

# Lewis Acidic Cationic Strontium and Barium Complexes

Katharina Thum,<sup>[a]</sup> Johannes Martin,<sup>[a]</sup> Holger Elsen,<sup>[a]</sup> Jonathan Eyselein,<sup>[a]</sup> Lena Stiegler,<sup>[a]</sup> Jens Langer,<sup>[a]</sup> and Sjoerd Harder<sup>\*[a]</sup>

Lewis acidic (BDI)Ae<sup>+</sup> cations of the heavier metals Sr and Ba, which are not stabilized by polar solvents, have been obtained by double deprotonation of (BDI)H<sub>2</sub><sup>+</sup> with either SrN"<sub>2</sub> or BaN"<sub>2</sub>; BDI = HC[C(Me)N(DIPP)]<sub>2</sub>, DIPP = 2,6-diisopropylphenyl, Ae = alkaline earth, N" = N(SiMe<sub>3</sub>)<sub>2</sub>. Due to clathrate formation [(BDI)Ae<sup>+</sup>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub><sup>-</sup>] could not be crystallized, but pyrene addition gave crystalline [(BDI)Ae<sup>+</sup>·pyrene][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub><sup>-</sup>] which was structurally characterized for Ae = Mg, Ca, Sr, Ba. (R<sub>2</sub>N)Ae<sup>+</sup> cations of the heavier metals Sr and Ba were obtained by reaction of Ae(NR<sub>2</sub>)<sub>2</sub> with [Ph<sub>3</sub>C<sup>+</sup>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub><sup>-</sup>] or [PhNMe<sub>2</sub>H<sup>+</sup>] [B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub><sup>-</sup>]. Following complexes were structurally characterized: [N"Ba<sup>+</sup>·(tol)<sub>2</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub><sup>-</sup>], [N\*Sr<sup>+</sup>·PhNMe<sub>2</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub><sup>-</sup>], [N\*Ba<sup>+</sup>·tol]

# Introduction

Alkaline earth (Ae) metal catalysis started to develop at the beginning of this century.<sup>[1-3]</sup> The field lately witnessed major breakthroughs especially in alkene and arene hydrogenation or functionalization.<sup>[4-13]</sup> Intermediate metal-alkene or arene  $\pi$ complexes play a superordinate role in substrate activation. For example, Ca-alkene interactions have been found crucial for successful catalytic alkene hydroamination.<sup>[14]</sup> Lately it also has been recognized that, especially for the heavier Ae metals Ca, Sr and Ba, the formation of Ae-arene interactions is the key to nucleophilic aromatic substitution reactions.[15-17] Unlike transition metals, the Ae metals do not dispose of partially filled dorbitals for small molecule activation. This is at least true for the  $Ae^{2+}$  ions. Recent observations indicate that *d*-orbitals may play a significant role for bond activation with electron-rich Ca<sup>I</sup> or  $Ca^0$  metal centers by strong  $\pi$ -backdonation.<sup>[18-20]</sup> Substrate activation with Ae<sup>2+</sup> cations relies fully on its strong Lewis acidic properties which by an electrostatic Ae<sup>2+</sup>...substrate interaction causes polarization of  $\pi$ -electron density in the substrate.<sup>[21,22]</sup>

 [a] K. Thum, Dr. J. Martin, Dr. H. Elsen, J. Eyselein, L. Stiegler, Dr. J. Langer, Prof. Dr. S. Harder
 Chair of Inorganic and Organometallic Chemistry, Universität Erlangen-Nürnberg, Egerlandstraße 1, 91058, Erlangen, Germany
 E-mail: sjoerd.harder@fau.de
 https://www.harder-research.com
 Supporting information for this article is available on the WWW under



Board Member Virtual Issue

$$\begin{split} & [B(C_6F_5)_4^{-1}] \text{ and } [N^*Ba^+ \cdot C_6H_6][B(C_6F_5)_4^{-1}]; \text{ tol} = \text{toluene and } N^* = \\ & N(SiiPr_3)_2. \text{ DFT calculations show that } Sr \cdots PhNMe_2 \text{ coordination} \\ & \text{is preferred over } Sr \cdots \text{toluene bonding. The } (R_2N)Ae^+ \text{ cations can} \\ & \text{be used as Brønsted bases (reaction with (BDI)H gave (BDI)Ae^+)} \\ & \text{and may be useful precursors for a variety of Lewis base-free} \\ & RAe^+ \text{ cations. DFT calculations, limited to monomeric model} \\ & \text{systems including } B(C_6F_5)_4^{-1} \quad (\omega B97XD/def2tzvpp//\omega B97XD/def2svp), show that there is negligible electron transfer from \\ & \text{the pyrene or toluene ligands to the } Ae^{2+} \text{ cation. Electrostatic} \\ & \text{attraction originates from charge-induced polarization of the} \\ & \pi\text{-electron density in the toluene and pyrene ligands.} \end{split}$$

Since Ae- $\pi$ -substrate complexes with weak, non-covalent cation... $\pi$ -interactions were rare and poorly understood, we started a comprehensive study on early main group metal---alkene and arene interactions. The vast majority of known Aealkene complexes is intramolecular.<sup>[21-29]</sup> Therefore, we developed synthetic methods to access highly Lewis acidic, cationic Ae complexes which allow for intermolecular Ae-alkene interactions. While most cationic Ae metal complexes are stabilized by strong Lewis bases or strongly chelating, multidentate neutral or anionic ligands,<sup>[30-41]</sup> our interest is directed to "naked", Lewis base-free, cationic complexes. We reported cationic  $\beta$ -diketiminate Ae metal complexes, (BDI)Ae<sup>+</sup>, that in the presence of the weakly coordinating anion (WCA)  $B(C_6F_5)_4^{-1}$ are highly Lewis acidic and strongly bind to neutral arenes (I);  $BDI = HC[C(Me)N(DIPP)]_2, DIPP = 2,6-diisopropylphenyl$ (Scheme 1).<sup>[42-44]</sup> At the same time, Hill and coworkers reported similar complexes with Krossing's WCA AI[OC(CF<sub>3</sub>)<sub>3</sub>]<sub>4</sub><sup>-[45]</sup> The very high Lewis acidity of their metal centers was not only demonstrated by bonding of  $\pi$ -arenes including benzene, toluene and *m*-xylene, [42-45] but also by coordination of 3hexyne<sup>[46]</sup> and hexamethyldisiloxane,<sup>[47]</sup> a silyl ether normally inert to metal bonding (II). Upon addition of a number of mono- and bis-alkenes, the first unsupported group 2 metal alkene complexes could be isolated and were fully characterized.  $^{[48]}$  Increasing the bulk of the  $\beta\text{-diketiminate}$ ligand allowed for isolation of the full series of Mg...XPh complexes (X=F, Cl, Br, I).<sup>[49]</sup> It was shown that the coordinated benzene ligand in (BDI)Ca<sup>+</sup>  $\cdot$  C<sub>6</sub>H<sub>6</sub> is activated for nucleophilic attack: reaction with the low-valent Al<sup>I</sup> species (BDI)Al gave 1,4addition to benzene resulting in a species containing the nonplanar, anti-aromatic  $C_6 H_6^{2-}$  anion which can be seen as a (BDI) Ca<sup>+</sup> cation interacting with an alumina-norbornadiene (III).<sup>[50]</sup> Furthermore, complexes of type (BDI)AeBPh<sub>4</sub> were isolated in which the Ae center mereley interacts with the tetraphenylborate anion via Ae--Ph-B contacts (Ae=Mg, Ca).<sup>[51]</sup> The latter Ae-

<sup>© 2021</sup> The Authors. European Journal of Inorganic Chemistry published by Wiley-VCH GmbH. This is an open access article under the terms of the Creative Commons Attribution License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited.



Scheme 1. Cationic alkaline earth metal complexes.

arene bonding is due to a negative charge on  $Ph_4B^-$  quite strong and although the complex was crystallized from toluene, no Ae--toluene interaction is observed. Substituting the BDI ligand in I for a chelating amidinate ligand gave the cationic Ca species (IV) which was shown active in hydroboration of ketones.<sup>[52]</sup>

While quite a number of examples of Mg and Ca-based cations have emerged in recent years, Lewis base-free cationic complexes of the heavier homologs Sr and Ba are underrepresented. This is immediately related to the considerably larger ion sizes for  $Sr^{2+}$  and  $Ba^{2+}$  which makes it challenging to saturate their coordination spheres without using polar solvents. Sarazin et al. reported cationic Sr and Ba complexes stabilized by multiple Lewis bases among which (BDI)Sr<sup>+</sup> · (pvridine) ... (pvridine). Most recently, Krossing reported the first "naked"  $Ae^{2+}$  cations (Ae = Ca, Sr, Ba) which are stabilized by  $(\eta^{6})$ -hexamethylbenzene bonding and interactions with fluorinated solvent and WCA's (V).<sup>[53]</sup> With a neutral chelating ansaarene ligand, a dicationic strontium complex (VI) was introduced that was successfully employed as a catalyst in isobutylene polymerization.<sup>[54]</sup> Here we describe the challenging syntheses and purification of borate complexes of the Lewis base-free cations (BDI)Ae<sup>+</sup> (Ae = Sr, Ba). Additionally, we introduce a series of complexes with the  $(R_2N)Ae^+$  cation (Ae =Sr, Ba). Their bonding with neutral arene ligands is discussed and has been subject of a theoretical study.

Chemistry Europe

European Chemica Societies Publishing

## **Results and Discussion**

### Syntheses

The (BDI)Mg<sup>+</sup> cation was obtained according to an earlier reported procedure: reaction of (BDI)MgnBu with [Ph<sub>3</sub>C<sup>+</sup>][B-(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub><sup>-</sup>] gave [(BDI)Mg<sup>+</sup>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub><sup>-</sup>], Ph<sub>3</sub>CH and 1-butene (Scheme 2).<sup>[42]</sup> Due to facile ligand exchange reactions, it is challenging to synthesize heteroleptic (BDI)AeR complexes for the heavier Ae metals (Ae = Ca, Sr, Ba).<sup>[39,55,56]</sup> We therefore developed a different approach for the synthesis of the heavier (BDI)Ae<sup>+</sup> cations.<sup>[42]</sup> In a first step the β-diketimine (BDI)H is protonated by Jutzi's oxonium acid [H<sup>+</sup> · (OEt<sub>2</sub>)<sub>2</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub><sup>-</sup>]<sup>[57]</sup> to give [(BDI)H<sub>2</sub><sup>+</sup>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub><sup>-</sup>] (Scheme 2). Double deprotonation with the homoleptic base AeN''<sub>2</sub> (Ae = Ca, Sr, Ba; N'' = N(SiMe<sub>3</sub>)<sub>2</sub>) in the polar but non-coordinating solvent chloroben-



Scheme 2. Syntheses of  $[(BDI)Ae^+ \cdot pyrene][B(C_6F_5)_4^-]$  (Ae = Mg, Ca, Sr, Ba).



zene led to  $[(BDI)Ae^+][B(C_6F_5)_4^-]$  in nearly quantitative yield. Although the cationic Mg complex  $[(BDI)Mg^+][B(C_6F_5)_4^-]$  has been crystallized and could be fully characterized by X-ray diffraction,<sup>[42]</sup> repeated attempts to obtain crystals of similar solvent-free complexes with the heavier Ae metals failed due to clathrate formation. For Ae = Ca we found that addition of small quantities of benzene led to facile crystallization of the benzene adduct  $[(BDI)Ca^+ \cdot C_6H_6][B(C_6F_5)_4^-]$ ,<sup>[42]</sup> but similar benzene adducts could not be obtained for Ae = Sr and Ba. Attempts to crystallize adducts of various other aromatic solvents (toluene, o- and m-xylene, mesitylene) also failed. However, using a larger extended polycyclic aromatic hydrocarbon (PAH) like pyrene gave crystals of [(BDI)Ae<sup>+</sup>·pyrene]  $[B(C_6F_5)_4]$  from a saturated chlorobenzene solution (yield: Sr 48%; Ba 69%). For comparison, also the lighter Ae complexes within the series have been prepared (yield: Mg 52%; Ca 39%).

In addition to these cationic  $\beta$ -diketiminate complexes, we also introduce a new series of Lewis base-free cations stabilized by monodentate amide ligands (Scheme 3). Bochmann and coworkers previously reported the isolation and structures of the cationic complexes  $[N''M^+ \cdot (Et_2O)_3][B(C_6F_5)_4^-]$  with M = Mgor Zn in which three Et<sub>2</sub>O ligands stabilize the metal cation (N"  $= N(SiMe_3)_2)$ .<sup>[30]</sup> Using a similar synthetic protocol in which the coordinating solvent Et<sub>2</sub>O was replaced by chlorobenzene, a less coordinating polar solvent, did not lead to isolation of welldefined cationic N"Sr<sup>+</sup> or N"Ba<sup>+</sup> complexes. Compared to bidendate  $\beta$ -diketiminate ligands, the smaller size and monodentate character of the amide ligand make stabilization of well-defined Lewis base-free complexes of larger cations considerably more challenging. However, using a mixture of chlorobenzene and toluene as the solvent, reaction of BaN", with  $[Ph_3C^+][B(C_6F_5)_4^-]$  led to amide abstraction and formation of the toluene adduct  $[N''Ba^+ \cdot (tol)_2][B(C_6F_5)_4^-]$  in 65% crystalline yield (Scheme 3). Due to steric hindrance the amide N" cannot attack the central trityl carbon but, as observed earlier,<sup>[45]</sup> reacts with the *p*-phenyl carbon to give a cyclohexadiene-like product. Complex  $[N''Ba^+ \cdot (tol)_2][B(C_6F_5)_4^-]$  is hardly soluble in halogenated aromatic solvents.

To increase its solubility, the substantially bulkier amide reagent BaN<sup>\*</sup><sub>2</sub> (N<sup>\*</sup> = N(Si*i*Pr<sub>3</sub>)<sub>3</sub>), which is even in alkanes highly soluble,<sup>[5]</sup> was reacted with  $[Ph_3C^+][B(C_6F_5)_4^-]$ . Under various conditions, this much bulkier amide ligand could not be abstracted by the trityl cation. However, addition of the anilinium salt [PhNMe<sub>2</sub>H<sup>+</sup>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub><sup>-</sup>] led to facile protonation of N\* to N\*H. The product  $[N*Ba^+ \cdot tol][B(C_6F_5)_4^-]$  could be crystallized in 52% yield; a similar product with a benzene ligand could be isolated and structurally characterized as well (Figure S68). The analogue reaction of SrN\*<sub>2</sub> with [PhNMe<sub>2</sub>H<sup>+</sup>]  $[B(C_6F_5)_4^-]$  gave  $[N*Sr^+ \cdot PhNMe_2][B(C_6F_5)_4^-]$  in which the metal cation is capped by  $\pi$ -bound PhNMe<sub>2</sub> instead of toluene. The neutral  $\pi$ -toluene and  $\pi$ -PhNMe<sub>2</sub> ligands in these complexes are only loosely bound to the metal and great care has to be taken in their isolation (drying under high vacuum should be avoided). In  $Ba_7H_7N''_7 \cdot (C_6H_6)_2$  the coordinated benzene molecules are also easily removed under vacuum.<sup>[58]</sup>

Since the amide ligands N" and N\* are strong Brønsted bases, the cationic Ae amide complexes are of interest as synthons for further preparation of cationic Ae complexes. Starting from  $[N"Ba^+ \cdot (tol)_2][B(C_6F_5)_4^-]$ ,  $[N*Ba^+ \cdot tol][B(C_6F_5)_4^-]$  or  $[N*Sr^+ \cdot PhNMe_2][B(C_6F_5)_4^-]$ , deprotonation of (BDI)H and addition of pyrene gave the  $\beta$ -diketiminate pyrene complexes in fair yields (Scheme 2). This synthetic pathway can also be followed in a one-pot procedure: *e.g.* a mixture of  $BaN''_{2,r}$  [Ph<sub>3</sub>C<sup>+</sup>]  $[B(C_6F_5)_4^-]$  and (BDI)H led to *in situ* formation of (BDI)Ba<sup>+</sup> which in the presence of pyrene gave  $[(BDI)Ba^+ \cdot pyrene][B(C_6F_5)_4^-]$ . The latter procedure avoids the tedious work-up of the intermediate complex  $[N"Ba^+ \cdot (tol)_2][B(C_6F_5)_4^-]$ . This straight forward method is likely applicable to the synthesis of a large variety of Lewis base-free cationic Ae metal complexes.

#### Crystal structures and solution studies

Representative crystal structures of cationic  $\beta$ -diketiminate Ae metal complexes stabilized with pyrene ligands are shown in Figure 1a–c (see Table 1 for selected bond distances). As shown schematically in Scheme 2, all metals in the series Mg–Ba are



Scheme 3. Syntheses of cationic amido Ae metal complexes.





**Figure 1.** (a) Crystal structure of  $[(BDI)Ca^+ \cdot pyrene][B(C_6F_5)_4^-]$ . (b) Crystal structure of  $[(BDI)Sr^+ \cdot pyrene][B(C_6F_5)_4^-]$ ; the  $B(C_6F_5)_4^-$  anions bridge between two metal centers. (c) The different Ae-pyrene coordination modes. (d) Crystal structure of  $[N^*Ba^+ \cdot (tol)_2][B(C_6F_5)_4^-]$  which forms a coordination polymer. (e) Crystal structure of  $[N^*Sr^+ \cdot PhNMe_2][B(C_6F_5)_4^-]$ . (f) Crystal structure of  $[N^*Ba^+ \cdot tol][B(C_6F_5)_4^-]$  which forms a polymer chain. For clarity, hydrogen atoms have been omitted and  $B(C_6F_5)_4^-$  anions are only partially shown.

<b>Table 1.</b> Comparison of shortest bond distances (Å) in [(BDI)Ae+·pyrene][B(C6F5)4-] (Ae=Mg, Ca, Sr, Ba).					
Ae	Mg	Ca	Sr	Ва	
Ae–N	1.983(1)	2.269(2)	2.466(2)	2.599(2)	
	1.991(1)	2.288(2)	2.495(2)	2.609(2)	
Ae–C	2.454(1)	2.767(3)	3.078(2)	3.241(2)	
	2.456(1)	2.931(3)	3.148(2)	3.300(2)	
		3.034(3)	3.356(2)	3.410(2)	
Ae-F (WCA1)	2.0417(9)	2.451(2)	2.565(1)	2.779(1)	
		2.552(1)			
Ae-F (WCA2)	-	-	2.915(1)	2.995(1)	
			2.987(1)	3.079(1)	

bound to the chelating BDI ligand, the borate anion  $B(C_6F_5)_4^$ and pyrene. The number of metal…F as well as metal…C contacts increase with metal size. Therefore, complexes of the smaller metals Mg and Ca are monomeric while those of the larger metals Sr and Ba form dimeric structures in which the two (BDI)Ae<sup>+</sup> · pyrene moieties are bridged by  $B(C_6F_5)_4^-$  anions. The molecular packing in these complexes is dominated by  $\pi$ -stacking of pyrene moieties with interplanar distances close to 3.5 Å, *i.e.* twice the van-der-Waals radius of C.

Discussing bond lengths in complexes with weak electrostatic bonds is bound to raise critical questions on hapticity due to the blurred border between bonding and non-bonding situations. Other than in covalent bonding, electrostatic bonds can be stretched considerably without breaking abruptly: the bond energy of an electrostatic bond is defined by Coulomb's law and inversely proportional to distance. Without clear cut-off criteria, the assignment of hapticity is merely based on comparisons with other examples for such weak interactions in literature. Analysis of Ae–N, Ae…C and Ae…F distances shows that the bond distances increase linear with  $Ae^{2+}$  cation size. Interestingly, the increase of the Ae…F distances is most pronounced (Figure S71). This may be explained by Hard-Soft-Acid-Base theory: the hard-hard match Mg–F gives shorter than expected bonds, while the soft-hard mismatch Ba–F gives rise to unusually long distances which should rather be regarded as weak interactions. The Mg–F distance in Mg…pyrene complex matches with literature known distance in I,<sup>[42]</sup> while the distances for Ca–F contacts are in agreement with values reported in V.<sup>[53]</sup> For the heavier Ae metals Sr and Ba, exceptionally long Sr–F and Ba–F interactions are found, which fall in the range reported for V (contacts to o-difluorobenzene: Sr–F: 2.625(3)–2.703(3) Å; Ba–F: 2.791(4)–2.939(5) Å)<sup>[53]</sup> and VI (Sr–F to o-difluorobenzene: 2.541(2) and 2.651(2) Å).

The hapticity and mode of metal-pyrene coordination is strongly dependent on metal size but even for the larger metals Sr and Ba a maximal hapticity of three is found (Figure 1c). This bonding motif is unusual compared to pyrene complexes of transition metals for which generally  $\eta^6$ -coordination is observed.<sup>[59-62]</sup>

Ca–C contacts in Ca—pyrene complex are in good agreement with distances reported in **V**.<sup>[53]</sup> They also fall in the range of Ca—C(Ph) distances in (BDI)CaBPh<sub>4</sub> (2.840(2)–3.249(2) Å) in which Ca is sandwiched between two Ph rings of a negatively charged tetraphenyborate anion.<sup>[51]</sup> One Ca—C(pyrene) bond is exceptionally short (shortest contact: 2.767(3) Å). For comparison, in **V** the shortest contact to  $\eta^6$ -coordinated hexameth-ylbenzene is 0.02 Å longer<sup>[53]</sup> and the shortest Ca–C contact in the benzene adducts of type I is 2.909(2) Å.<sup>[42]</sup> The Ca—C(pyrene) contact in [(BDI)Ca<sup>+</sup> · pyrene][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>–] is even shorter than the



Ca…arene contacts in complexes of type III and IV in which the metal cation is considerably less shielded by ligands.<sup>[50,52]</sup> It is nearly as short as the average Ca–C bond of 2.633(8) Å in Cp\*<sub>2</sub>Ca in which Ca<sup>2+</sup> binds a negatively charged Cp\* anion (Cp\*=C<sub>5</sub>Me<sub>5</sub>).<sup>[63]</sup> To the best of our knowledge, the Ca…C(pyrene) bond length is the shortest value reported for an unsupported Ca…arene bond. Despite this short contact, there is no significant influence of the metal-pyrene coordination on the C–C bond distances (Figure S70), indicating a purely electrostatic interaction between the metal cation and the extended  $\pi$ -system.

Although the metal-C contacts in Ae--pyrene complexes (Ae = Sr, Ba) are longer than in complexes of type V,<sup>[53]</sup> which have a very open coordination sphere at the metal and therefore enable rather short Ae--C contacts to  $\eta^6$ -coordinated hexameth-ylbenzene, the herein reported Ae--C distances fall in the typical range reported for Ae--C(arene) contacts in benzylic complexes.<sup>[64-66]</sup> *E.g.*, Sr--C(Ph) contacts in (PhCH<sub>2</sub>)<sub>4</sub>Sr<sub>2</sub>(THF)<sub>3</sub> vary from 2.907(2) to 3.382(3) Å while Ba--C(arene) contacts in (PhCH<sub>2</sub>)<sub>6</sub>Ba<sub>3</sub>(THF)<sub>5</sub> or in (DMAT)<sub>2</sub>Ba(THF<sub>2</sub>) (DMAT=2-dimeth-ylamino- $\alpha$ -trimethylsilylbenzyl) are in the 3.067(2)-3.309(2) Å range.<sup>[67]</sup> Longer Ba--C contacts in the range of 3.286(3)-3.430(3) Å have been reported for barium complex bearing a triazene ligand with bulky aryl substituents.<sup>[66]</sup> These values are in good agreement with those found in the Ba--pyrene complex.

The full series of cationic Ae metal pyrene complexes [(BDI)  $Ae^+ \cdot pyrene$ ][ $B(C_6F_5)_4^-$ ] (Ae = Mg, Ca, Sr, Ba) is soluble in bromobenzene- $d_5$  and the heavier complexes (Ae = Ca, Sr, Ba) even dissolve surprisingly well in  $C_6D_6$ . NMR spectra of the complexes in these solvents show in all cases signals for free, uncoordinated, pyrene. Even for the most Lewis acidic metal cation,  $Mg^{2+}$ , pyrene is more weakly bound than the solvent which is present in large excess. These cationic Sr and Ba complexes could therefore be seen as arene solvates.

Representative crystal structures of cationic amido Ae metal complexes are shown in Figure 1d–f (see Table 2 for selected bond distances). The Ba atom in  $[N''Ba^+ \cdot (tol)_2][B(C_6F_5)_4^-]$  is symmetrically sandwiched by two toluene ligands (Figure 1d). The shorter Ba–C(toluene) contacts range from 3.279(9) Å to

Table 2. Selected shortest bond distances (Å) for cationic Ae metal amido complexes.					
Complex	$[N''Ba^+ \cdot (tol)_2] \\ [B(C_6F_5)_4^-]$	$[N*Sr^+ \cdot PhNMe_2] \\ [B(C_6F_5)_4^-]$	$[N*Ba^+ \cdot tol] \\ [B(C_6F_5)_4^-]$		
Ae–N Ae–C (arene1)	2.502(8) 3.279(9) 3.281(9) 3.323(9)	2.408(2) 3.033(2) 3.040(2) 3.095(2) 3.119(2) 3.182(2) 3.244(3)	2.559(3) 3.321(8) 3.353(7) 3.385(6)		
Ae–C (arene2)	3.23(3) <sup>[a]</sup> 3.25(3) <sup>[a]</sup> 3.29(4) <sup>[a]</sup>	-	-		
Ae–F (WCA1)	3.077(8)	2.676(1) 2.695(1)	2.783(3)		
Ae-F (WCA2)	3.046(5) 3.072(5)	-	2.941(3)		
[a] Toluene ligand disordered.					

3.323(9) Å and are comparable to the Ba-pyrene contacts (vide supra). Interestingly, they are only marginally longer than the average Ba–C bond distances in [BaCp<sub>3</sub><sup>-</sup>][NBu<sub>4</sub><sup>+</sup>] (3.129 Å)<sup>[68]</sup> or  $[BaCp_2]$  (3.151 Å),<sup>[69]</sup> both complexes with  $Ba^{2+}$ ...Cp<sup>-</sup> contacts. They are also slightly longer than the average Ba-C contact (3.141 Å) in the Ba bis-ylide complex [Ph<sub>2</sub>P(4-methylbenzylide)<sub>2</sub>]<sub>2</sub>Ba.<sup>[70]</sup> However, the Ba--toluene contacts are considerably longer than the Ba-C bonds in the sandwich complex  $Ba(C_{5}Ph_{5})_{2}$  in which the rings attract each other by dispersive forces.<sup>[71]</sup> Note that the reported Ba–C distances to neutral coordinating toluene ligands are reported in the 3.18-3.36 Å range and are in good agreement with our values.<sup>[72-74]</sup> The coordination sphere of Ba in  $[N''Ba^+ \cdot (tol)_2][B(C_6F_5)_4^-]$  is completed by three relatively long Ba--F interactions with two bridging  $B(C_6F_5)_4^-$  anions, giving rise to a coordination polymer. Replacing the amide ligand N" for the bulkier ligand N\* does not change this structure type but leads to loss of one of the toluene ligands (Figure 1f). In contrast, the analogue complex with the somewhat smaller Sr metal is monomeric (Figure 1e). In  $[N*Sr^+ \cdot PhNMe_2][B(C_6F_5)_4^-]$  the Sr coordination sphere in N\*Sr<sup>+</sup> is completed by capping with a N,N-dimethylaniline ligand with Sr...C contacts in the range of 3.033(2) to 3.244(3) Å. These distances are in good agreement with Sr-C contacts in VI (2.945(3)–3.117(3) Å).<sup>[54]</sup> A similar coordination mode is observed for transition metal complexes of N,N-dimethylaniline.[75-77] Preference for dimethylaniline versus toluene coordination may be explained by the mesomeric effect of the Me<sub>2</sub>N-substituent which is coplanar with the ring, releasing electron density by resonance. In contrast, Sr-NMe<sub>2</sub> coordination results in localization of the electron lone pair on N, giving rise to pyramidalization of the N atom.<sup>[78]</sup> The coordination sphere of Sr is complemented by two Sr...F-C contacts to the borate anion, which are in agreement with values reported in V.<sup>[53]</sup>

The cationic amido Ae metal complexes with the bulky N\* ligands dissolve well in bromobenzene- $d_5$ . In contrast, the complex with the less bulky N" ligand,  $[N''Ba^+ \cdot (tol)_2][B(C_6F_5)_4^-]$ , is insoluble in bromobenzene- $d_5$  and even hardly dissolves in the more polar solvents  $C_6H_5F$  or  $C_6H_4F_2$ . NMR studies in these solvents reveal in all cases signals for free, uncoordinated, toluene or PhNMe<sub>2</sub> ligands due to excess of coordinating solvent.

## Theoretical considerations

DFT calculations were performed at the  $\omega$ B97XD/def2tzvpp level of theory. The complexes have been fully optimized, the presence of B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub><sup>-</sup> was considered in all cases. Although we incorporated the WCA in all cases, our studies are limited to monomeric model systems for practical reasons. Bond energies as well as NPA charges have been calculated, Atoms-in-Molecules (AIM) analyses have been performed. A comparison between crystal structures and calculated structures can be found in Table S2 and Table S3.

The complexation enthalpies and free energies for pyrene have been calculated (Scheme 4a). While pyrene coordination is in all cases exothermic,  $\Delta H$  ranges from -15.4 to -24.5 kcal/





Scheme 4. (a) Complexation enthalpies (and free energies) for pyrene bonding. (b) Complexation enthalpies (and free energies) for toluene and *N*,*N*-dimethylaniline bonding.

mol, it is for larger metals nearly thermoneutral in case entropy is considered:  $\Delta G$  ranges from -0.5 to -9.0 kcal/mol. There is, however, no clear correlation with Ae<sup>2+</sup> cation size. According to expectation, the Ae<sup>2+</sup>...pyrene bond energy should decrease down group 2: Mg > Ca > Sr > Ba. However, the following trend is calculated: Mg > Ca < Sr > Ba; *i.e.* the maximum complexation energies are found for Sr<sup>2+</sup>. This irregularity is due to competition between Ae<sup>2+</sup>...pyrene and Ae<sup>2+</sup>...B(C<sub>6</sub>F<sub>s</sub>)<sub>4</sub><sup>-</sup> bonding. At least within the limitations of our model system, the larger metals (Sr and Ba) are still able to maintain short Ae<sup>2+</sup>...F

Complexation enthalpies and free energies have also been calculated for bonding of toluene and *N*,*N*-dimethylaniline to cationic amido Ae metal complexes (Scheme 4b, Figure S89). While toluene bonding to the least bulky (Me<sub>3</sub>Si)<sub>2</sub>NBa<sup>+</sup> cation is highly exothermic ( $\Delta H = -37.8$  kcal/mol), bonding of a second toluene ligand is substantially less favorable ( $\Delta H = -11.5$  kcal/mol). If one considers loss of entropy, coordination of the second toluene ligand is even slightly endergonic and a temperature dependent equilibrium is expected ( $\Delta G = +1.0$  kcal/mol). Toluene coordination to the sterically hindered cation ( $iPr_3Si)_2NBa^+$  is considerably less exothermic and considering the free energy it should be regarded thermoneutral ( $\Delta G = -1.8$  kcal/mol). Bonding of a second toluene ligand was

not possible. The same holds for toluene coordination to  $(iPr_3Si)_2NSr^+$ . For this cation, it was calculated that  $\pi$ -coordination of *N*,*N*-dimethylaniline is preferred over toluene bonding, as observed by experiment.

From the NPA charge analysis it is evident that metal-ligand bonding in the (BDI)Ae<sup>+</sup>  $\cdot$  pyrene (Ae = Mg, Ca, Sr, Ba) and the (amide)Ae<sup>+</sup> · arene (Ae = Sr, Ba; amide = N'' or N\*) complexes is mainly electrostatic. Regardless of the anionic ligand, which is either a bidentate  $\beta$ -diketiminate or monodentate amide, or the coordinated arenes (pyrene, toluene or aniline) the charges on the metal centers vary from +1.80 to +1.86, those on the neutral ligands from +0.008 to +0.03 and those on the negatively charged ligands from -0.86 to -0.92 (Figure S72-S73). This means that there is negligible charge transfer from the neutral arene ligand to the Ae<sup>2+</sup> metal cation. Metal-arene bonding arises from strong polarization of the arene  $\pi$ -electron density by the  $Ae^{2+}$  cation (Figure S74–S87). Metal coordination also leads in general to a slightly increased ellipticity of the pyrene C-C bonds involved (compared to similar pyrene C-C bonds that are non-coordinating); see Figures S74–S80. Although the calculated coordination geometries differ from the crystal structures (Table S2-S3), it can be seen that small Ae<sup>2+</sup> cations like Mg<sup>2+</sup> result in the strongest polarization of the pyrene  $\pi$ -electron density (Figure 2a). Atoms-In-Molecules





(a) changes in C charges due to pyrene coordination

**Figure 2.** (a) Polarization of the pyrene ligand on account of metal coordination. The numbers show the increase of the electron density in comparison with free pyrene (NPA charges). (b) AIM analyses: Laplacian of the electron density in [(BDI)Mg<sup>+</sup> · pyrene][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub><sup>-</sup>] (left) and [(BDI)Ba<sup>+</sup> · pyrene][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub><sup>-</sup>] (right). Blue dots represent bond-critical-points.  $\pi$ -Electron density polarization towards the metal is indicated by orange arrows.

(AIM) analyses show that there is not only a shift of  $\pi$  -electron density within the pyrene plane but also perpendicular to this plane (Figure 2b). This is exemplary shown for the small, strongly polarizing, Mg<sup>2+</sup> cation in [(BDI)Mg<sup>+</sup>·pyrene][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub><sup>-</sup>] but is also evident in [N"Ba<sup>+</sup>·(tol)<sub>2</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub><sup>-</sup>] with the much larger Ba<sup>2+</sup> cation (Figure S83).

# Conclusion

Lewis base-free (BDI)Ae<sup>+</sup> cations of the heavier metals Sr and Ba are accessible by double deprotonation of  $(BDI)H_2^+$  with either SrN"<sub>2</sub> or BaN"<sub>2</sub>. Although the salts  $[(BDI)Ae^+][B(C_6F_5)_4^-]$  could not be crystallized due to clathrate formation, addition of pyrene enabled the full characterization of the arene adducts:  $[(BDI)Ae^+ \cdot pyrene][B(C_6F_5)_4^-]$  for Ae = Mg, Ca, Sr, Ba. Crystal structures show that the coordination sphere of all metals consists of a chelating BDI ligand and several Ae---pyrene and Ae---F interactions.

Lewis base-free (R<sub>2</sub>N)Ae<sup>+</sup> cations of the heavier metals Sr and Ba were available by removal of a single amide ligand from Ae(NR<sub>2</sub>)<sub>2</sub>. For less bulky amide ligands (N" = N(SiMe<sub>3</sub>)<sub>2</sub>) this can be achieved by reaction with [Ph<sub>3</sub>C<sup>+</sup>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub><sup>-</sup>]. Thus, the toluene stabilized complex [N"Ba<sup>+</sup> · (tol)<sub>2</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub><sup>-</sup>] was obtained which forms a coordination polymer. For the bulky amide ligand N\* (= N(SiiPr<sub>3</sub>)<sub>2</sub>), protonation with [PhN(H)Me<sub>2</sub><sup>+</sup>] [B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub><sup>-</sup>] was imperative. Accordingly, reaction of SrN\*<sub>2</sub> with the anilinium salt led to [N\*Sr<sup>+</sup> · PhNMe<sub>2</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub><sup>-</sup>] which

crystallized as a monomer with a  $\pi$ -bound PhNMe<sub>2</sub> ligand. DFT calculations show that Sr…PhNMe<sub>2</sub> coordination is preferred over Sr…toluene bonding. The analogue Ba complex crystallized as the toluene complex [N\*Ba<sup>+</sup>·tol][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub><sup>-</sup>]. Since the amide ligand is a moderately strong Brønsted base, (R<sub>2</sub>N)Ae<sup>+</sup> cations can be used as versatile precursors for a variety of Lewis base-free RAe<sup>+</sup> cations.

All cationic Sr and Ba complexes have been studied by NMR in either benzene, bromobenzene, fluorbenzene or difluorobenzene. In all cases, metal-pyrene or toluene coordination cannot compete with solvation and only signals for free pyrene and toluene were observed.

DFT calculations, limited to monomeric model systems including  $B(C_6F_5)_4^-(\omega B97XD/def2tzvpp)$ , demonstrate that metal-ligand bonding is of electrostatic nature. There is negligible electron transfer from the pyrene or toluene ligands to the  $Ae^{2+}$  cation. Electrostatic attraction originates from charge-induced polarization of the  $\pi$ -electron density in the toluene and pyrene ligands.

The herein presented Lewis base-free cationic Sr and Ba complexes feature large open coordination spheres around the metal. Complexes with the (BDI)Ae<sup>+</sup> cations (Ae = Ca, Sr, Ba) are even soluble in benzene. This makes them ideally suited as soft Lewis acids for complexation and activation of larger  $\pi$ -systems which is a topic we currently investigate. In this role they contribute to our understanding of the role of the alkaline earth metal in catalysis.



# **Experimental Section**

## **General Experimental Procedures**

All experiments were conducted under an inert nitrogen atmosphere using standard Schlenk and glovebox techniques (MBraun, Labmaster SP). Hexane (isomeric mixture), pentane (isomeric mixture), toluene and benzene were degassed with nitrogen, dried over activated aluminum oxide (Solvent Purification System: Pure Solv 400-4-MD, Innovative Technology) and stored over 3 Å molecular sieves. Chlorobenzene and were dried over calcium hydride, distilled under N<sub>2</sub> atmosphere and stored over molecular sieves 3 Å. C<sub>6</sub>D<sub>5</sub>Br and C<sub>6</sub>D<sub>6</sub> (99.6% D, Sigma Aldrich) were dried over 3 Å molecular sieves. Pyrene (Alfa Aesar, 98%) was obtained commercially, sublimed under reduced pressure and stored under  $N_2$  atmosphere.  $[Ph_3C^+][B(C_6F_5)_4^-]$  and  $[PhNMe_2H^+][B(C_6F_5)_4^-]$ (Boulder Scientific) were used as received.  $[(BDI)H_2^+][B(C_6F_5)_4^-]$  (BDI =  $HC[C(Me)N(DIPP)]_2$ , DIPP = 2,6-diisopropylphenyl),<sup>[42]</sup>  $SrN''_2$  and  $BaN''_2 (N'' = N(SiMe_3)_2),^{[79]} SrN_2 and <math display="inline">BaN_2 (N^* = N(SiiPr_3)_2)^{[5]}$  and  $[(BDI)Mg^+ \cdot C_6H_6][B(C_6F_5)_4^-]^{[42]}$  were synthesized according to literature procedures. NMR spectra were recorded with a Bruker Avance III HD 400 MHz or a Bruker Avance III HD 600 MHz spectrometer. The spectra were referenced to the respective residual signals of the deuterated solvents.<sup>[80]</sup> Elemental analysis was performed with a Euro EA 3000 (Euro Vector) analyzer. All crystal structures have been measured on a SuperNova (Agilent) diffractometer with dual Cu and Mo microfocus sources and either an Atlas or Atlas S2 detector.

Deposition Numbers 207217 {for [(BDI)Mg<sup>+</sup>·pyrene][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub><sup>-</sup>]}, 2072218 {for [(BDI)Ca<sup>+</sup>·pyrene][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub><sup>-</sup>]}, 2072219 {for [(BDI)Sr<sup>+</sup>·pyrene][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub><sup>-</sup>]}, 2072220 {for [(BDI)Ba<sup>+</sup>·pyrene][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub><sup>-</sup>]}, 2072221 {for [N"Ba<sup>+</sup>·(tol)]2][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub><sup>-</sup>]}, 2072222 {for [N\*Ba<sup>+</sup>·tol][B-(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub><sup>-</sup>]}, 2072223 {for [N\*Ba<sup>+</sup>·C<sub>6</sub>H<sub>6</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub><sup>-</sup>]}, and 2072224 {for [N\*Sr<sup>+</sup>·PhNMe<sub>2</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub><sup>-</sup>]} contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

Synthesis of  $[(BDI)Ba^+ \cdot pyrene][B(C_6F_5)_4^-]$ :  $[(BDI)H_2^+][B(C_6F_5)_4^-]$ (0.1620 g, 0.1480 mmol) and BaN"<sub>2</sub> (0.0744 g, 0.1630 mmol, 1.1 eq.) were dissolved in chlorobenzene (3 mL). A yellow slime formed, which was dissolved again after the mixture was heated to 60 °C for 4 h. All volatiles were removed in vacuo. Hexane (2 mL) was added to the resulting orange-brown foam and upon scratching the glass wall of the reaction vessel solid formation was initiated. The solid was washed with hexane (2×3 mL) and dried in vacuo to obtain the crude product in 95% yield. After dissolving 0.0305 g (0.0247 mmol) in chlorobenzene (0.3 mL) and adding pyrene (0.0285 g, 5.7 eq.), yellow crystals grew at room temperature overnight, which were washed with cold pentane and dried in vacuo (0.0244 g, 0.0170 mmol, 69%). Note: In some attempts the solution oversaturated and seeding crystals were necessary. An alternative synthetic procedure is given in the supplementary information. <sup>1</sup>H NMR (600 MHz, C<sub>6</sub>D<sub>5</sub>Br, 298 K)  $\delta$  8.00 (d, <sup>3</sup>J<sub>HH</sub>= 7.5 Hz, 4H, ArH (pyrene)), 7.90 (s, 4H, ArH (pyrene)), 7.85 (t, <sup>3</sup>J<sub>HH</sub>= 7.5 Hz, 2H, ArH (pyrene)), 7.12-7.08 (m, 6H, ArH), 4.82 (s, 1H, CCHC), 2.73 (hept, <sup>3</sup>J<sub>HH</sub>=6.8 Hz, 4H, CHMe<sub>2</sub>), 1.63 (s, 6H, CH<sub>3</sub>), 1.08 (d, <sup>3</sup>J<sub>HH</sub>= 6.8 Hz, 12H, CHCH<sub>3</sub>), 1.00 (d,  ${}^{3}J_{HH}$  = 6.8 Hz, 12H, CHCH<sub>3</sub>) ppm.  ${}^{13}C{}^{1}H{}$ NMR (151 MHz,  $C_6D_5Br$ , 298 K)  $\delta$  163.0 (s, NC(CH<sub>3</sub>)), 148.7 (br. d,  ${}^{1}J_{CF} = 242 \text{ Hz}, B(C_{6}F_{5})_{4}), 142.0 \text{ (s, ArC)}, 141.1 \text{ (s, ArC)}, 138.6 \text{ (br. d,}$  ${}^{1}J_{CF} = 243 \text{ Hz}, B(C_{6}F_{5})_{4}), 136.7 \text{ (br. d, } {}^{1}J_{CF} = 242 \text{ Hz}, B(C_{6}F_{5})_{4}), 128.8 \text{ (s,}$ ArCH), 127.7 (s, ArC (pyrene)), 126.2 (s, ArCH (pyrene)), 125.7 (s, ArCH), 125.3 (s, ArCH (pyrene)), 125.0 (s, ArC (pyrene)), 100.0 (s, CCHC), 28.5 (s, CHMe2), 24.9 (s, CHCH3), 24.2 (s, NC(CH3)), 24.1 (s, CHCH<sub>3</sub>) ppm. B–C of  $B(C_6F_5)_4$  was not detected. <sup>19</sup>F{<sup>1</sup>H} NMR (376 MHz, C<sub>6</sub>D<sub>5</sub>Br, 298 K)  $\delta$  -130.8 (s, 8F, o-CF), -159.8 (t,  ${}^{3}J_{FF} =$ 21 Hz, 4F, p-CF), -163.9 (s, 8F, m-CF) ppm. <sup>11</sup>B{<sup>1</sup>H} NMR (128 MHz,  $C_6 D_5 Br,~298$  K)  $\delta~-16.1$  (s,  $\textit{B}(C_6 F_5)_4)$  ppm.  $^1\text{H}$  NMR (600 MHz,  $C_6 D_{6\prime}$ 298 K)  $\delta$  7.93 (d,  ${}^{3}J_{HH} =$  7.5 Hz, 4H, ArH (pyrene)), 7.83 (s, 4H, ArH (pyrene)), 7.76 (t,  ${}^{3}J_{HH} = 7.5$  Hz, 2H, ArH (pyrene)), 7.08–7.03 (m, 6H, ArH), 4.48 (s, 1H, CCHC), 2.41 (hept, <sup>3</sup>J<sub>HH</sub>=6.8 Hz, 4H, CHMe<sub>2</sub>), 1.43 (s, 6H, CH<sub>3</sub>), 1.06 (d, <sup>3</sup>J<sub>HH</sub>=6.8 Hz, 12H, CHCH<sub>3</sub>), 1.04 (d, <sup>3</sup>J<sub>HH</sub>=6.8 Hz, 12H, CHCH<sub>3</sub>) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (151 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K) δ 163.1 (s, NC(CH<sub>3</sub>)), 149.1 (br. d, <sup>1</sup>J<sub>CF</sub> = 242 Hz, B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>), 145.1 (s, ArC), 139.8 (s, ArC), 138.8 (br. d,  ${}^{1}J_{CF} = 243$  Hz, B( $C_{6}F_{5}$ )<sub>4</sub>), 137.3 (br. d,  ${}^{1}J_{CF} = 242$  Hz, B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>), 131.7 (s, ArC (pyrene)), 127.8 (s, ArCH (pyrene)), 126.1 (s, ArCH (pyrene)), 125.6 (s, ArCH), 125.3 (s, ArC (pyrene)), 124.5 (s, ArCH), 89.5 (s, CCHC), 28.8 (s, CHMe<sub>2</sub>), 24.7 (s, CHCH<sub>3</sub>), 24.4 (s, NC(CH<sub>3</sub>)), 24.2 (s, CHCH<sub>3</sub>) ppm. B–C of B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub> was not detected. <sup>19</sup>F  $\{^{1}\text{H}\}$  NMR (565 MHz, C\_6D\_6, 298 K)  $\delta$  -131.6 (s, 8F, o-CF), -161.1 (t, <sup>3</sup>J<sub>FF</sub>=21 Hz, 4F, *p*-CF), -165.1 (s, 8F, *m*-CF) ppm. <sup>11</sup>B{<sup>1</sup>H} NMR (193 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K)  $\delta$  –16.0 (s, B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>) ppm. FT-IR (ATR, pure):  $\tilde{\nu} = 2972$  (m), 2928 (w), 2873 (w), 1649 (m), 1554 (m), 1514 (vs), 1462 (s), 1386 (m), 1364 (m), 1310 (m), 1267 (m), 1174 (m), 1089 (s), 977 (vs), 847 (m), 773 (m), 755 (m), 722 (m), 707 (m), 660 (m) cm <sup>-1</sup>. Color change to black at 80°C, m.p.: 159°C with decomposition. Elemental analysis Found: C, 57.65; H, 3.62; N, 1.97. Calc. for C<sub>69</sub>H<sub>49</sub>BBaF<sub>20</sub>N<sub>2</sub> (M = 1434.27 g/mol): C, 57.78; H, 3.44; N, 1.95.

Synthesis of  $[(BDI)Sr^+ \cdot pyrene][B(C_6F_5)_4^-]$ :  $[(BDI)H_2^+][B(C_6F_5)_4^-]$ (0.1880 g, 0.1710 mmol) and SrN"<sub>2</sub> (0.0768 g, 0.1880 mmol, 1.1 eq.) were dissolved in chlorobenzene (3 mL). A yellow slime formed, which was dissolved again after the mixture was heated to 60 °C overnight. All volatiles were removed in vacuo and hexane (2 mL) was added to the resulting orange-brown foam. Upon scratching the glass wall of the reaction vessel solid formation was initiated. The solid was washed with hexane (3×2 mL) and dried in vacuo to obtain the crude product in 92% yield. After dissolving 0.0175 g (0.0148 mmol) in chlorobenzene (0.2 mL) and adding pyrene (0.0163 g, 5.7 eq.), the orange solution was layered with hexane (0.2 mL) at room temperature and left overnight after which time no crystals could be observed. Within the inert atmosphere of a glovebox, the vial was placed in a container with hexane (0.5 mL) for slow gas diffusion. Yellow crystals grew within 2 days at room temperature, which were isolated and dried in vacuo (0.0098 g, 0.00708 mmol, 48%). Note: In some attempts the solution oversaturated and additonal hexane diffusion or seeding crystals were necessary. An alternative synthetic procedure is given in the supplementary information. <sup>1</sup>H NMR (600 MHz, C<sub>6</sub>D<sub>5</sub>Br, 298 K) δ 8.00 (d, <sup>3</sup>J<sub>HH</sub> = 7.5 Hz, 4H, ArH (pyrene)), 7.90 (s, 4H, ArH (pyrene)), 7.85 (t, <sup>3</sup>J<sub>HH</sub> = 7.5 Hz, 2H, ArH (pyrene)), 7.07 (m, 6H, ArH), 4.82 (s, 1H, CCHC), 2.80 (hept, <sup>3</sup>J<sub>HH</sub>=6.8 Hz, 4H, CHMe<sub>2</sub>), 1.60 (s, 6H, CH<sub>3</sub>), 1.07 (m, 24H, CHCH<sub>3</sub>) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (151 MHz, C<sub>6</sub>D<sub>5</sub>Br, 298 K)  $\delta$  165.8 (s, NC(CH<sub>3</sub>)), 148.5 (br. d, <sup>1</sup>J<sub>CF</sub> = 242 Hz, B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>), 143.0 (s, ArC), 141.0 (s, ArC), 138.5 (br. d,  ${}^{1}J_{CF} = 243$  Hz, B( $C_{6}F_{5})_{4}$ ), 136.8 (br. d,  ${}^{1}J_{CF} = 242$  Hz, B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>), 128.6 (s, ArCH), 127.7 (s, ArC (pyrene)), 126.2 (s, ArCH (pyrene)), 126.1 (s, ArCH), 125.3 (s, ArCH (pyrene)), 125.0 (s, ArC (pyrene)), 94.2 (s, CCHC), 28.7 (s, CHMe<sub>2</sub>), 25.0 (s, CHCH<sub>3</sub>), 24.2 (s, NC(CH<sub>3</sub>)), 24.1 (s, CHCH<sub>3</sub>) ppm. B–C of B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub> was not detected. <sup>19</sup>F {<sup>1</sup>H} NMR (376 MHz, C<sub>6</sub>D<sub>5</sub>Br, 298 K)  $\delta$  –131.3 (s, 8F, o-CF), –159.8 (t,  ${}^{3}J_{FF} = 21$  Hz, 4F, p-CF), -164.2 (s, 8F, m-CF) ppm.  ${}^{11}B{}^{1}H{}$  NMR (128 MHz,  $C_6D_5Br$ , 298 K)  $\delta$  -16.1 (s,  $B(C_6F_5)_4$ ) ppm. <sup>1</sup>H NMR (600 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K)  $\delta$  7.94 (d, <sup>3</sup>J<sub>HH</sub>=7.5 Hz, 4H, ArH (pyrene)), 7.82 (s, 4H, ArH (pyrene)), 7.76 (t,  ${}^{3}J_{HH}$ =7.5 Hz, 2H, ArH (pyrene)), 7.10-7.01 (m, 6H, ArH), 4.47 (s, 1H, CCHC), 2.44 (hept, <sup>3</sup>J<sub>HH</sub>=6.9 Hz, 4H, CHMe<sub>2</sub>), 1.40 (s, 6H, CH<sub>3</sub>), 1.06 (d, <sup>3</sup>J<sub>HH</sub> = 6.9 Hz, 12H, CHCH<sub>3</sub>), 1.00 (d,  ${}^{3}J_{HH} = 6.9$  Hz, 12H, CHCH<sub>3</sub>) ppm.  ${}^{13}C{}^{1}H$  NMR (151 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K)  $\delta$  166.0 (s, NC(CH<sub>3</sub>)), 149.1 (br. d,  ${}^{1}J_{CF} = 244$  Hz, B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>), 145.0 (s, ArC), 140.3 (s, ArC), 138.9 (br. d,  ${}^{1}J_{CF} = 244$  Hz, B( $C_{6}F_{5}$ )<sub>4</sub>), 137.3 (br. d, <sup>1</sup>J<sub>CF</sub>=244 Hz, B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>), 131.7 (s, ArC (pyrene)), 127.8 (s, ArCH (pyrene)), 126.1 (s, ArCH (pyrene)), 125.8 (s, ArCH), 125.3 (s, ArC (pyrene)), 124.3 (s, ArCH), 89.8 (s, CCHC), 28.7 (s, CHMe<sub>2</sub>), 24.7 (s,



CHCH<sub>3</sub>), 24.5 (s, NC(CH<sub>3</sub>)), 24.3 (s, CHCH<sub>3</sub>) ppm. B–C of B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub> was not detected. <sup>19</sup>F{<sup>1</sup>H} NMR (565 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K)  $\delta$  –131.7 (s, 8F, o-CF), -161.1 (t, <sup>3</sup>J<sub>FF</sub>=21 Hz, 4F, p-CF), -165.4 (s, 8F, m-CF) ppm. <sup>11</sup>B {<sup>1</sup>H} NMR (193 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K)  $\delta$  –16.0 (s, B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>) ppm. FT-IR (ATR, pure):  $\tilde{\nu}$  = 2965 (m), 2927 (w), 2873 (w), 1647 (m), 1548 (m), 1517 (s), 1462 (vs), 1384 (m), 1369 (m), 1309 (m), 1269 (m), 1174 (m), 1084 (s), 968 (vs), 857 (m), 776 (m), 750 (m), 724 (m), 681 (m), 652 (m) cm <sup>-1</sup>. Color change to black at 82 °C, m.p.: 150 °C with decomposition. Elemental analysis Found: C, 59.70; H, 3.83; N, 1.91. Calc. for C<sub>72</sub>H<sub>54</sub>BCl<sub>0.33</sub>SrF<sub>20</sub>N<sub>2</sub> (M = 1434.27 g/mol): C, 60.04; H, 3.82; N, 1.95.

**Synthesis of [(BDI)Ca<sup>+</sup>** · C<sub>6</sub>H<sub>6</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub><sup>-</sup>]: [(BDI)Ca<sup>+</sup> · C<sub>6</sub>H<sub>6</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub><sup>-</sup>] was synthesized by an optimized literature procedure.<sup>[42,50]</sup> [(BDI)H<sub>2</sub><sup>+</sup>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub><sup>-</sup>] (0.2160 g, 0.1830 mmol) and CaN"<sub>2</sub> (0.0780 g, 0.2010 mmol, 1.1 eq.) were dissolved in chlorobenzene (2 mL). A yellow slime formed, which dissolved again after the mixture was heated to 60 °C for 5 h. All volatiles were removed *in vacuo* and the resulting yellow-brown foam was dissolved in benzene (0.5 mL). Upon storage at room temperature small crystals grew, that were washed with a mixture of benzene/hexane (1:1) and dried *in vacuo* (0.1790 g, 0.1480 mmol, 81%). The NMR data match those of material obtained by the original method.

[(BDI)Ca<sup>+</sup>·pyrene][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub><sup>-</sup>]: Synthesis of  $[(BDI)Ca^+ \cdot C_6H_6]$ (0.0254 g, 0.0209 mmol) and pyrene (0.0241 g,  $[B(C_6F_5)_4^{-}]$ 0.1192 mmol, 5.7 eq.) were stirred in methylcyclohexane (3.5 mL) at room temperature for 2 h. After formation of a clear solution and filtration, the filtrate was left at -20°C overnight. Scratching the glass vial with a spatula initiated crystallization, the product was washed with cold pentane (3×0.3 mL) and dried in vacuo to afford  $[(BDI)Ca^+ \cdot pyrene][B(C_6F_5)_4^-]$  as off-white powder (0.0106 g, 0.00792 mmol, 39%). An alternative synthetic procedure is given in the supplementary information. <sup>1</sup>H NMR (600 MHz,  $C_6D_5Br$ , 298 K)  $\delta$ 8.00 (d, <sup>3</sup>J<sub>HH</sub>=7.5 Hz, 4H, ArH (pyrene)), 7.90 (s, 4H, ArH (pyrene)), 7.85 (t, <sup>3</sup>J<sub>HH</sub>=7.5 Hz, 2H, ArH (pyrene)), 7.10–7.06 (m, 6H, ArH), 4.86 (s, 1H, CCHC), 2.78 (hept,  ${}^{3}J_{HH}$  = 6.8 Hz, 4H, CHMe<sub>2</sub>), 1.58 (s, 6H, CH<sub>3</sub>), 1.07 (m, 24H, CHCH<sub>3</sub>) ppm.  ${}^{13}C{}^{1}H$  NMR (151 MHz, C<sub>6</sub>D<sub>5</sub>Br, 298 K)  $\delta$ 167.9 (s, NC(CH<sub>3</sub>)), 148.7 (br. d,  ${}^{1}J_{CF} = 242$  Hz, B( $C_{6}F_{5}$ )<sub>4</sub>), 143.1 (s, ArC), 141.3 (s, ArC), 138.6 (br. d,  ${}^{1}J_{CF} = 243$  Hz, B( $C_{6}F_{5})_{4}$ ), 136.9 (br. d,  ${}^{1}J_{CF} =$ 242 Hz, B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>), 128.6 (s, ArCH), 127.7 (s, ArC (pyrene)), 126.2 (s, ArCH (pyrene)), 125.3 (s, ArCH (pyrene)), 125.0 (s, ArC (pyrene)), 124.7 (s, ArCH), 94.2 (s, CCHC), 28.9 (s, CHMe2), 24.8 (s, CHCH3), 24.4 (s, NC(CH<sub>3</sub>)), 24.2 (s, CHCH<sub>3</sub>) ppm. B–C of  $B(C_6F_5)_4$  was not detected.  $^{19}\text{F}\{^{1}\text{H}\}$  NMR (376 MHz, C\_6D\_5Br, 298 K)  $\delta$  -131.2 (s, 8F, o-CF), -159.8(t, <sup>3</sup>J<sub>FF</sub>=21 Hz, 4F, p-CF), -164.3 (s, 8F, m-CF) ppm. <sup>11</sup>B{<sup>1</sup>H} NMR (128 MHz,  $C_6D_5Br$ , 298 K)  $\delta$  -15.7 (s,  $B(C_6F_5)_4$ ) ppm. <sup>1</sup>H NMR (600 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K)  $\delta$  7.94 (d, <sup>3</sup>J<sub>HH</sub>=7.5 Hz, 4H, ArH (pyrene)), 7.83 (s, 4H, ArH (pyrene)), 7.76 (t,  ${}^{3}J_{HH} = 7.5$  Hz, 2H, ArH (pyrene)), 7.08-6.98 (m, 6H, ArH), 4.68 (s, 1H, CCHC), 2.51 (hept, <sup>3</sup>J<sub>HH</sub>=6.9 Hz, 4H, CHMe<sub>2</sub>), 1.38 (s, 6H, CCH<sub>3</sub>), 1.00 (d, <sup>3</sup>J<sub>HH</sub>=6.9 Hz, 12H, CHCH<sub>3</sub>), 0.93 (d,  ${}^{3}J_{HH} = 6.9$  Hz, 12H, CHCH<sub>3</sub>) ppm.  ${}^{13}C{}^{(1)}H{}$  NMR (151 MHz,  $C_{6}D_{6}$ , 298 K)  $\delta$  167.8 (s, NC(CH<sub>3</sub>)), 149.1 (br. d,  ${}^{1}J_{CF} = 238$  Hz, B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>), 144.4 (s, ArC), 141.2 (s, ArC), 138.9 (br. d,  ${}^{1}J_{CF} = 238$  Hz, B( $C_{6}F_{5})_{4}$ ), 137.2 (br. d,  ${}^{1}J_{CF} = 238$  Hz, B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>), 131.7 (s, ArC (pyrene)), 126.3 (s, ArCH (pyrene)), 126.1 (ArCH (pyrene)), 125.4 (s, ArCH), 125.3 (s, ArC (pyrene)), 124.4 (s, ArCH), 94.1 (s, CCHC), 28.8 (s, CHMe<sub>2</sub>), 24.4 (s, CHCH<sub>3</sub>), 24.1 (s, NC(CH<sub>3</sub>)), 24.0 (s, CHCH<sub>3</sub>) ppm. B-C of B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub> not observed.  $^{19}\text{F}$  NMR (565 MHz,  $\text{C}_6\text{D}_6\text{r},$  298 K)  $\delta$  -131.4 (s, 8F, o-CF), -160.7 (t, <sup>3</sup>J<sub>FF</sub>=21 Hz, 4F, p-CF), -165.5 (s, 8F, m-CF) ppm. <sup>11</sup>B NMR (193 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K)  $\delta$  –16.0 (s, B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>) ppm. FT-IR (ATR, pure):  $\tilde{\nu} =$  2966 (m), 2932 (w), 2875 (w), 1643 (m), 1517 (s), 1460 (vs), 1431 (m), 1389 (m), 1310 (m), 1270 (m), 1174 (m), 1082 (s), 1020 (m), 980 (vs), 950 (m), 927 (m), 850 (m), 775 (m), 714 (m), 681 (m), 652 (m) <sup>-1</sup>. M.p.: 139°C. Elemental analysis (vacuum dried sample) cm Found: C, 61.83; H, 4.11; N, 2.03. Calc. for  $C_{69}H_{51}BCaF_{20}N_2$  (M = 1339.04 g/mol): C, 61.89; H, 3.84; N, 2.09.

Synthesis of [(BDI)Mg<sup>+</sup>·pyrene][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub><sup>-</sup>]:  $[(BDI)Mg(nBu)]_{2}$ (0.0260 a. 0.0260 mmol) and  $[Ph_{3}C^{+}][B(C_{6}F_{5})_{4}^{-}]$ (0.0458 a 0.0497 mmol) were dissolved in chlorobenzene (0.3 mL) and stirred until the solution became almost colorless (1 min). After addition of pyrene (0.0300 g, 0.1490 mmol) and filtration, the reaction mixture was left at room temperature overnight. Repeatedly layering with hexane portions (3×0.5 mL) and scratching the glass wall of the vial with a spatula initiated crystallization. The crystalline product was washed with pentane (3×0.2 mL) and dried under vacuum (0.0342 g, 0.0258 mmol, 52%). <sup>1</sup>H NMR (600 MHz,  $C_6D_5Br_2$  298 K)  $\delta$ 8.00 (d, <sup>3</sup>J<sub>HH</sub>=7.5 Hz, 4H, ArH (pyrene)), 7.89 (s, 4H, ArH (pyrene)), 7.85 (t,  ${}^{3}J_{HH} = 7.5$  Hz, 2H, ArH (pyrene)), 7.19–7.14 (m, 3H, ArH), 7.06– 7.05 (m, 3H, ArH), 4.95 (s, 1H, CCHC), 2.76 (hept, <sup>3</sup>J<sub>HH</sub>=6.6 Hz, 4H, CHMe<sub>2</sub>), 1.58 (s, 6H, CCH<sub>3</sub>), 1.06 (d, <sup>3</sup>J<sub>HH</sub> = 6.6 Hz, 24H, CHCH<sub>3</sub>), 0.88 (d,  ${}^{3}J_{HH} = 6.6$  Hz, 24H, CHCH<sub>3</sub>) ppm.  ${}^{13}C{}^{1}H$  NMR (151 MHz,  $C_{6}D_{5}Br$ , 298 K)  $\delta$  173.1 (s, NC(CH<sub>3</sub>)), 148.6 (br. d,  ${}^{1}J_{CF} = 242$  Hz, B( $C_{6}F_{5})_{4}$ ), 141.9 (s, ArC), 141.3 (s, ArC), 138.4 (br. d,  ${}^{1}J_{CF} = 243$  Hz, B( $C_{6}F_{5})_{4}$ ), 137.1 (br. d, <sup>1</sup>J<sub>CF</sub>=242 Hz, B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>), 128.6 (s, ArCH), 127.5 (s, ArC (pyrene)), 127.1 (ArCH), 125.1 (s, ArCH (pyrene)), 124.6 (s, ArC (pyrene)), 96.6 (s, CCHC), 28.6 (s, CHMe<sub>2</sub>), 24.1 (s, CHCH<sub>3</sub>), 24.0 (s, NC(CH<sub>3</sub>)), 23.9 (s, CHCH<sub>3</sub>) ppm. B-C of B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub> and one signal of pyrene were not detected.  $^{19}\text{F}$  NMR (565 MHz,  $C_6D_5\text{Br},$  298 K)  $\delta$  -131.9 (s, 8F, o-CF), -159.7 (s, 4F, p-CF), -165.0 (s, 8F, m-CF) ppm. <sup>11</sup>B NMR (193 MHz,  $C_6D_5Br$ , 298 K)  $\delta$  –16.0 (s,  $B(C_6F_5)_4$ ) ppm. FT-IR (ATR, pure):  $\tilde{\nu} = 2961$ (m), 2928 (w), 2878 (w), 1647 (m), 1512 (m), 1460 (vs), 1440 (m), 1383 (m), 1313 (m), 1262 (m), 1182 (m), 1087 (s), 1027 (m), 973 (vs), 950 (m), 931 (m), 857 (m), 753 (m), 720 (m), 681 (m), 652 (m) cm <sup>-1</sup>. M.p.: 135 °C. Elemental analysis (1 complex and 0.5 molecules hexane) Found: C, 63.23; H, 4.10; N, 2.03. Calc. for C<sub>144</sub>H<sub>116</sub>B<sub>2</sub>F<sub>40</sub>Mg<sub>2</sub>N<sub>4</sub> (M = 2732.71 g/mol): C, 63.29; H, 4.28; N, 2.05.

Synthesis of  $[N''Ba^+ \cdot (tol)_2][B(C_6F_5)_4^-]$ :  $[Ph_3C^+][B(C_6F_5)_4^-]$  (0.0581 g, 0.0630 mmol, 1.0 eq.) and BaN"<sub>2</sub> (0.0320 g, 0.0690 mmol, 1.1 eq.) were dissolved in a mixture of chlorobenzene (1 mL) and toluene (1 mL). After stirring the suspension for 2 h at room temperature a clear yellow solution was obtained. Upon filtration and storage at  $-20\,^{\circ}\text{C}$  crystals grew, which were washed with cold pentane (5imes0.3 mL) and dried under nitrogen flow. Note: Drying in vacuo leads to decompositon due to removal of the coordinating solvent molecules (0.0473 g, 0.0407 mmol, 65 %). <sup>1</sup>H NMR (600 MHz, PhF/ C<sub>6</sub>D<sub>6</sub> (400/200 μL), 298 K) δ 2.27 (s, 6H, CH<sub>3</sub> (toluene)), 0.17 (s, 18H, CH<sub>3</sub>) ppm. All signals in the aromatic region were obscured by PhF.  $^{19}\text{F}\{^1\text{H}\}$  NMR (376 MHz, PhF/C\_6D\_6 (400/200  $\mu\text{L})$ , 298 K)  $\delta$  -131.9 (br. s, 8F, o-CF), -161.2 (t,  ${}^{3}J_{FF}$ =21 Hz, 4F, p-CF), -165.3 (t,  ${}^{3}J_{FF}$ =21 Hz, 8F, *m*-CF) ppm. <sup>11</sup>B{<sup>1</sup>H} NMR (128 MHz, PhF/C<sub>6</sub>D<sub>6</sub> (400/200 μL), 298 K)  $\delta$  –16.2 (s,  $B(C_6F_5)_4$ ) ppm. <sup>13</sup>C{<sup>1</sup>H} and <sup>29</sup>Si NMR data were not obtained due to the poor solubility of this compound. FT-IR (ATR, pure):  $\tilde{\nu} = 2947$  (m), 2899 (w), 1643 (m), 1519 (m), 1462 (vs), 1372 (m), 1272 (m), 1248 (m), 1087 (s), 1056 (m), 975 (vs), 873 (m), 825 (m), 813 (m), 757 (m), 737 (m), 678 (m), 658 (m), 582 (m) cm <sup>-1</sup>. M.p.: 127 °C. Elemental analysis Found: C, 46.04; H, 3.02 N, 1.02. Calc. for C<sub>44</sub>H<sub>34</sub>BBaF<sub>20</sub>NSi<sub>2</sub> (M = 1161.04 g/mol): C, 45.52; H, 2.95; N, 1.21.

**Synthesis of [N\*Ba<sup>+</sup>·tol][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub><sup>-</sup>]:** [PhN(H)Me<sub>2</sub><sup>+</sup>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub><sup>-</sup>] (0.1190 g, 0.1490 mmol, 1.0 eq.) and BaN\*<sub>2</sub> (0.1300 g, 0.1640 mmol, 1.1 eq.) were dissolved in a mixture of chlorobenzene (2 mL) and toluene (2 mL). After stirring the suspension overnight at room temperature a colorless solution was obtained. Upon filtration and storage at room temperature crystals grew, which were washed with cold pentane (2×0.1 mL) and dried under nitrogen flow. Note: In some attempts the solution oversaturated and seeding crystals were necessary. Drying *in vacuo* leads to decompositon due to removal of the coordinating solvent molecule (0.0960 g, 0.0776 mmol, 52%). <sup>1</sup>H NMR (600 MHz, C<sub>6</sub>D<sub>5</sub>Br, 298 K)  $\delta$  7.15–7.07 (m, 5H, ArH (toluene)), 2.17 (s, 3H, CH<sub>3</sub> (toluene)), 1.01 (d, <sup>3</sup>J<sub>HH</sub>= 6.9 Hz, 36H, CHCH<sub>3</sub>), 0.73 (hept, <sup>3</sup>J<sub>HH</sub>=6.9 Hz, 6H, CHMe<sub>2</sub>) ppm. <sup>13</sup>C



{<sup>1</sup>H} NMR (151 MHz, C<sub>6</sub>D<sub>5</sub>Br, 253 K)  $\delta$  148.7 (br. d, <sup>1</sup>J<sub>CF</sub>=231 Hz,  $B(C_6F_5)_4)$ , 138.6 (br. d,  ${}^{1}J_{CF} = 231$  Hz,  $B(C_6F_5)_4)$ , 137.9 (s, ArC (toluene)), 137.1 (br. d,  ${}^{1}J_{CF} = 244$  Hz, B( $C_{6}F_{5})_{4}$ ), 129.4 (s, ArCH (toluene)), 128.6 (s, ArCH (toluene)), 125.7 (s, ArCH (toluene)), 21.8 (s, CH<sub>2</sub> (toluene)), 19.7 (s, CHCH<sub>3</sub>), 15.9 (s, CHCH<sub>3</sub>) ppm. B–C of  $B(C_6F_5)_4$  was not detected.  $^{19}\text{F}\{^{1}\text{H}\}$  NMR (376 MHz, C6D5Br, 298 K)  $\delta$  –130.5 (br. s, 8F, o-CF), -158.3 (t, <sup>3</sup>J<sub>FF</sub>=21 Hz, 4F, p-CF), -162.6 (t, <sup>3</sup>J<sub>FF</sub>=21 Hz, 8F, m-CF) ppm. <sup>11</sup>B{<sup>1</sup>H} NMR (128 MHz,  $C_6D_5Br$ , 298 K)  $\delta$  -15.7 (s,  $B(C_6F_5)_4$ ) ppm. <sup>29</sup>Si NMR (119 MHz, C<sub>6</sub>D<sub>5</sub>Br, 298 K)  $\delta$  –8.50 (s, SiiPr<sub>3</sub>) ppm. FT-IR (ATR, pure):  $\tilde{\nu} = 2968$  (m), 2950 (m), 2872 (m), 2775 (w), 1642 (m), 1522 (m), 1454 (vs), 1374 (m), 1278 (m), 1247 (m), 1085 (s), 1050 (m), 974 (vs), 884 (m), 773 (m), 751 (m), 705 (m), 652 (m), 611 (m), 507 (m) cm  $^{-1}$ . Color change to black at 130 °C, m.p.: 170 °C with decomposition. Elemental analysis Found: C, 47.69; H, 4.07; N, 1.26. Calc. for for C<sub>49</sub>H<sub>50</sub>BBaF<sub>20</sub>NSi<sub>2</sub> (M = 1237.22 g/mol): C, 47.57; H, 4.07; N, 1.13.

Synthesis of  $[N*Ba^+ \cdot C_6H_6][B(C_6F_5)_4^-]$ :  $[PhN(H)Me_2^+][B(C_6F_5)_4^-]$ (0.0891 g, 0.1110 mmol, 1.0 eq.) and BaN\*2 (0.0970 g, 0.1220 mmol, 1.1 eq.) were dissolved in a mixture of chlorobenzene (1.9 mL) and benzene (1.9 mL). After stirring the suspension overnight at room temperature a colorless solution was obtained, which was filtrated and stored at room temperature for crystallization. Washing the crystals with cold pentane (2×0.2 mL) and drying under nitrogen flow gave the product. Note: In some attempts the solution oversaturated and seeding crystals were necessary. Drying in vacuo leads to decompositon due to removal of the coordinating solvent molecule (0.0731 g, 0.0598 mmol, 54%). <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>5</sub>Br, 298 K) δ 7.22 (s, 6H, ArH (C<sub>6</sub>H<sub>6</sub>)), 1.01 (d, <sup>3</sup>J<sub>HH</sub>=7.3 Hz, 36H, CHCH<sub>3</sub>), 0.73 (hept,  ${}^{3}J_{HH} = 7.3 \text{ Hz}$ , 6H, CHMe<sub>2</sub>) ppm.  ${}^{13}C{}^{1}H$  NMR (101 MHz, C<sub>6</sub>D<sub>5</sub>Br, 253 K) & 128.6 (s, ArCH (benzene)), 19.8 (s, CHCH<sub>3</sub>), 16.0 (s, CHCH<sub>3</sub>) ppm. C–F and B–C of  $B(C_6F_5)_4$  were not detected. <sup>19</sup>F{<sup>1</sup>H} NMR (376 MHz, C<sub>6</sub>D<sub>5</sub>Br, 298 K) δ -130.5 (br. s, 8F, o-CF), -158.3 (t,  ${}^{3}J_{FF} = 21$  Hz, 4F, p-CF), -162.6 (t,  ${}^{3}J_{FF} = 21$  Hz, 8F, m-CF) ppm.  ${}^{11}B{}^{1}H{}$ NMR (128 MHz, C<sub>6</sub>D<sub>5</sub>Br, 298 K)  $\delta$  –15.7 (s, B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>) ppm. <sup>29</sup>Si NMR (119 MHz, C<sub>6</sub>D<sub>5</sub>Br, 298 K) δ -8.90 (s, SiiPr<sub>3</sub>) ppm. FT-IR (ATR, pure):  $\tilde{\nu} = 2966$  (m), 2951 (m), 2871 (m), 2799 (w), 1642 (m), 1517 (m), 1462 (vs), 1379 (m), 1277 (m), 1244 (m), 1082 (s), 1051 (m), 973 (vs), 881 (m), 778 (m), 757 (m), 712 (m), 651 (m), 613 (m), 508 (m) cm <sup>-1</sup>. Color change to black at 127 °C, m.p.: 165 °C with decomposition. Elemental analysis Found: C, 47.05; H, 3.97; N, 1.29. Calc. for C<sub>48</sub>H<sub>48</sub>BBaF<sub>20</sub>NSi<sub>2</sub> (M = 1223.19 g/mol): C, 47.13; H, 3.96; N, 1.15.

Synthesis of  $[N*Sr^+ \cdot PhNMe_2][B(C_6F_5)_4^-]$ :  $[PhNMe_2H^+][B(C_6F_5)_4^-]$ (0.0721 g, 0.0899 mmol, 1.0 eq.) and SrN\*<sub>2</sub> (0.0737 g, 0.0989 mmol, 1.1 eq.) were dissolved in a mixture of chlorobenzene (1 mL) and toluene (1 mL). After stirring the suspension for 15 minutes at room temperature a colorless solution was obtained. Concentration of the reaction volume to half, filtration and layering with hexane (0.5 mL) gave colorless crystals at room temperature after 7 days, which were washed with cold pentane and dried under nitrogen flow (3×0.5 mL, 0.0237 g, 0.0195 mmol, 22%). Note: In some attempts the solution oversaturated and seeding crystals were necessary. Drying in vacuo leads to decompositon due to removal of the coordinating aniline molecule. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>5</sub>Br 298 K) δ 7.16 (m, 2H, ArH (PhNMe<sub>2</sub>)), 6.61 (t, <sup>3</sup>J<sub>HH</sub>=7.2 Hz, 1H, ArH (PhNMe<sub>2</sub>)), 6.50 (d,  ${}^{3}J_{HH} = 8.2$  Hz, 2H, ArH (PhNMe<sub>2</sub>)), 2.50 (s, 6H, CH<sub>3</sub> (PhNMe<sub>2</sub>)), 0.99 (d,  ${}^{3}J_{HH} = 7.3$  Hz, 36H, CHCH<sub>3</sub>), 0.64 (hept,  ${}^{3}J_{HH} =$ 7.3 Hz, 6H, CHMe<sub>2</sub>) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (151 MHz, C<sub>6</sub>D<sub>5</sub>Br, 253 K) δ 151.6 (s, CN (PhNMe<sub>2</sub>)), 148.5 (br. d,  ${}^{1}J_{CF} = 244$  Hz, B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>), 138.8 (br. d,  ${}^{1}J_{CF} = 244$  Hz, B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>), 137.1 (br. d,  ${}^{1}J_{CF} = 244$  Hz, B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>), 121.1 (s, ArCH (PhNMe<sub>2</sub>)), 115.4 (s, ArCH (PhNMe<sub>2</sub>)), 112.3 (s, ArCH (PhNMe2)), 39.8 (s, CH3 (PhNMe2), 19.5 (s, CHCH3), 15.9 (s, CHCH3) ppm. <sup>19</sup>F{<sup>1</sup>H} NMR (376 MHz, C<sub>6</sub>D<sub>5</sub>Br, 298 K) δ –131.1 (br. s, 8F, *o*-C*F*), -158.7 (t,  ${}^{3}J_{FF} = 21$  Hz, 4F, p-CF), -163.2 (br. s, 8F, m-CF) ppm.  ${}^{11}B$  $\{^1\text{H}\}$  NMR (128 MHz,  $C_6D_5\text{Br},$  298 K)  $\delta$  -15.8 (s,  $\textit{B}(C_6F_5)_4)$  ppm.  $^{29}\text{Si}$ NMR (119 MHz, C<sub>6</sub>D<sub>5</sub>Br, 298 K)  $\delta$  -7.8 (s, SiiPr<sub>3</sub>) ppm. FT-IR (ATR, pure):  $\tilde{\nu} = 2971$  (m), 2939 (m), 2869 (m), 1649 (m), 1594 (m), 1515 (m), 1456 (vs), 1371 (m), 1276 (m), 1196 (w), 1086 (s), 1052 (m), 976 (vs), 886 (m), 775 (m), 751 (m), 708 (m), 659 (m), 608 (m), 530 (m) cm<sup>-1</sup>. Color change to black at 130 °C, m.p.: 171 °C with decomposition. Elemental analysis Found: C, 50.00; H, 4.49; N, 2.30. Calc. for  $C_{50}H_{53}BF_{20}N_2Si_2Sr$  (M = 1216.56 g/mol): C, 49.36; H, 4.39; N, 2.30.

# **Supporting Information**

(see footnote on the first page of this article): Alternative synthetic routes,  ${}^{1}H$ ,  ${}^{11}B$ ,  ${}^{19}F$ ,  ${}^{13}C$  NMR and FT-IR spectra, crystallographic details including ORTEP plots, details for the DFT calculations including XYZ-files.

# **Author Information**

The authors declare no competing financial interest.

## Acknowledgements

We acknowledge C. Wronna and A. Roth for CHN analyses and Dr. C. Färber and J. Schmidt for assistance with NMR analyses. Open access funding enabled and organized by Projekt DEAL.

# **Conflict of Interest**

The authors declare no conflict of interest.

**Keywords:** Ab initio calculations  $\cdot$  Arene coordination  $\cdot$  Barium  $\cdot$  Cations  $\cdot$  Strontium

- Early Main Group Metal Catalysis Concepts and Reactions (Ed. S. Harder), Wiley-VCH, Weinheim, Germany, 2020.
- [2] M. S. Hill, D. J. Liptrot, C. Weetman, Chem. Soc. Rev. 2016, 45, 972-988.
- [3] S. Harder, Chem. Rev. 2010, 110, 3852-3876.
- [4] H. Bauer, M. Alonso, C. Fischer, B. Rösch, H. Elsen, S. Harder, Angew. Chem. Int. Ed. 2018, 57, 15177–15182; Angew. Chem. 2018, 130, 15397– 15402.
- [5] J. Martin, C. Knüpfer, J. Eyselein, C. Färber, S. Grams, J. Langer, K. Thum, M. Wiesinger, S. Harder, Angew. Chem. Int. Ed. 2020, 59, 9102–9112; Angew. Chem. 2020, 132, 9187–9197.
- [6] H. Bauer, K. Thum, M. Alonso, C. Fischer, S. Harder, Angew. Chem. Int. Ed. 2019, 58, 4248–4253; Angew. Chem. 2019, 131, 4292–4297.
- [7] D. Schuhknecht, C. Lhotzky, T. P. Spaniol, L. Maron, J. Okuda, Angew. Chem. Int. Ed. 2017, 56, 12367–12371; Angew. Chem. 2017, 129, 12539– 12543.
- [8] D. Schuhknecht, T. P. Spaniol, L. Maron, J. Okuda, Angew. Chem. Int. Ed. 2020, 59, 310–314; Angew. Chem. 2020, 132, 317–322.
- [9] F. Buch, J. Brettar, S. Harder, Angew. Chem. Int. Ed. 2006, 45, 2741–2745; Angew. Chem. 2006, 118, 2807–2811.
- [10] X. Shi, G. Qin, Y. Wang, L. Zhao, Z. Liu, J. Cheng, Angew. Chem. Int. Ed. 2019, 58, 4356–4360; Angew. Chem. 2019, 131, 4400–4404.
- [11] X. Shi, J. Cheng, Dalton Trans. 2019, 48, 8565-8568.
- [12] X. Shi, C. Hou, L. Zhao, P. Deng, J. Cheng, Chem. Commun. 2020, 56, 5162–5165.
- [13] T. X. Gentner, A. R. Kennedy, E. Hevia, R. E. Mulvey, *ChemCatChem* 2021, DOI: 10.1002/cctc.202100218.



- [14] J. Penafiel, L. Maron, S. Harder, Angew. Chem. Int. Ed. 2015, 54, 201–206; Angew. Chem. 2015, 127, 203–208.
- [15] A. S. S. Wilson, M. S. Hill, M. F. Mahon, C. Dinoi, L. Maron, Science 2017, 358, 1168–1171.
- [16] B. Rösch, T. X. Gentner, H. Elsen, C. A. Fischer, J. Langer, M. Wiesinger, S. Harder, Angew. Chem. Int. Ed. 2019, 58, 5396–5401; Angew. Chem. 2019, 131, 5450–5455.
- [17] J. Martin, J. Eyselein, S. Grams, S. Harder, ACS Catal. 2020, 10, 7792– 7799.
- [18] B. Rösch, T. X. Gentner, J. Langer, C. Färber, J. Eyselein, L. Zhao, C. Ding, G. Frenking, S. Harder, *Science* **2021**, *371*, 1125–1128.
- [19] Q. Wang, S. Pan, S. Lei, J. Jin, G. Deng, G. Wang, L. Zhao, M. Zhou, G. Frenking, *Nat. Commun.* 2019, *10*, 3375.
- [20] Q. Wang, S. Pan, Y. Wu, G. Deng, J. Bian, G. Wang, L. Zhao, M. Zhou, G. Frenking, *Angew. Chem. Int. Ed.* **2019**, *58*, 17365–17374; *Angew. Chem.* **2019**, *131*, 17526–17535.
- [21] B. Freitag, H. Elsen, J. Pahl, G. Ballmann, A. Herrera, R. Dorta, S. Harder, Organometallics 2017, 36, 1860–1866.
- [22] J. Martin, J. Langer, M. Wiesinger, H. Elsen, S. Harder, Eur. J. Inorg. Chem. 2020, 2582–2595.
- [23] H. Schumann, S. Schutte, H.-J. Kroth, D. Lentz, Angew. Chem. Int. Ed. 2004, 43, 6208–6211; Angew. Chem. 2004, 116, 6335–6338.
- [24] M. Wiecko, C. Eidamshaus, R. Köppe, P. W. Roesky, Dalton Trans. 2008, 4837–4839.
- [25] M.-K. Chung, O. C. Lightbody, J. M. Stryker, Org. Lett. 2008, 10, 3825– 3828.
- [26] M. Fujita, O. C. Lightbody, M. J. Ferguson, R. McDonald, J. M. Stryker, J. Am. Chem. Soc. 2009, 131, 4568–4569.
- [27] S. C. Roşca, C. Dinoi, E. Caytan, V. Dorcet, M. Etienne, J. F. Carpentier, Y. Sarazin, Chem. Eur. J. 2016, 22, 6505–6509.
- [28] S.-C. Roşca, E. Caytan, V. Dorcet, T. Roisnel, J.-F. Carpentier, Y. Sarazin, Organometallics 2017, 36, 1269–1277.
- [29] S.-C. Roşca, V. Dorcet, T. Roisnel, J.-F. Carpentier, Y. Sarazin, *Dalton Trans.* 2017, 46, 14785–14794.
- [30] Y. Sarazin, M. Schormann, M. Bochmann, Organometallics 2004, 23, 3296–3302.
- [31] D. Mukherjee, J. Okuda, Chem. Commun. 2018, 54, 2701-2714.
- [32] P. Jochmann, J. P. Davin, T. P. Spaniol, L. Maron, J. Okuda, Angew. Chem. Int. Ed. 2012, 51, 4452–4455; Angew. Chem. 2012, 124, 4528–4531.
- [33] D. Martin, K. Beckerle, S. Schnitzler, T. P. Spaniol, L. Maron, J. Okuda, Angew. Chem. Int. Ed. 2015, 54, 4115–4118; Angew. Chem. 2015, 127, 4188–4191.
- [34] D. Mukherjee, T. Höllerhage, V. Leich, T. P. Spaniol, U. Englert, L. Maron, J. Okuda, J. Am. Chem. Soc. 2018, 140, 3403–3411.
- [35] S. Banerjee, A. Ankur, A. Andrews, A. Venugopal, Chem. Commun. 2018, 54, 5788–5791.
- [36] S. Banerjee, A. Ankur, A. P. Andrews, B. Varghese, A. Venugopal, *Dalton Trans.* 2019, 48, 7313–7319.
- [37] A. D. Obi, J. E. Walley, N. C. Frey, Y. O. Wong, D. A. Dickie, C. E. Webster, R. J. Gilliard, Organometallics 2020, 39, 4329–4339.
- [38] B. Liu, V. Dorcet, L. Maron, J.-F. Carpentier, Y. Sarazin, Eur. J. Inorg. Chem. 2012, 3023–3031.
- [39] B. Liu, T. Roisnel, Y. Sarazin, Inorg. Chim. Acta 2012, 380, 2-13.
- [40] Y. Sarazin, V. Poirier, T. Roisnel, J.-F. Carpentier, Eur. J. Inorg. Chem. 2010, 3423–3428.
- [41] Y. Sarazin, B. Liu, T. Roisnel, L. Maron, J.-F. Carpentier, J. Am. Chem. Soc. 2011, 133, 9069–9087.
- [42] J. Pahl, S. Brand, H. Elsen, S. Harder, Chem. Commun. 2018, 54, 8685– 8688.
- [43] J. Pahl, A. Friedrich, H. Elsen, S. Harder, Organometallics 2018, 37, 2901– 2909.
- [44] A. Friedrich, J. Pahl, H. Elsen, S. Harder, Dalton Trans. 2019, 48, 5560– 5568.
- [45] L. Garcia, M. D. Anker, M. F. Mahon, L. Maron, M. S. Hill, *Dalton Trans.* 2018, 47, 12684–12693.
- [46] J. Pahl, T. E. Stennett, M. Volland, D. M. Guldi, S. Harder, Chem. Eur. J. 2019, 25, 2025–2034.
- [47] J. Pahl, H. Elsen, A. Friedrich, S. Harder, Chem. Commun. 2018, 54, 7846– 7849.
- [48] K. Thum, A. Friedrich, J. Pahl, H. Elsen, J. Langer, S. Harder, Chem. Eur. J. 2021, 27, 2513–2522.

- [49] A. Friedrich, J. Pahl, J. Eyselein, J. Langer, N. van Eikema Hommes, A. Görling, S. Harder, Chem. Sci. 2021, 12, 2410–2418.
- [50] S. Brand, H. Elsen, J. Langer, W. A. Donaubauer, F. Hampel, S. Harder, Angew. Chem. Int. Ed. 2018, 57, 14169–14173; Angew. Chem. 2018, 130, 14365–14369.
- [51] R. J. Schwamm, M. P. Coles, M. S. Hill, M. F. Mahon, C. L. McMullin, N. A. Rajabi, A. S. S. Wilson, *Angew. Chem. Int. Ed.* **2020**, *59*, 3928–3932; *Angew. Chem.* **2020**, *132*, 3956–3960.
- [52] S. Brand, A. Causero, H. Elsen, J. Pahl, J. Langer, S. Harder, Eur. J. Inorg. Chem. 2020, 1728–1735.
- [53] M. Schorpp, I. Krossing, Chem. Sci. 2020, 11, 2068–2076.
- [54] P. Dabringhaus, M. Schorpp, H. Scherer, I. Krossing, Angew. Chem. Int. Ed. 2020, 59, 22023–22027; Angew. Chem. 2020, 132, 22207–22211.
- [55] A. G. Avent, M. R. Crimmin, M. S. Hill, P. B. Hitchcock, Dalton Trans. 2005, 278–284.
- [56] T. X. Gentner, B. Rösch, K. Thum, J. Langer, G. Ballmann, J. Pahl, W. A. Donaubauer, F. Hampel, S. Harder, *Organometallics* 2019, 38, 2485– 2493.
- [57] P. Jutzi, C. Müller, A. Stammler, H.-G. Stammler, Organometallics 2000, 19, 1442–1444.
- [58] M. Wiesinger, B. Maitland, C. Färber, G. Ballmann, C. Fischer, H. Elsen, S. Harder, Angew. Chem. Int. Ed. 2017, 56, 16654–16659; Angew. Chem. 2017, 129, 16881–16886.
- [59] A. Arrais, E. Diana, G. Gervasio, R. Gobetto, D. Marabello, P. L. Stanghellini, *Eur. J. Inorg. Chem.* 2004, 1505–1513.
- [60] E. V. Dikarev, B. Li, A. Y. Rogachev, H. Zhang, M. A. Petrukhina, Organometallics 2008, 27, 3728–3735.
- [61] B. E. Kucera, R. E. Jilek, W. W. Brennessel, J. E. Ellis, Acta Crystallogr. 2014, C70, 749–753.
- [62] A. Woolf, A. B. Chaplin, J. E. McGrady, M. A. M. Alibadi, N. Rees, S. Draper, F. Murphy, A. S. Weller, *Eur. J. Inorg. Chem.* **2011**, 1614–1625.
- [63] R. Pal, S. Mebs, M. W. Shi, D. Jayatilaka, J. M. Krzeszczakowska, L. A. Malaspina, M. Wiecko, P. Luger, M. Hesse, Y.-S. Chen, J. Beckmann, S. Grabowsky, *Inorg. Chem.* 2018, *57*, 4906–4920.
- [64] K. Izod, P. G. Waddell, Organometallics 2015, 34, 2726–2730.
- [65] A. Torvisco, K. Ruhlandt-Senge, Inorg. Chem. 2011, 50, 12223-12240.
- [66] S.-O. Hauber, F. Lissner, G. B. Deacon, M. Niemeyer, Angew. Chem. Int. Ed. 2005, 44, 5871–5875; Angew. Chem. 2005, 117, 6021–6025.
- [67] B. Rösch, J. Martin, J. Eyselein, J. Langer, M. Wiesinger, S. Harder, Organometallics 2021, 40, 1395–1401.
- [68] S. Harder, Angew. Chem. Int. Ed. 1998, 37, 1239–1241; Angew. Chem. 1998, 110, 1357–1359.
- [69] K. Fichtel, K. Hofmann, U. Behrens, Organometallics 2004, 23, 4166– 4168.
- [70] S. Harder, M. Lutz, Organometallics 1997, 16, 225-230.
- [71] L. Orzechowski, D. F. J. Piesik, C. Ruspic, S. Harder, Dalton Trans. 2008, 4742.
- [72] M. Westerhausen, M. Kroftaa, N. Wiberga, J. Knizeka, Z. Naturforsch. B 1998, 53, 1489–1493.
- [73] O. Michel, S. König, K. W. Törnroos, C. Maichle-Mössmer, R. Anwander, *Chem. Eur. J.* 2011, 17, 11857–11867.
- [74] O. Michel, K. W. Törnroos, C. Maichle-Mössmer, R. Anwander, Eur. J. Inorg. Chem. 2012, 44–47.
- [75] M. Zeller, A. D. Hunter, Acta Crystallogr. 2005, E61, m23-m24.
- [76] N. Yu, M. Nishiura, X. Li, Z. Xi, Z. Hou, *Chem. Asian J.* 2008, 3, 1406–1414.
  [77] M. W. Drover, E. G. Bowes, J. A. Love, L. L. Schafer, *Organometallics* 2017,
- 36, 331–341.
- [78] F. Feil, S. Harder, Organometallics 2001, 20, 4616–4622.
- [79] M. Westerhausen, Inorg. Chem. 1991, 30, 96–101.
- [80] G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw, K. I. Goldberg, *Organometallics* 2010, 29, 2176– 2179.

Manuscript received: April 27, 2021 Revised manuscript received: May 4, 2021 Accepted manuscript online: May 5, 2021