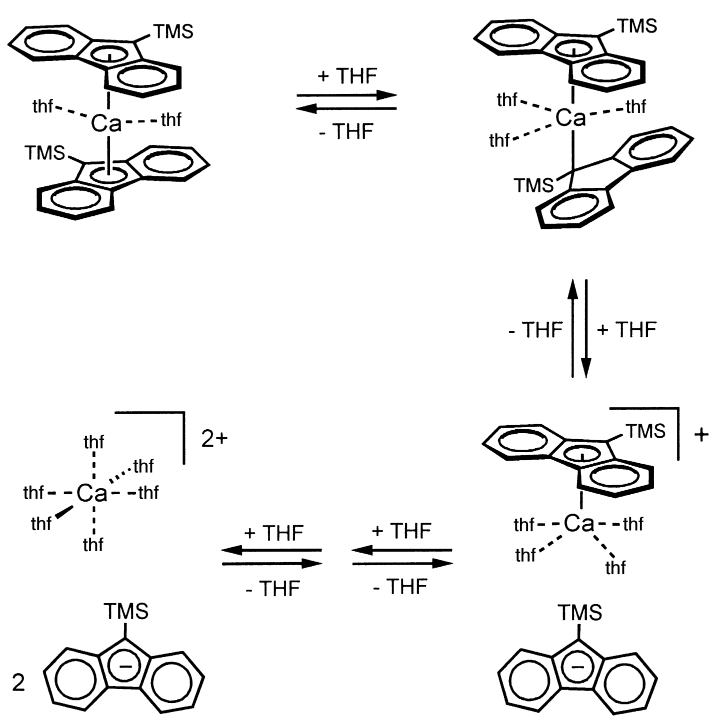


Figure 3. The hydrogen-bond network in the crystal structure of $[Ca^{2+}(thf)_6][Me_3Si(fluorenyl^-)]_2 \cdot C_6H_6$. Only half of the structure is shown (the other half is generated by inversion at the Ca center) and only hydrogen atoms involved in short C–H ··· π interactions are shown. The shortest C–H ··· $ring_{center}$ contacts are indicated by dashed lines. The C–H ··· $ring_{center}$ distances (angles) are H1: 2.725 Å (142.3°), H2: 2.730 Å (149.6°) and H3: 2.777 Å (158.1°). The shortest C–H ··· C contact involves H3 and amounts to 2.615 Å (133.5°). Values for the isostructural Mg analogue are H1: 2.759 Å (137.8°) H2: 2.761 Å (146.9°) and H3: 2.731 Å (154.6°). The shortest H ··· C contact involves H3 and amounts to 2.656 Å (130.0°).



(2)

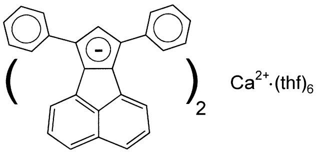
A relationship exists with the structure of the SSIP [fluorenyl$^-$][(ethylenediamine)$_2$Li$^+$].[1e] The ethylenediamine ligands in this structure are not chelating but bridge between Li$^+$ ions. This gives rise to a three-dimensional sponge structure of bridged Li$^+$ ions. Thus, in this structure the framework is not built from the anions but from the solvated cations. The fluorenyl anions are fixed in the cavities of the sponge by strong N–H ··· π interactions (the higher acidity of N–H compared to C–H bonds make such interactions much more important than C–H ··· π interactions).

Crystals of [**8** · (thf)$_6$] are slightly soluble in benzene, and the compound was studied in this solvent by NMR spectroscopy. If anion–cation bonding in solution is sufficiently strong, a preferential arrangement could exist between the plane of the fluorenyl ring and the solvated Ca^{2+} ion. In that case 2D-ROESY ^{1}H NMR spectroscopy might reveal short contacts between the [Me$_3$Si(fluorenyl)]$^-$ ion and hydrogen atoms of THF. Only dinuclear relaxation between the Me$_3$Si group of the fluorenyl anion and the α-hydrogen atoms of THF was observed, and no NOEs could be found to the β-hydrogens of THF. This might suggest that C–H$_\alpha$ ··· π hydrogen bonding, as observed in the solid state, is still present in solution. However, we would also expect weak NOEs for the β-hydrogen atoms of THF. A better explanation might be the presence of species in which at least one of the Me$_3$Si(fluorenyl) ligands is bound to a [Ca^{2+}(thf)$_x$] unit, either [Me$_3$Si(fluorenyl)$_2$]Ca · (thf)$_2$ or the cation [Me$_3$Si(fluorenyl)]$_2$Ca · (thf)$_4$. We therefore propose an equilibrium in solution in benzene between neutral, monocationic, and dicationic species [Eq. (2)]. The position of the equilibrium is strongly dependent on the THF concentration. Addition of THF drives all equilibria to the side of the completely solvent-separated ion pair, which precipitates from solution.

The Mg analogue **9** crystallizes from THF/benzene as yellow-orange needles and is isostructural to the calcium complex. It has similar crystal data, the same space group, the same composition ($[Mg^{2+}(thf)_6][Me_3Si(fluorenyl^-)]_2 \cdot C_6H_6$), and a very similar structure and crystal packing. The Mg^{2+} ion, situated on a crystallographic center of inversion, shows nearly perfect octahedral coordination by THF ligands: the Mg–O bond lengths are in the narrow range of 2.082(2)–2.109(2) Å, and the bond angles between neighboring THF ligands deviate from 90° by at most 1.4°. The solvated cation is enclosed in a box consisting of four [Me$_3$Si(fluorenyl)]$^-$ ions and two benzene molecules. A three-dimensional hydrogen-bond network, very similar to that in the Ca analogue (Figure 3), is observed here as well: the C–H ··· $ring_{center}$ distances (angles) are H1: 2.759 Å (137.8°), H2: 2.761 Å (146.9°), and H3: 2.731 Å (154.6°). The shortest C–H ··· C contact involves H3 (2.656 Å, 130.0°). The structures and crystal packing of the Mg and Ca analogues are strikingly similar in even the smallest detail. The puckering of the THF ligands in both structures is exactly the same. Although THF ligands usually show a high degree of disorder and anisotropy, those in both structures reported here have a high degree of order. The average anistropic displacement factors for the atoms of the THF molecules in the Mg and Ca structures are

0.052 and 0.037, respectively (the maximum anistropic displacement factors are 0.062 (Mg) and 0.101 (Ca)). This high degree of order and the close similarity of the two structures are likely due to the fixation of the $[M^{2+}(thf)_6]$ ions in their cavities by C–H···π interactions.

Bis(7,9-diphenylcyclopenta[*a*]acenaphthadienyl)calcium $[(ACp)_2Ca]$ (**10**) crystallizes with the composition $[\mathbf{10}\cdot(thf)_6]\cdot C_6H_6$. It contains a $[Ca^{2+}(thf)_6]$ ion with a crystallographic twofold axis running through Ca^{2+} and two of the THF oxygen atoms (Figure 2b). The octahedral coordination sphere around the Ca^{2+} ion is slightly distorted (Ca–O 2.327(2)–2.369(2) Å), and the bond angles between neighboring THF ligands deviate from 90° by maximally 5.1°. The overall structure of $[\mathbf{10}\text{-}(thf)_6]\cdot C_6H_6$ can also be described with the box model. The box is made of four negatively charged walls and two neutral, highly ordered benzene caps, which are slightly off-center. Likewise, the $[Ca^{2+}(thf)_6]$ ion is fixed in the cavity by C–H···π interactions, the most important of which are shown in Figure 4. Only short distances to the four negatively charged ligands are observed. The shortest C–H···π interaction with the center of the neutral benzene molecule is 2.977 Å. The ACp^- ligands themselves are pairwise connected by C–H···π interactions (H1).



$[\mathbf{10}\cdot(thf)_6]$

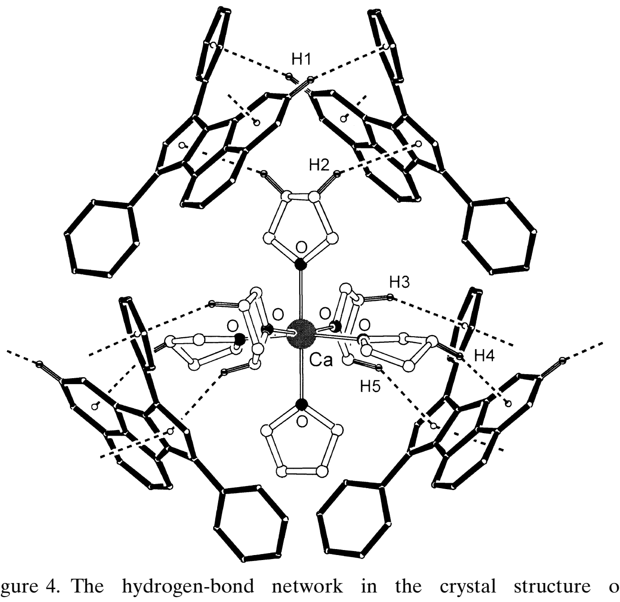


Figure 4. The hydrogen-bond network in the crystal structure of $[Ca^{2+}(thf)_6][ACp^-]_2\cdot C_6H_6$. The shortest C–H···ring$_{center}$ contacts are indicated by dashed lines. The C–H···ring$_{center}$ distances (angles) are H1: 2.783 Å (158.9°), H2: Å 2.816 (155.0°), H3: 2.741 Å (153.9°), H4: 2.549 Å (161.1°), H5: 2.679 Å (145.1°). The shortest H···C contact involves H5 and amounts to 2.587 Å (149.1°).

The box model and the incorporation of benzene seem to be general features in the structures of SSIPs consisting of fully solvated alkaline-earth metal cations and planar delocalized carbanions. We investigated the crystal packing of the earlier reported **4**.[4c] This is also a SSIP including a fluorenyl anion and, interestingly, also a cocrystallized benzene molecule. Its overall composition $[Me_2Mg_2{}^{2+}(pmdta)_2][fluorenyl^-]_2[C_6H_6]$ (PMDTA = pentamethyldiethylenetriamine) is the same as those of the compounds discussed above. The crystal structure shows a solvated $Me_2Mg_2{}^{2+}$ ion (situated on a center of inversion) surrounded by four negatively charged fluorenyl rings and two neutral benzene molecules (Figure 5a). Some of the hydrogen atoms of the chelating PMDTA ligand are involved in C–H···π interactions and show very short distances to the centers of the aromatic rings. The size and especially the elongated form of the cation disrupts the box of π ligands. The ligands surround the cation within the plane of projection. The three-dimensional arrangement of the fluorenyl anions and the benzene molecules is such that a honeycomb structure exists, that is, aromatic molecules that from parallel channels which are filled with stacks of solvated cations (Figure 5b). A similar channel

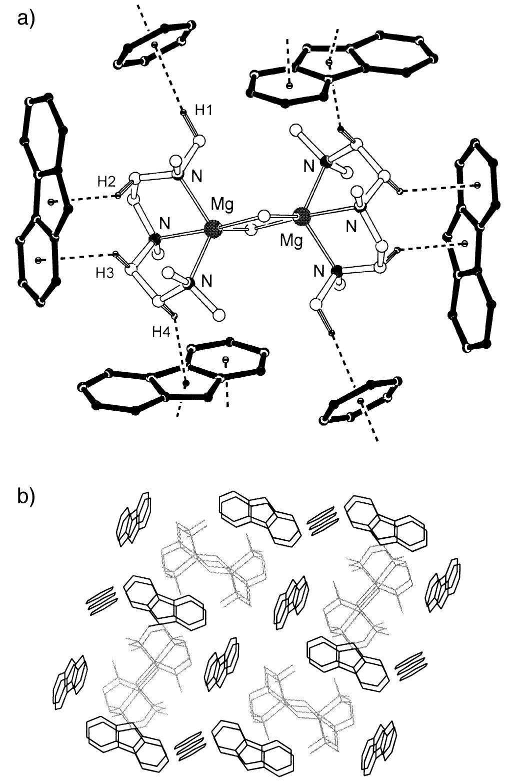
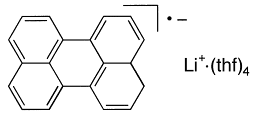


Figure 5. a) The hydrogen-bond network in the crystal structure of $[(pmdta)MgMe^+][fluorenyl^-]_2\cdot C_6H_6$.[4c] The shortest C–H···ring$_{center}$ contacts are indicated by dashed lines. The C–H···ring$_{center}$ distances (angles) are H1: 2.589 Å (150.1°), H2: 2.432 Å (143.2°), H3: 2.588 Å (125.5°), H4: 2.542 Å (145.5°). The shortest H···C contact involves H3 and amounts to 2.598 Å (104.4°). b) The packing model shows a honeycomb framework of anions (black), the channels of which are filled with solvated cations (gray).



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structure was reported for the alkali metal SSIP **11**.[1h] Likewise, SSIPs of bridged-fluorenyl anions with $[Li^+(thf)_4]$ countercations exhibit encapsulation of the solvated cation.[1b]

We prepared and structurally investigated two other SSIPs containing the weakly or noncoordinating anion Ph_4B^-. The phenyl-rich Ph_4B^- ion can coordinate directly to the metal cation, as in $Ph_4B^-K^+$ and $Ph_4B^-Rb^+$,[7] or can be free and function as an efficient acceptor for $C{-}H\cdots\pi$ interactions.

The complex $(Ph_4B^-)_2Mg^{2+}$ (**12**) was obtained by reaction of $MgBr_2$ with two equivalents of $Na^+Ph_4B^-$ in THF. Crystallization of the product from THF/hexane yielded crystals of composition $[Mg^{2+}(thf)_6][Ph_4B^-]_2\cdot$hexane. The structure contains a $[Mg^{2+}(thf)_6]$ ion, situated on a center of inversion and with a nearly perfect octahedral coordination geometry: the Mg–O bond lengths lie in the narrow range of 2.075(1)–2.115(1) Å, and the bond angles between neighboring THF ligands deviate from 90° by at most 1.1°. The boron atoms of the eight borate anions surrounding the cation can be regarded as the eight corners of a distorted cube (Figure 6).

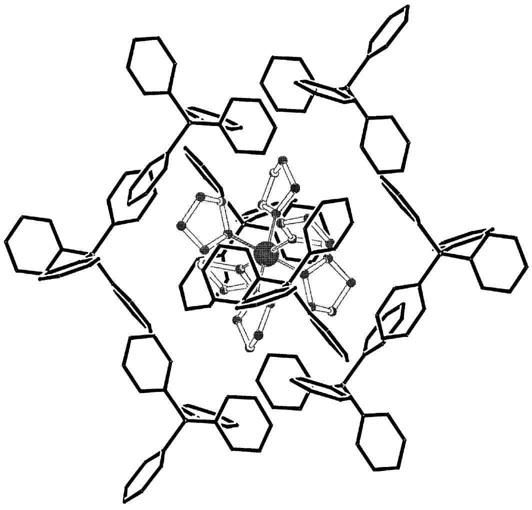

Figure 6. Packing of anions and cations in the crystal structure of $[Mg^{2+}(thf)_6][Ph_4B^-]_2$ (cation in gray and anions in black; a heavily disordered hexane molecule is not shown).

Thus, a solvated metal cation in a box is also present here. Each solvated cation is embedded in a framework of eight Ph_4B^- anions: six that encircle it within a plane, and one each below and above the plane. Many short $H\cdots C$ contacts are observed between the THF protons and the numerous phenyl ring carbon atoms (the shortest contact is 2.518 Å). At least eight $C{-}H\cdots\pi$ interactions have $C{-}H\cdots ring_{center}$ distances shorter than 2.8 Å.

The complex $[CaBr(thf)_4]^+Ph_4B^-$ ([**13**-$(thf)_4$]) was obtained by reaction of anhydrous $CaBr_2$ with one equivalent of $Ph_4B^-Na^+$ in THF and crystallized from THF/hexane. The crystal structure of this heteroleptic calcium compound is depicted in Figure 7. It shows a centrosymmetric dimeric $Ca_2Br_2^{2+}$ cation in which the bromine anions bridge the metal centers (Br-Ca-Br 83.9(3)°). Each Ca^{2+} ion is solvated by four THF ligands that complete its octahedral coordination sphere. All O-Ca-O angles are smaller than 90° (largest deviation 14.5°) due to repulsive interactions with the large Br^- ions. The $[Ca_2Br_2^{2+}(thf)_8]$ species is encircled by six borate anions (Figure 7a), but below and above the plane of projection are neighboring cations. Thus, the crystal packing can be best described as a honeycomb framework of borate anions, the channels of which are filled with cations (Figure 7b). In this respect, the structure is quite similar to that of $[Me_2Mg_2(pmdta)_2]^{2+}[fluorenyl^-]_2\cdot C_6H_6$ (Figure 5). This underscores the importance of size and shape of the cation: the $[Me_2Mg_2(pmdta)_2]^{2+}$ and $[Ca_2Br_2(thf)_8]^{2+}$ ions both have elongated forms.

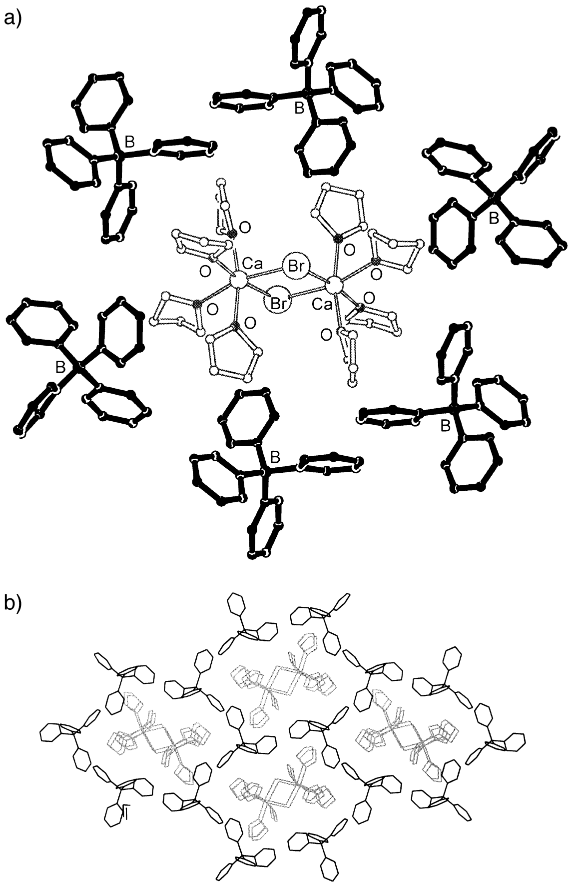

Figure 7. The dimeric entity $[CaBr^+(thf)_4]_2$ surrounded by six Ph_4B^- anions. b) The packing model shows a honeycomb framework of anions (black), the channels of which are filled with solvated cations (gray).

Each THF ligand is disordered over two positions and this complicates the discussion on $C{-}H\cdots\pi$ interactions between cations and anions. Apparently, several geometries of the solvated cation fit in the cavity. Both disordered models for the THF ligand display numerous short $C{-}H\cdots C$ bonds ($H\cdots C < 2.8$ Å).

Conclusion

We have found that fluorenylcalcium complexes show unusual behavior in solution and precipitate from nonpolar solvents on addition of THF. Their solid-state structures reveal the unexpected rupture of both metal–carbanion bonds to give completely solvent-separated ion pairs. The solid-state structures of these compounds are described by the "metal-in-a-box" model. This model, in which the solvated Group 2 cation is encapsulated in a box made of anionic ligands and benzene molecules, seems to be a general feature of structures of solvent-separated ion pairs with large planar anions. Numerous short C–H ··· π interactions between THF hydrogen atoms and the walls of the box fixate the solvated cation in its cavity and significantly stabilize this form of crystal packing.

Experimental Section

All experiments were carried out under argon using predried solvents and Schlenk techniques. Bis[bis(trimethylsilyl)amide]calcium(thf)$_2$,[16] 9-trimethylsilylfluorene,[17] and 7,9-diphenylcyclopenta[*a*]acenaphthadiene (ACpH)[18] were prepared according to literature procedures. Anhydrous CaI_2 was obtained from Strem. Anhydrous $MgBr_2$ was prepared in situ by treating 1,2-dibromoethane with Mg in THF.

Synthesis of 9-trimethylsilylfluorenylpotassium: A solution of 9-trimethylsilylfluorene (2.0 g, 8.39 mmol) and potassium bis(trimethylsilyl)amide (1.67 g, 8.37 mmol) in THF (15 mL) was refluxed for 2 h, during which the color changed to deep red. Evaporation of the solvent resulted in a dark red, foamy substance that became a powder after heating under vacuum (0.01 Torr, 60 °C, 1 h, quantitative yield). ^{1}H NMR (250 MHz, [D$_6$]benzene/[D$_8$]THF, 20 °C): $\delta = 0.60$ (s, 9H; Me$_3$Si), 6.78 (t, ^3J(H,H) = 7.2 Hz, 2H; aromatics), 7.09 (t, ^3J(H,H) = 7.4 Hz, 2H; aromatics), 7.72 (d, ^3J(H,H) = 8.1 Hz, 2H; aromatics), 7.89 (d, ^3J(H,H) = 7.8 Hz, 2H; aromatics). ^{13}C NMR: $\delta = 2.5$, 85.6, 111.4, 118.5, 119.2, 121.3, 123.9, 142.1.

Synthesis of hexakis(tetrahydrofuran)calcium bis(9-trimethylsilylfluorenide) ([8 · (thf)$_6$]): A solution of 9-trimethylsilylfluorenylpotassium (2.32 g, 8.39 mmol) in THF (20 mL) was stirred overnight with anhydrous CaI_2 (1.21 g, 4.12 mmol). The THF was completely removed from the yellow-brown suspension, and the resulting brown, sticky product was dried under vacuum (0.01 Torr, 60 °C, 1 h). Addition of benzene (30 mL) and subsequent centrifugation resulted in a orange-red mother liquor, which was concentrated to 20 mL. Addition of THF (4 mL) and cooling to 5 °C resulted in a crop of large orange crystals (yield: 2.45 g, 58 %). ^{1}H NMR (600 MHz, [D$_6$]benzene, 20 °C): $\delta = 0.56$ (s, 9H; Me$_3$Si), 1.27 (m, 4H; THF), 3.24 (m, 4H; THF), 6.87 (t, ^3J(H,H) = 7.1 Hz, 2H; aromatics), 7.15 (s, 6H; benzene), 7.18 (t, ^3J(H,H) = 7.2 Hz, 2H; aromatics), 7.80 (d, ^3J(H,H) = 8.2 Hz, 2H; aromatics), 7.83 (d, ^3J(H,H) = 7.7 Hz, 2H; aromatics). ^{13}C NMR: $\delta = 2.4$, 25.4, 68.4, 88.6, 113.2, 120.7, 120.8, 122.4, 124.5, 128.3 (benzene), 142.3.

Synthesis of hexakis(tetrahydrofuran)magnesium bis(9-trimethylsilylfluorenide) ([9 · (thf)$_6$]): A solution of 9-trimethylsilylfluorenylpotassium (1.11 g; 4.01 mmol) and $MgBr_2$ (8.0 mL, 0.25 M in THF, 2.00 mmol) in THF (20 mL) was refluxed for 1 h. The orange-brown mother liquor was separated from the KBr by centrifugation and concentrated to ca. 10 mL. Cooling to 4 °C yielded a large crop of yellow-orange blocks (1.98 g, 49 %). ^{1}H NMR (250 MHz, [D$_4$]methanol, 20 °C): $\delta = 0.10$ (s, 9H; Me$_3$Si), 1.85 (m, 4H; THF), 3.68 (m, 4H; THF), 7.22–7.35 (m, 4H; aromatics), 7.33 (s, 6H; benzene), 7.51 (t, ^3J(H,H) = 6.7 Hz, 2H; aromatics), 7.78 (d, ^3J(H,H) = 7.3 Hz, 2H; aromatics). ^{13}C NMR: $\delta = -1.1$ (Me$_3$Si), 26.5 (THF), 68.8 (THF), 120.7, 125.1, 126.1, 127.0, 127.8, 138.1 (^1J(C,D) = 21.7 Hz), 143.0 (aromatics), 129.3 (benzene).

Synthesis of hexakis(tetrahydrofuran)calcium bis(7,9-diphenylcyclopenta[*a*]acenaphthadienide) ([10 · (thf)$_6$]): A solution of bis[bis(trimethylsilyl)amide]calcium(thf)$_2$ (0.51 g, 1.00 mmol) and 7,9-diphenylcyclopenta[*a*]acenaphthadiene (ACpH, 0.68 g, 1.99 mmol) in benzene (40 mL) was refluxed for 3 h. Evaporation of the solvent and drying under vacuum (0.01 Torr, 75 °C, 1 h) gave the crude product in the form of a red-brown powder as the THF disolvate (ACp)$_2$Ca · (thf)$_2$ in essentially quantitative yield. Large black (intense dark red) crystals of the SSIP were obtained by dissolving the crude product in THF/benzene (9/1) and cooling to 4 °C (yield: 0.78 g, 63 %). ^{1}H NMR (600 MHz, [D$_6$] benzene, 20 °C): $\delta = 1.31$ (m, 4H; THF), 3.42 (m, 4H; THF), 6.34 (s, 1H; ACp), 7.12 (t, ^3J(H,H) = 7.4 Hz, 2H; ACp), 7.15 (s, 6H; benzene), 7.18 (t, ^3J(H,H) = 7.6 Hz, 2H; ACp), 7.27 (t, ^3J(H,H) = 7.6 Hz, 2H; ACp), 7.37 (d, ^3J(H,H) = 8.1 Hz, 2H; ACp), 7.68 (d, ^3J(H,H) = 8.3 Hz, 2H; ACp), 7.70 (d, ^3J(H,H) = 7.1 Hz, 2H; ACp). ^{13}C NMR: $\delta = 25.6$ (THF), 68.0 (THF), 110.9, 117.3, 123.2, 123.4, 125.4, 127.2, 127.6, 128.5, 128.7, 131.0, 137.0, 137.3, 138.8 (ACp), 128.3 (C$_6$H$_6$).

Synthesis of hexakis(tetrahydrofuran)magnesium bis(tetraphenylborate) ([12 · (thf)$_6$]): A solution of $Ph_4B^-Na^+$ (0.70 g; 2.05 mmol) and $MgBr_2$ (4.1 mL, 0.25 M in THF, 1.03 mmol) in THF (20 mL) was refluxed for 1 h. The colorless mother liquor was separated from NaBr by centrifugation. Vapour diffusion of hexane into the mother liquor yielded a crop of large colorless crystals (0.58 g, 51.0 %) of the SSIP. ^{1}H NMR (250 MHz, [D$_8$]THF, 20 °C): $\delta = 1.76$ (m, 4H; THF), 3.62 (m, 4H; THF), 6.71 (t, ^3J(H,H) = 7.1 Hz, 4H; *p*-H), 6.85 (t, ^3J(H,H) = 7.3 Hz, 8H; *m*-H), 7.25 (m, 8H; *o*-H). ^{13}C NMR: $\delta = 26.7$, 68.1, 121.6, 125.5, 137.1, 165.1 (q, ^1J(C,B) = 7.3 Hz).

Synthesis of bromotetrakis(tetrahydrofuran)calcium tetraphenylborate ([13 · (thf)$_4$]): A suspension of anhydrous $CaBr_2$ (0.49 g, 2.45 mmol) in THF (20 mL) was combined with a solution of $Ph_4B^-Na^+$ (0.84 g, 2.45 mmol) in THF (20 mL) and stirred at 65 °C for 24 h. The resulting white suspension was centrifuged, and the separated mother liquor was concentrated to ca. 50 % of its original volume and layered with hexane (20 mL). An oil that later transformed into large platelike colorless crystals separated from the solution (1.18 g; 33 %). ^{1}H NMR (250 MHz, [D$_4$]methanol, 20 °C): $\delta = 1.82$ (m, 16H; THF), 3.69 (m, 16H; THF), 6.83 (t, ^3J(H,H) = 7.1 Hz, 4H; *p*-H), 6.96 (t, ^3J(H,H) = 7.3 Hz, 8H; *m*-H), 7.29 (m, 8H; *o*-H). ^{13}C NMR: $\delta = 26.3$, 68.0, 121.2, 125.3, 137.0, 165.4 (q, ^1J(C,B) = 7.2 Hz).

Crystal structure determinations: Data were recorded on an Enraf-Nonius CAD4 diffractometer ($\lambda = 0.71073$ nm). The structures were solved by automatic Patterson methods (DIRDIF)[19] or by direct methods (SHELX-S)[20] and refined with SHELXL-97[21] against F^2 for all reflections. Molecular illustrations and geometry calculations were performed with the PLATON package.[22] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-169838–169842. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[8 · thf)$_6$]: ($C_{24}H_{48}CaO_6$)($C_{16}H_{17}Si$)$_2$(C_6H_6), $M_r = 1025.58$, orange-red block, 0.3 × 0.4 × 0.5 mm, monoclinic, space group $P2_1/c$, $a = 12.569(2)$, $b = 16.550(2)$, $c = 18.121(2)$ Å, $\beta = 128.555(7)°$, $V = 2947.8(7)$ Å^3, $Z = 2$, $\rho = 1.156$ g cm^{-3}, $\mu(\mathrm{Mo_{K\alpha}}) = 0.195$ mm^{-1}. A total of 6059 reflections were measured (Mo$_{K\alpha}$ radiation, graphite monochromator, $T = -90$ °C, $\theta_{max} = 26.0°$), 5789 independent reflections ($R_{int} = 0.031$), 3966 observed reflections with $I > 2.0\sigma(I)$. Refinement to $R_1 = 0.041$, $wR_2 = 0.108$ and GOF = 1.03 (498 parameters). All hydrogen atoms were removed from the difference Fourier map and refined isotropically with free displacement factors; max./min. residual electron density: −0.39/0.23 e Å^{-3}.

[9 · (thf)$_6$]: ($C_{24}H_{48}MgO_6$)($C_{16}H_{17}Si$)$_2$(C_6H_6), $M_r = 1009.81$, yellow needle, 0.2 × 0.3 × 0.4 mm, monoclinic, space group $P2_1/c$, $a = 12.2863(14)$, $b = 16.3355(9)$, $c = 17.9291(18)$ Å, $\beta = 127.951(6)°$, $V = 2837.5(5)$ Å^3, $Z = 2$, $\rho = 1.182$ g cm^{-3}, $\mu(\mathrm{Mo_{K\alpha}}) = 0.123$ mm^{-1}. A total of 6076 reflections were measured (Mo$_{K\alpha}$ radiation, graphite monochromator, $T = -90$ °C, $\theta_{max} = 26.5°$), 5804 independent reflections ($R_{int} = 0.018$), 4032 observed reflections with $I > 2.0\sigma(I)$. Refinement to $R_1 = 0.043$, $wR_2 = 0.109$ and GOF = 1.02 (498 parameters). All hydrogen atoms were removed from the difference Fourier map and refined isotropically with free displacement factors; max./min. residual electron density: −0.33/0.27 e Å^{-3}.

[10 · (thf)$_6$]: ($C_{24}H_{48}CaO_6$)($C_{27}H_{17}$)$_2$(C_6H_6), $M_r = 1233.62$, black (dark red) block, 0.4 × 0.4 × 0.5 mm, monoclinic, space group $C2/c$, $a = 17.330(2)$, $b = 18.985(2)$, $c = 21.210(2)$ Å, $\beta = 106.88(1)°$, $V = 6677.6(1)$ Å^3, $Z = 4$, $\rho = 1.227$ g cm^{-3}, $\mu(\mathrm{Mo_{K\alpha}}) = 0.150$ mm^{-1}. A total of 4742 reflections were measured (Mo$_{K\alpha}$ radiation, graphite monochromator, $T = -90$ °C, $\theta_{max} = 25.0°$), 4597 independent reflections ($R_{int} = 0.016$), 3254 observed reflections with $I > 2.0\sigma(I)$. Refinement to $R_1 = 0.038$, $wR_2 = 0.094$ and GOF = 1.02 (588 parameters). All hydrogen atoms were removed from the difference Fourier map and refined isotropically with free displacement factors; max./min. residual electron density: −0.25/0.17 e Å^{-3}.

[12 · (thf)$_6$]: ($C_{24}H_{48}MgO_6$)($C_{24}H_{20}B$)$_2$(C_6H_{12}), $M_r = 1179.51$, white block, 0.6 × 0.7 × 0.8 mm^3, monoclinic, space group $P2_1/c$, $a = 11.937(4)$, $b = 13.227(3)$, $c = 23.371(6)$ Å, $\beta = 116.82(2)°$, $V = 3293(2)$ Å^3, $Z = 2$, $\rho = 1.190$ g cm^{-3}, $\mu(\mathrm{Mo_{K\alpha}}) = 0.076$ mm^{-1}. A total of 7529 reflections were measured ($Mo_{K\alpha}$ radiation, graphite monochromator, $T = -90\,^{\circ}C$, $\theta_{max} = 27.0^{\circ}$), 7187 independent reflections ($R_{int} = 0.022$), 5119 observed reflections with $I > 2.0\sigma(I)$. Refinement to $R_1 = 0.049$, $wR_2 = 0.128$ and GOF = 1.04 (543 parameters). The structure contains a cocrystallized hexane molecule with severe disorder. This disordered solvent was treated with the bypass procedure using the program SQUEEZE[23] (incorporated in PLATON[22]). All hydrogen atoms were removed from the difference Fourier map and refined isotropically with free displacement factors. Max./min. residual electron density: $-0.24/0.41$ e Å^{-3}.

[13 · (thf)$_4$]: $(C_{32}H_{64}Br_2Ca_2O_8)(C_{24}H_{20}B)_2$, $M_r = 1455.07$, colorless block, $0.4 \times 0.4 \times 0.4$ mm, monoclinic, space group $P2_1/c$, $a = 9.952(2)$, $b = 28.446(2)$, $c = 15.441(2)$ Å, $\beta = 120.49(1)^{\circ}$, $V = 3767(1)$ Å^3, $Z = 2$, $\rho = 1.283$ g cm^{-3}, $\mu(Mo_{K\alpha}) = 1.266$ mm^{-1}. A total of 8649 reflections were measured ($Mo_{K\alpha}$ radiation, graphite monochromator, $T = -90\,^{\circ}C$, $\theta_{max} = 27.0^{\circ}$), 8186 independent reflections ($R_{int} = 0.020$), 5467 observed reflections with $I > 2.0\,\sigma(I)$. Refinement to $R_1 = 0.058$, $wR_2 = 0.171$ and GOF = 1.04 (474 parameters). Absorption correction with PLATON[22] based on psi scans (0.94–0.98 transmission). All THF ligands showed disorder over two positions and were refined isotropically as such. All borate hydrogen atoms were removed from the difference Fourier map and were refined isotropically with free displacement factors. The THF hydrogen atoms were calculated and refined in a riding model; max./min. residual electron density: $-0.33/0.27$ e Å^{-3}.

Acknowledgements

This work was generously supported by BASF AG (Ludwigshafen, Germany), the Deutsche Forschungsgemeinschaft and the University of Konstanz. We would like to acknowledge the following for discussions: Prof. Dr. H.-H. Brintzinger (Konstanz), Dr. K. Knoll (BASF, Ludwigshafen), and Ms. A. Friemel for recording 600 MHz NMR spectra.

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Received: September 12, 2001 [F3551]