



HAL
open science

Heteroleptic carbazolato-barium hydroborates and a related separated ion pair

Peter.M. Chapple, Thierry Roisnel, Marie Cordier, Jean-François Carpentier,
Yann Sarazin

► **To cite this version:**

Peter.M. Chapple, Thierry Roisnel, Marie Cordier, Jean-François Carpentier, Yann Sarazin. Heteroleptic carbazolato-barium hydroborates and a related separated ion pair. *Polyhedron*, 2022, 217, pp.115731. 10.1016/j.poly.2022.115731 . hal-03607938

HAL Id: hal-03607938

<https://univ-rennes.hal.science/hal-03607938>

Submitted on 14 Mar 2022

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Heteroleptic Carbazolato-Barium Hydroborates and a Related Separated Ion Pair

Peter. M. Chapple, Thierry Roisnel, Marie Cordier, Jean-François Carpentier and Yann Sarazin*

Univ Rennes, CNRS, ISCR-UMR 6226, 35000 Rennes, France.

* Corresponding author. E-mail address: yann.sarazin@univ-rennes1.fr (Y. Sarazin)

Dedicated to Professor Ionel Haiduc, a main contributor to organometallic chemistry from the University Babeş-Bolyai, Cluj-Napoca, Romania.

Keywords: barium – hydroborate – cation – carbazolate ligand

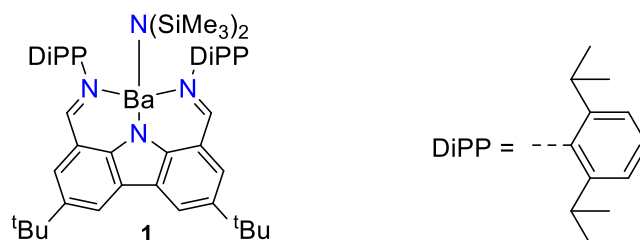
Abstract

The syntheses and characterisation of two molecular barium-hydroborate complexes supported by a bulky bis(imino)carbazolate ligand, namely $[\{\text{Carb}^{\text{Dipp}}\}\text{Ba}(\mu\text{-H}_2\text{Bpin})]_3$ (**2**₃) and $[\{\text{Carb}^{\text{Dipp}}\}\text{Ba}(\text{H}_2\text{-9BBN})\cdot\text{Et}_2\text{O}]$ (**3**·Et₂O), are presented. These two complexes are obtained in high yields upon reaction of the amido precursor $[\{\text{Carb}^{\text{Dipp}}\}\text{BaN}(\text{SiMe}_3)_2]$ (**1**) with the commercially available pinacolborane or $[\text{H-9BBN}]_2$, respectively. The solid-state molecular structures of the complexes were solved, and show **2**₃ to form a solvent-free cyclic trimer, whereas the monomeric **3**·Et₂O is solvated by one molecule of diethyl ether. Furthermore, the well-defined ion pair $[\{\text{Carb}^{\text{Dipp}}\}\text{Ba}(\text{Et}_2\text{O})_2]^+[\text{H}_2\text{N}\{\text{B}(\text{C}_6\text{F}_5)_3\}_2]^-$ (**4**), a rare occurrence of soluble barium cation, was also obtained in good yield upon treatment of **1** with Bochmann's acid. Its X-ray structure was solved and reveals the absence of interaction between the metal cation and its counter-ion. Finally, the structure of the seven-coordinated, dicationic $[\text{Ba}(\text{thf})_7]^{2+}[\text{H}_2\text{N}\{\text{B}(\text{C}_6\text{F}_5)_3\}_2]^{-2}$ (**5**) is also presented.

1. Introduction

The chemistry of the large alkaline-earth metals (=Ae) calcium, strontium and barium has been enjoying tremendous momentum for 15 years. This success stems in large parts from the recognition that well-defined complexes of these elements, often supported by stabilising and solubilising bulky ligands, display unique structural and reactivity patterns, and also generate competent molecular catalysts that can mediate a multitude of organic transformations [1-13]. Barium, the largest of these three metals ($r_{\text{ionic}} = 1.38 \text{ \AA}$ for C.N. = 6), has proved more complicated to tame than its smaller congeners Ca and Sr (1.00 and 1.18 \AA , respectively). This owes much to the very large size and electropositivity of the Ba^{2+} ion, which generates highly ionic complexes where bonding is weak and almost entirely non-directional. Yet, increasingly effective ligand design has allowed for significant breakthroughs in the area of barium organometallic/coordination chemistry and barium-mediated homogeneous catalysis [14].

Although the highly versatile Dipp-substituted β -diketiminate $\{\text{BDI}^{\text{Dipp}}\}^-$ has proved amazingly effective for calcium ($\text{DiPP} = 2,6\text{-}i\text{Pr}_2\text{-C}_6\text{H}_3$), e.g. to obtain heteroleptic Ca-hydrides [12,15], it is unable to prevent completely ligand scrambling in solution in the case of heteroleptic barium complexes [16]. The synthesis of stable and soluble barium hydrides is hence in comparison very recent, and the utilisation of extremely bulky cyclopentadienyl or trispyrazolylborate ligands was required to obtain complexes of low nuclearity [17-19]. The development of specifically designed ancillary ligands, with many of them being nitrogen-based, for the synthesis of stable heteroleptic complexes, has recently been reviewed [14]. We have introduced a bulky, bis(imino)carbazolate (hereafter referred to as $\{\text{Carb}^{\text{Dipp}}\}^-$) as a stabilising ligand for molecular barium chemistry, and have shown that it afforded the syntheses of stable compounds that had remained elusive until then, e.g. the heteroleptic Ba-fluoride $[\{\text{Carb}^{\text{Dipp}}\}\text{Ba}(\mu\text{-F})_2(\mu\text{-thf})]$ and Ba-stannylide $[\{\text{Carb}^{\text{Dipp}}\}\text{BaSn}(\text{SiMe}_3)_3\text{.thf}]$ [20-21]. The unsolvated amido complex $[\{\text{Carb}^{\text{Dipp}}\}\text{BaN}(\text{SiMe}_3)_2]$ (**1**) proved a remarkable hydrophosphination precatalyst and a very useful precursor. Yet, the synthesis of a stable Ba-hydride supported by this ligand upon treatment of **1** with PhSiH_3 could not be achieved, as the imine functional groups was sensitive both to reduction by the sought Ba-H species and to barium-catalysed hydrosilylation [21]. As part of our continued interest in barium chemistry, we next turned our attention to the use of hydroboranes.



Beyond regular barium bis(tetrahydroborate)s supported by polyethers [22], a number of homoleptic Ba-hydroborates have been described. Notable examples include hydroborates

$[\text{Ba}\{\text{HB}(\text{C}_6\text{F}_5)_3\}_2(\text{thf})_4]$ [23] and its bis(3,5-di-*tert*-butylpyrazolyl)dihydroborate parent [24], as well as a variety of phosphine-borane stabilised anions. Representative examples (Fig. 1) include the dinuclear $[\{\text{PhP}(\text{BH}_3)\{\text{CH}(\text{SiMe}_3)\}_2\text{Ba}(\text{OEt}_2)_{1.75}(\text{thf})_{0.25}\}_2]$ (**A**), $[\{\text{(Me}_3\text{Si)}_2\{\text{Me}_2(\text{H}_3\text{B})\text{P}\}\text{C}\}_2\text{Ba}(\text{thf})_5]$ (**B**), and $[\{\text{N}(\text{R-CHMePh})\text{P}(\text{BH}_3)\text{Ph}_2\}_2\text{Ba}(\text{thf})_2]$ (**C**) [25-27]; in these complexes, the (boro)hydride is able to complement or compete with the carbanion or the amide for coordination onto the metal. The diamido phosphine-borane barium complex $[\{\text{Ph}_2\text{P}(\text{BH}_3)\text{N}\}_2\text{C}_6\text{H}_4]\text{Ba}(\text{thf})_3$ (**D**) was shown to promote the ring-opening polymerisation of ϵ -caprolactame [28]. Finally, an unusual case of barium-bis(carborate) (**E**), obtained by reaction of 2,3-bis(trimethylsilyl)-2,3-dicarba-*nido*-hexaborane with a barium zincate, was also reported [29]. Yet, to date, no example of structurally authenticated, heteroleptic barium borohydride has been disclosed to our knowledge.

We report here on the synthesis and molecular solid-state structures of two heteroleptic Ba-hydroborates supported by the $\{\text{Carb}^{\text{DiPP}}\}^-$ bis(imino)carbazolate ancillary ligand. Along this line of work, we have come to interrogate the strength of Ba-to-ligand bonds in this family of compounds, and we have been led to prepare a charge-separated cationic barium-carbazolate paired with a weakly-coordinating anion, the synthesis and structure of which are also presented here. This latter compound adds up to the limited set of well-defined cationic barium complexes structurally characterised to date, which, despite recent advances in the area of soluble cations with the smaller alkaline earths [30-40], remains otherwise mostly limited to Ba-phenoxides and fluoroalkoxides [39, 41-44].

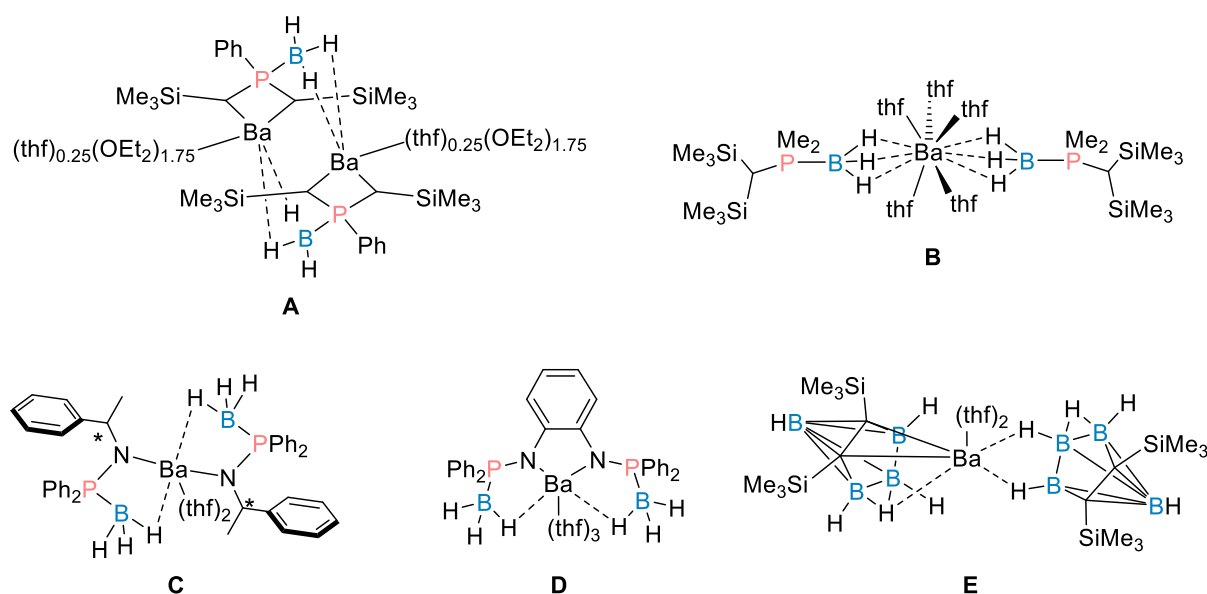
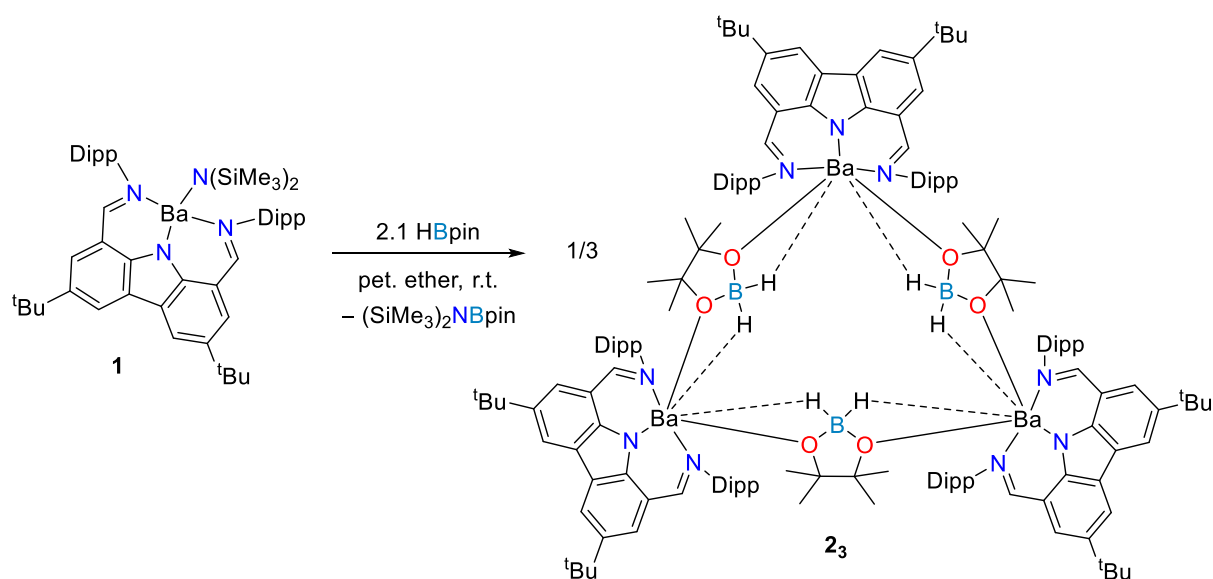


Fig. 1. Examples of barium complexes with phosphine-borane-stabilised anions.

2. Results and Discussion

Commercially available boranes such as pinacolborane (HBpin) and 9-borabicyclo[3.3.1]nonane dimer ($[\text{H-9BBN}]_2$) are relatively mild hydride sources. The reaction between $[\{\text{BDI}^{\text{Dipp}}\}\text{CaN}(\text{SiMe}_3)_2\cdot\text{thf}]$ and one equivalent of the dimer $[\text{H-9BBN}]_2$ has previously been reported to generate the corresponding dihydroborate complex [45]. The reaction of **1** with HBPin was attempted, with the hope that using only one equivalent of the monomeric HBpin, a borane with reduced Lewis acidity compared to H-9BBN due to partial $O(p)$ - $B(p)$ orbital overlap, would generate a Ba-hydride species. The dropwise addition of one equivalent of HBpin to a stirred solution of **1** at room temperature immediately generated a bright yellow precipitate. After being washed with hexanes and dried, ^1H and ^{11}B NMR analysis in benzene- d_6 was run on the solid sample; however, the compound was poorly soluble, with only the by-product $(\text{SiMe}_3)_2\text{NBpin}$ being clearly identifiable in the spectra ($\delta_{11\text{B}}$ 24.5 ppm) [18]. The identity of the complex was established as $[\{\text{Carb}^{\text{Dipp}}\}\text{Ba}(\mu\text{-H}_2\text{Bpin})_3]$ (**2₃**), a trimeric unsolvated dihydroborate species with C_3 -symmetry, by X-ray diffraction methods (vide infra); the recorded NMR data were consistent with this formulation. The synthesis of **2₃** is reproducible and can be achieved almost quantitatively (isolated yield 95%) by using 2.1 equivalents of HBpin vs **1** (Scheme 1). It is structurally very similar to the calcium trimer $[\{\text{BDI}^{\text{Dipp}}\}\text{Ca}(\mu\text{-H}_2\text{BPin})_3]$ isolated in 2012 by Harder and co-workers following the reaction of HBpin and $[\{\text{BDI}^{\text{Dipp}}\}\text{Ca}(\mu\text{-H})\cdot\text{thf}]_2$ [46].



Scheme 1. Synthesis of $[\{\text{Carb}^{\text{Dipp}}\}\text{Ba}(\mu\text{-H}_2\text{Bpin})_3]$ (**2₃**) from $[\{\text{Carb}^{\text{Dipp}}\}\text{BaN}(\text{SiMe}_3)_2]$ (**1**) and HBPin.

Compound **2₃** is soluble in thf, although it decomposes within a few hours to a number of unidentifiable products. Collecting exploitable NMR spectra hence proved difficult. However, satisfactory data could eventually be collected by using an extremely concentrated solution in thf- d_8 and maintaining the collection of ^{13}C NMR data under 15 min. Yet, even after this short time, decomposition of the sample started to become visible. The large number of products that formed (with more than 100

different ^{13}C resonances detected after 40 h) made identification of potential decomposition pathways difficult. The characteristic resonance in the ^1H NMR spectrum of **2**₃ is a broad signal for the dihydroborate Bpin methyl resonance at δ_{H} 0.39 ppm, whereas the signal for the H_2BPin hydrides could not be detected. The ^{11}B NMR spectrum displays a broad triplet at δ_{B} 3.66 ppm, with a $^1J_{\text{BH}}$ coupling constant of 92.9 Hz, similar to that in $[\{\text{BDI}^{\text{Dipp}}\}\text{Ca}(\mu\text{-H}_2\text{BPin})\text{Bpin}]_3$ (δ_{B} 2.1, $^1J_{\text{BH}} = 91$ Hz) [46]. Unlike Harder's complex, **2**₃ is insoluble in diethyl ether and in hydrocarbons, including aromatic ones. The synthesis of the tmeda and dabco adducts of **2**₃ were both attempted in order to make stable adducts and gather better NMR data. However, the resulting compounds also proved insoluble in diethyl ether and aromatic solvents, and again were unstable in thf, precluding their isolation and characterisation.

X-ray quality crystals of **2**₃ were grown from the petroleum ether washings. The molecular solid-state structure of **2**₃ (Fig. 2) has two similar -although non-equivalent- molecules in the unit cell; only one will be discussed here. The structure is essentially the $\{\text{Carb}^{\text{Dipp}}\}\text{Ba}$ equivalent of the calcium trimeric $[\{\text{BDI}^{\text{Dipp}}\}\text{Ca}(\mu\text{-H}_2\text{BPin})\text{Bpin}]_3$ [46], having three $\{\text{Carb}^{\text{Dipp}}\}\text{Ba}$ fragments being bridged by three H_2BPin units. The bridging occurs through the oxygen atoms of the H_2BPin moiety.

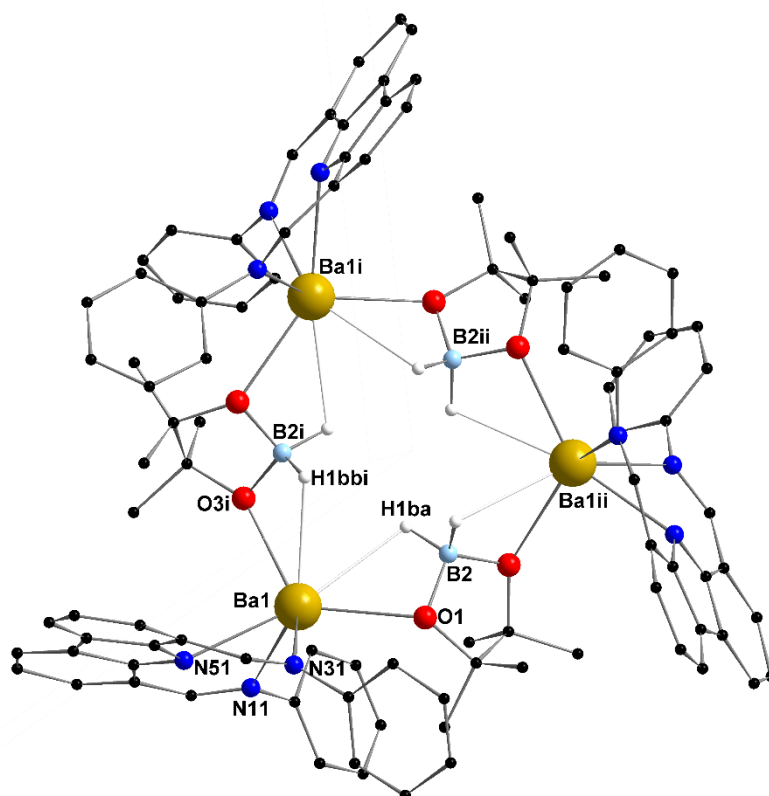
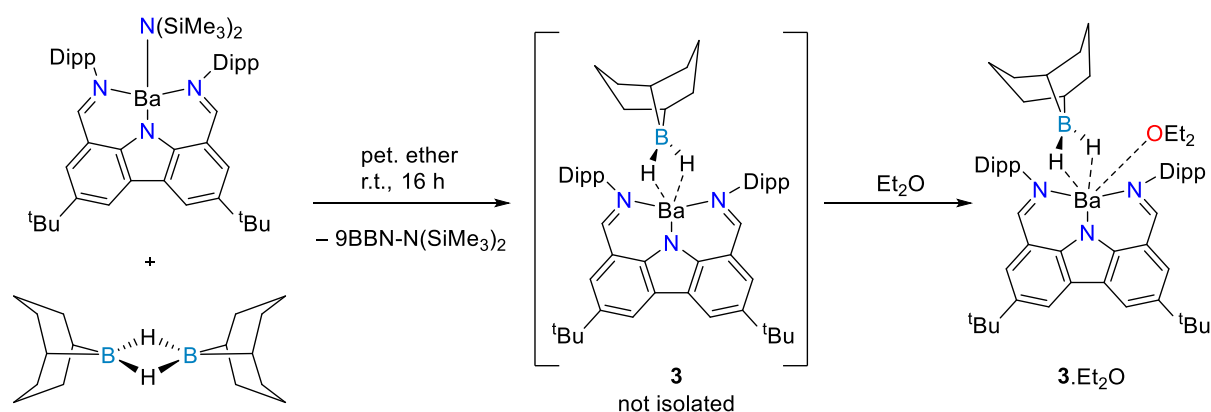


Fig. 2. Representation of the molecular solid-state structure of $[\{\text{Carb}^{\text{Dipp}}\}\text{Ba}(\mu\text{-H}_2\text{BPin})\text{Bpin}]_3$ (**2**₃). H atoms (except those bound to B), ^iPr and ^tBu groups omitted for clarity. Only one of the two similar molecules in the asymmetric unit cell shown. Selected bond lengths (\AA) and angles ($^\circ$): Ba1-N51 = 2.700(5), Ba1-N11 = 2.902(5), Ba1-N31 = 2.887(5), Ba1-O1 = 2.688(5), Ba1-BaO3i = 2.693(5), Ba1-H1ba = 2.83(9), Ba1-H1bbⁱ = 3.81(11), Ba1-B2 = 3.225(9), Ba1-B2i = 3.319(9); O1-Ba1-O3ⁱ = 122.38(16), N11-Ba1-

N31 = 114.46(14), N11-N51-N31 = 103.7(3); Ba1- NNN_{plane} = 1.535(4). Symmetry operations: $X' = 1/2 + z, 3/2 - x, 1 - y$; $X'' = 3/2 - y, 1 - z, -1/2 + x$.

The geometry around each Ba is five-coordinate and forms a distorted square pyramid. The primary interaction between the metal cation and the ‘twisted’ dihydroborate is through the O-atoms (Ba1 \cdots O1 = 2.688(5); Ba1 \cdots O3' = 2.693(5) Å). The twisting of the dihydroborate results in the two hydrides being located at different distances from the Ba²⁺ centre. Although the uncertainty on their exact location is relatively high, the hydrides were placed using electronic density in the Fourier difference map, and the interatomic distances between these H-atoms and Ba are significantly lower than the sum of the van der Waals radii (3.78 Å). Unlike Harder’s complex, both BH hydrides are involved in Ba \cdots HB stabilising interactions (Ba1 \cdots H1ba = 2.83(9), Ba1 \cdots H1bbi = 2.81(11) Å), which is consistent with the larger ionic radius of Ba²⁺. The solvated dihydroborates [Ba(BH₄)₂.(diglyme)₂] and [Ba(BH₄)₂.18-c-6] are also known [22], with Ba-H interatomic distances in the range 2.60(4)-2.98(5) Å. A final notable bonding feature in **2**₃ is how far the Ba atom protrudes out of the pocket delineated by the three nitrogen atoms of the ligand, at a Ba- NNN_{plane} distance of 1.535(4) Å.

When an equimolar amount of [H-9BBN]₂ dimer was used in place of HBpin, the reaction with **1** proceeded slowly upon elimination of 9BBN-N(SiMe₃)₂, taking 16 h to reach full conversion of the starting materials. However, unlike **2**₃, the reaction product, assumed to be [{Carb^{Dipp}}Ba(H₂-9BBN)] (**3**), was extremely soluble in aliphatic solvents, precluding its recrystallisation and hence its characterisation by XRD. Yet, addition of a minimal amount of diethyl ether to a concentrated solution in petroleum ether led to the isolation of the ether adduct [{Carb^{Dipp}}Ba(H₂-9BBN).Et₂O] (**3**.Et₂O) as large yellow blocks (Scheme 2).



Scheme 2. Synthesis of [{Carb^{Dipp}}Ba(H₂-9BBN).Et₂O] (**3**.Et₂O) from **1** and [H-9BBN]₂.

The ¹H NMR spectrum of **3**.Et₂O recorded in benzene-*d*₆ displays characteristic resonances for the {Carb^{Dipp}}⁻ ligand at δ_{H} 8.35 (CH=N) and 3.03 (CH(CH₃)₂), while the resonances for CH(CH₃)₂

methyl groups consist of two doublets at 1.40 and 1.12 ppm. The 9-BBN moiety gives rise to a number of broad multiplets in the region 2.20-0.90 ppm. The BH_2 hydrogens generate a broad singlet at 0.54 ppm, i.e. at a chemical shift very similar to those of related heteroleptic alkaline-earth dihydroborates, e.g. $[\{BDI^{Dipp}\}Ca(H_2-9BBN).thf]$ (δ_H 0.67 ppm in toluene- d_8) and $[\{BDI^{Dipp}\}Mg(H_2-9BBN).thf]$ (δ_H 0.47 ppm in thf- d_8) [45,47]. The ^{11}B NMR spectrum of $3.Et_2O$ displays a single broad triplet at δ_B -6.76 ppm ($^1J_{BH} = 74.5$ Hz), slightly downfield of $[\{BDI^{Dipp}\}Ca(H_2-9BBN).thf]$ (δ_B -12.5 ppm) and $[\{BDI^{Dipp}\}Mg(H_2-9BBN).thf]$ (δ_B -17.4 ppm). The complex does not lose either molecule of diethyl ether under vacuum (50 °C, 1×10^{-3} mbar, 1 h), in contrast to $[\{BDI^{Dipp}\}Mg(H-9-BBN).thf]$ which readily loses its coordinated thf molecule. Unlike **2**₃, complex **3**.Et₂O is stable in solution at room temperature, showing no sign of decomposition nor reduction of the ligand backbone. X-ray diffraction analysis revealed the molecular solid-state structure of **3**.Et₂O as having one molecule of $[\{Carb^{Dipp}\}Ba(H-9-BBN).Et_2O]$ with another non-coordinating molecule of disordered diethyl ether in the unit cell (Fig. 3).

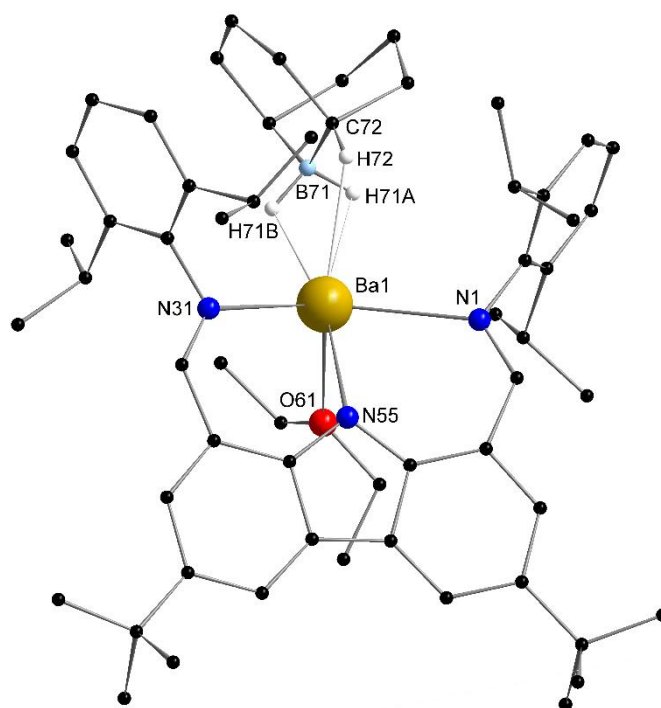
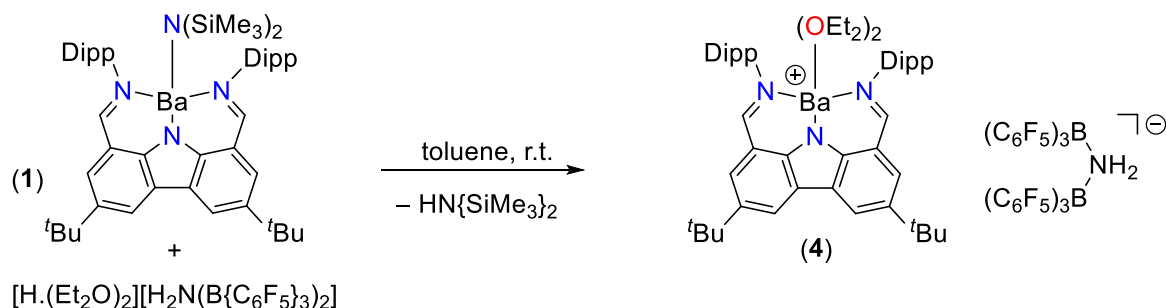


Fig. 3. Representation of the molecular structure of $[\{Carb^{Dipp}\}Ba(H_2-9BBN).Et_2O]$ (**3**.Et₂O). Non-coordinated Et₂O molecule and H atoms (except those interacting with Ba) omitted for clarity. Selected bond lengths (Å) and angles (°): Ba1-N55 = 2.713(4), Ba1-N1 = 2.787(5), Ba1-N31 = 2.781(5), Ba1-O61 = 2.739(4), Ba1-B71 = 3.077(9), Ba1-C72 = 3.260(9), Ba1-H71B = 2.5112(6), Ba1-H71a = 3.0426(6), Ba1-H72 = 2.6291(6); N1-Ba1-N31 = 126.15(13), N55-Ba1-O61 = 82.83(13), N1-N55-N31 = 104.67(16); Ba1- NNN_{plane} = 1.136(5). Note that the positions of H atoms were idealised, and therefore the Ba1-H interatomic distances given here are merely approximative and not further discussed.

The contribution of the disordered diethyl ether molecule was removed from the final data set using the *SQUEEZE* option in *PLATON*. Unlike in complex **2**₃, the two hydrides could in this case not be located using electron density in the Fourier difference map, and were instead placed in calculated positions; as such, the relevant Ba···H bond lengths are not discussed. Compound **3**.Et₂O has a 5-coordinate distorted square pyramidal geometry at Ba, with the molecule of diethyl ether molecular as the pyramid cap. A common feature of the solid-state structures of Ae-9BBN dihydroborates is a secondary interaction with a hydrogen atom on the α-carbon atom (methine) of the 9-BBN molecule [45]. In the case of **3**.Et₂O, this interaction cannot be confirmed with certainty due to the inability to locate the hydrogen atom using electron density. Nonetheless, there is some evidence for the interaction based on the twisted geometry of the 9-BBN moiety, and the relatively short distance to the carbon atom in α position (Ba1-C72 = 3.260(9) Å). The distance from the metallic cation to the mean plane delineated by the three N-atoms is much shorter in **3**.Et₂O (1.136(5) Å) than in **2**₃ (1.535(4) Å). Although **2**₃ and **3**.Et₂O are likely reasonably strong hydride sources, their reactivity has yet to be explored. Such complexes may also be relevant dormant or off-cycle species in the barium-catalysed dehydrocoupling of hydroboranes with amines [45,47] or, potentially, borinic acids.

The synthesis of the Ba-dihydroborate **3**.Et₂O, where, due to the relative weakness of the Ae-to-H bonds and overall high ionicity of the bonding, the metal could (potentially) be considered as a cation associated to a negatively charged borate, prompted us to synthesise an actual separated ion pair built on a Ba-carbazolate cation. With the aim of expanding on this niche area of discrete barium cations, the {Carb^{Dipp}}⁻ ligand was then used in conjunction with the weakly coordinating anion (WCA) H₂N{B(C₆F₅)₃}₂⁻ to synthesise a well-defined cation. We have often used the anion H₂N{B(C₆F₅)₃}₂⁻ because of its easy access, good solubility and desirable crystallisation properties (attributed to the presence of a dipole moment) relative to other commonly used WCA's such as B(C₆F₅)₄⁻ or Al{OC(CF₃)₃}₄⁻ [48-50]. The ion pair [{Carb^{Dipp}}Ba.(Et₂O)₂]⁺[H₂N{B(C₆F₅)₃}₂]⁻ (**4**) was isolated as orange crystals upon reaction of **1** with one equivalent of Bochmann's acid [H.(Et₂O)₂]⁺[H₂N{B(C₆F₅)₃}₂]⁻ [51] in toluene (Scheme 3), followed by recrystallisation in a mixture of toluene and a small amount of dichloromethane (see experimental section for details). Partial desolvation of the crystals under high vacuum gave [{Carb^{Dipp}}Ba.(Et₂O)_{0.25}]⁺[H₂N{B(C₆F₅)₃}₂]⁻ in 75% yield.



Scheme 3. Synthesis of [{Carb^{Dipp}}Ba.(Et₂O)₂]⁺[H₂N{B(C₆F₅)₃}₂]⁻ (**4**).

Compound **4** has poor solubility in aliphatic hydrocarbon solvents, but is soluble in aromatic solvents and dichloromethane. Despite repeated attempts from many different solvent mixtures, solvent-free crystals could not be obtained; besides, it proved impossible to remove all of the coordinated Et₂O molecules in **4**, even after prolonged drying under dynamic vacuum. The ¹H NMR spectrum in benzene-*d*₆ displays characteristic {Carb^{Dipp}}⁻ ligand resonances at δ_H 8.13 (CH=N), 2.51 (CH(CH₃)₂), 1.44 (C(CH₃)₃) and two doublets at 1.17 and 0.99 ppm. The presence of the coordinated Et₂O molecule is corroborated by typical resonances of expected intensities at δ_H 3.18 and 1.02 ppm. There is only a single resonance visible for the anion, a broad singlet at δ_H 6.36 ppm corresponding to NH₂. The ¹⁹F NMR spectrum displays three sharp resonances expected for a perfluorinated phenyl ring at δ_F -132.22, -158.77 and -164.48 ppm (*o*-, *p*- and *m*-F, respectively), while the ¹¹B NMR spectrum has a single broad resonance centred on δ_B -7.62 ppm. The molecular structure of the cationic fragment in **4**, that is, [{Carb^{Dipp}}Ba.(Et₂O)₂]⁺, is depicted in Fig. 4; as expected [42-44,48], there is no interaction between the cation and the anion, and the compound therefore characteristically forms a well-separated ion pair.

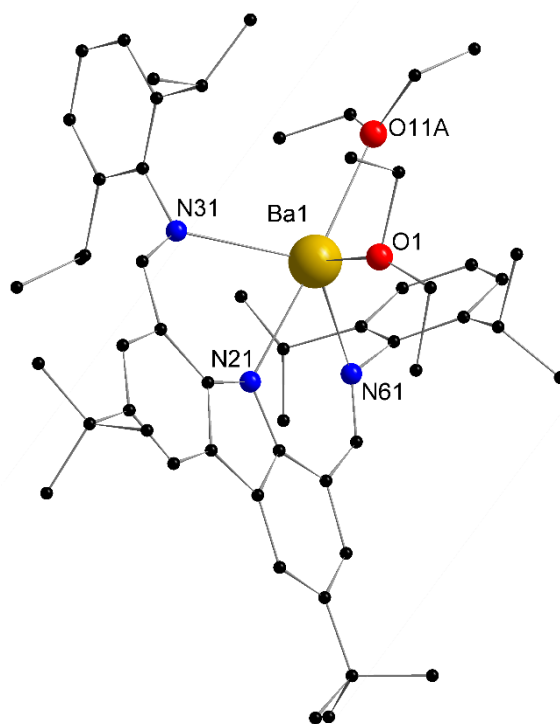


Fig. 4. Representation of the structure of the cation in the molecular solid-state structure of [{Carb^{Dipp}}Ba.(Et₂O)₂]⁺[H₂N{B(C₆F₅)₃}₂]⁻ (**4**). Non-interacting dichloromethane molecule and the non-coordinating anion [H₂N{B(C₆F₅)₃}₂]⁻ are not depicted; only the main component of the disordered Et₂O molecule is shown. H atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Ba1-N21 = 2.624(3), Ba1-N31 = 2.729(3), Ba1-N61 = 2.750(4), Ba1-O1 = 2.669(6), Ba1-O11A = 2.763(4); N21-Ba1-N31 = 70.70(10), N21-Ba1-N61 = 68.87(10), N21-Ba1-O1 = 89.0(2), N21-Ba1-O11A = 174.16(12), N31-Ba1-N61 = 123.85(10), N31-Ba1-O1 = 98.9(2), N31-Ba1-O11A = 106.88(13), N61-Ba1-O1 = 117.4(2), N61-Ba1-O11A = 109.41(14), O1-Ba1-O11A = 96.7(2). Ba1-*NNN*_{plane} = 1.2141(6).

The geometry about the metal in **4** forms a distorted trigonal bipyramid, with one molecule of diethyl ether and the $N_{\text{carbazolate}}$ occupying the two apical positions ($N21\text{-Ba1-O11A} = 174.16(12)^\circ$). The various $\text{Ba-N}_{\text{carbazolate}}$ ($\text{Ba1-N21} = 2.624(3) \text{ \AA}$) and $\text{Ba-N}_{\text{imine}}$ ($\text{Ba1-N31} = 2.729(3)$ and $\text{Ba1-N61} = 2.750(4) \text{ \AA}$) interatomic distances in **4** are comparatively shorter than those in **2₃** and **3.Et₂O**, which reflects stronger bonding in the case of the highly electron-deficient metal cation in the former. The distance from barium to the best average NNN_{plane} plane in **4** ($1.2141(6) \text{ \AA}$) is slightly longer than in **3.Et₂O** ($1.136(5) \text{ \AA}$), but still much shorter than in **2₃** ($1.535(4) \text{ \AA}$). The structure of the non-coordinating counter-ion $\text{H}_2\text{N}\{\text{B}(\text{C}_6\text{F}_5)_3\}_2^-$ is very similar to that already described [48-51] and shows the typical pattern of stabilising intramolecular $\text{H}\cdots\text{F}$ interactions. The Ba-O_{eq} interatomic distance to the O-atom in equatorial position is substantially shorter than that to the O-atom located at the apex ($\text{Ba1-O1} = 2.669(6)$ and $\text{Ba1-O11A} = 2.763(4) \text{ \AA}$, respectively), but both are in the range of similar Ba-O distances described so far for related barium complexes ligated by $\{\text{Carb}^{\text{DiPP}}\}^-$ [20-21].

Of note, other attempts to recrystallise the product of the reaction between **1** and Bochmann's acid in a mixture of toluene and thf yielded a small crop (yield not recorded) of colourless crystals of $[\text{Ba}(\text{thf})_7][\text{H}_2\text{N}\{\text{B}(\text{C}_6\text{F}_5)_3\}_2]_2$ (**5**) that contains a carbazolate-free, solvated barium dication. It is likely that the formation of **5** results from ligand scrambling in a complex akin to **4** in the presence of thf. Compound **5** is poorly soluble. Its NMR data were recorded in dichloromethane-*d*₂. The ¹H NMR spectrum features only three resonances for the amido NH_2 ($\delta_{\text{H}} 5.68 \text{ ppm}$) and thf (3.80 and 2.01 ppm) hydrogens. A single resonance is located at $\delta_{\text{B}} -8.38 \text{ ppm}$ in the ¹¹B NMR spectrum, whereas the *o*-, *p*- and *m*-F atoms give rise to resonances at $\delta_{\text{F}} -132.82$, -161.11 and -165.64 ppm in the ¹⁹F NMR spectrum. The solid-state structure of **5** was revealed by XRD. The unit cell contains a single Ba^{2+} cation solvated by seven thf molecules in a pseudo pentagonal bipyramidal geometry, with O4a and O1 at the axial positions (Fig. 5), along with two non-interacting anions and two molecules of severely disordered dichloromethane. The bond lengths for the Ba-O interatomic distances in the range $2.715(3)\text{-}2.748(4) \text{ \AA}$, are similar to those of other seven-coordinate barium complexes with metal-bound thf molecules, such as $[\text{BaI}_2(\text{thf})_5]$ ($2.706(8)\text{-}2.738(8) \text{ \AA}$) or $[\text{Ba}(\text{PPh}_2)_2(\text{thf})_5]$ ($2.716(4)\text{-}2.782(4) \text{ \AA}$) [52-53]. The thf solvated eight-coordinate complex $[\text{Ba}(\text{thf})_8][\text{B}(\text{C}_6\text{F}_5)_4]_2$, which has a square antiprismatic geometry at Ba, has also been reported [54]. It features longer Ba-O interatomic distances ($2.765(2) \text{ \AA}$) than **5**, as would be expected from the higher coordination number. The difference in thf solvation between these two compounds is unexpected. It cannot be justified by the different choice of anions, since both $\text{B}(\text{C}_6\text{F}_5)_4^-$ and $\text{H}_2\text{N}\{\text{B}(\text{C}_6\text{F}_5)_3\}_2^-$ are poorly coordinating and do not show any $\text{Ba}\cdots\text{F}$ interaction with the metallic dication. The gain in stabilising energy linked to the binding of an eighth thf molecule must be low, and it is quite likely that this additional solvent molecule is only loosely associated to the metal.

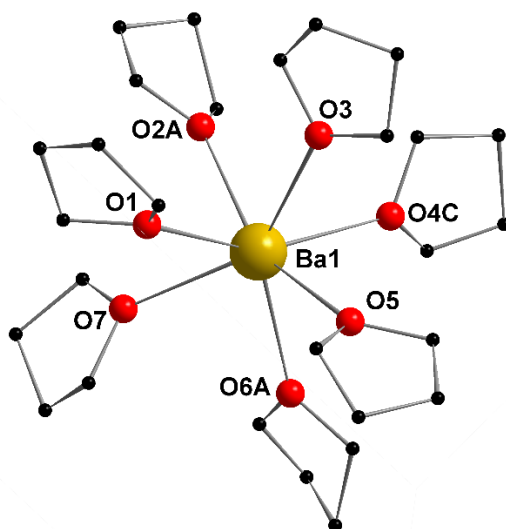


Fig. 5. Representation of the molecular structure of the cation in $[\text{Ba}(\text{thf})_7]^{2+}[\text{H}_2\text{N}\{\text{B}(\text{C}_6\text{F}_5)_3\}_2]^-_2$ (**5**). H atoms omitted for clarity. Only major component of disorder on thf molecules shown. Selected bond lengths (Å) and angles (°): Ba1-O1 = 2.745(4), Ba1-O2a = 2.722(3), Ba1-O3 = 2.715(3), Ba1-O4a = 2.741(4), Ba1-O5 = 2.740(3), Ba1-O6 = 2.726(3), Ba1-O7 = 2.748(8); O1-Ba1-O4a = 153.67(12), O1-Ba1-O5 = 89.93(12), O1-Ba1-O2a = 87.38(12), O1-Ba1-O3 = 75.90(11), O1-Ba1-O7 = 75.42(11), O1-Ba1-O6a = 124.78(12).

3. Conclusion

Two barium-dihydroborate complexes supported by a bulky bis(imino)carbazolate ligand have been prepared and structurally characterised. They are new additions to the family of compounds that can be effectively stabilised by this bulky ancillary ligand, and, more generally, also complement the range of soluble, molecular barium complexes. They should open new areas of investigations linked to the reactivity of the hydroborate moieties, and the outcome of related investigations will be disclosed in a forthcoming report. The bis(imino)carbazolate ligand has also allowed for the synthesis and crystallisation of a rare case of soluble barium cation paired with a weakly coordinating fluorinated anion, which bears the potential to be used in Lewis acid-mediated catalysis [42-44].

4. Experimental

All manipulations were performed under an inert atmosphere by using standard Schlenk techniques or in a dry, solvent-free glovebox (Jacomex; O₂ < 1 ppm, H₂O < 3 ppm). Petroleum ether, toluene, dichloromethane, and Et₂O were collected from MBraun SPS-800 purification alumina columns and thoroughly degassed with argon before being stored on 4 Å molecular sieves; thf was distilled under argon from Na/benzophenone prior to use. Deuterated solvents (Eurisotop, Saclay, France) were stored in sealed ampoules over activated 4 Å molecular sieves or a potassium mirror, and degassed by a minimum of three freeze–thaw cycles. NMR spectra were recorded with Bruker AM-400 or AM-500 spectrometers. All chemical shifts (δ) [ppm] were determined relative to the residual signal of the deuterated solvent in benzene-*d*₆ or dichloromethane-*d*₂ or to FCCL₃ for ¹⁹F NMR. Assignment of the signals was assisted by 1D and 2D NMR experiments. The complex [{Carb^{DiPP}}BaN(SiMe₃)₂] (**1**) and [H.(Et₂O)₂]⁺[H₂N{B(C₆F₅)₃}₂]⁻ were prepared according to literature procedures [20,51]. Pinacolborane and [H-9BBN]₂ were purchased from Sigma-Aldrich or Acros and used as received. Reliable and reproducible elemental analyses for the complexes could not be obtained, most probably on account of their high sensitivity.

[[Carb^{DiPP}}Ba(μ-H₂Bpin)]₃ (2₃**). HBpin (83 mg, 59 μL, 0.65 mmol) was added dropwise to a solution of [{Carb^{DiPP}}Ba(N{SiMe₃)₂]₂] (**1**; 300 mg, 0.32 mmol) in petroleum ether (30 mL), resulting in the formation of a yellow suspension. The suspension was stirred for 30 min, then the solid was isolated by cannula filtration and washed with petroleum ether (2 × 10 mL). The resulting yellow solid was dried under reduced pressure to constant weight, to give the title compound as a bright yellow solid. Yield: 294 mg (95%). Single-crystals suitable from X-ray diffraction were grown from petroleum ether washings. The crystals are extremely reactive, and quickly decompose in crystal mineral oil with the evolution of (presumably hydrogen) gas.**

¹H NMR (400.16 MHz, thf-*d*₈, 25 °C): δ 8.52 (s, 2H, CH=N), 8.47 (d, ⁴J_{HH} = 2.0 Hz, 2H, Ar-H), 7.64 (d, ⁴J_{HH} = 2.1 Hz, 2H, Ar-H), 7.24 (m, 4H, Ar-H), 7.15 (m, 2H, Ar-H), 3.14 (hept, ³J_{HH} = 6.8 Hz, 4H, CH(CH₃)₂), 1.49 (s, 18H, C(CH₃)₃), 1.28 (d, ³J_{HH} = 7.0 Hz, 12H, CH(CH₃)₂), 1.15 (d, ³J_{HH} = 6.8 Hz, 12H, CH(CH₃)₂), 0.39 (s, 12H, OC(CH₃)₂) ppm. The BH₂ resonance could not be observed.

¹³C{¹H} J-MOD NMR (125.77 MHz, thf-*d*₈, 27 °C; 256 scans): δ 172.16 (CH=N), 149.50 (Ar-C), 148.71 (Ar-C), 141.23 (Ar-C), 138.86 (Ar-C), 132.30 (Ar-C), 126.49 (Ar-C), 124.78 (Ar-C), 123.71 (Ar-C), 122.71 (Ar-C), 120.74 (Ar-C), 79.16 (O-C), 32.58 (C(CH₃)₃), 29.48 (CH(CH₃)₂), 26.03 (CH(CH₃)₂), 25.72 (C(CH₃)₃), 25.32 (OC(CH₃)₂), 24.70 (CH(CH₃)₂)k ppm.

¹¹B NMR (128.38 MHz, thf-*d*₈, 27 °C): δ 3.66 (t, ¹J_{BH} = 92.9 Hz) ppm.

[[Carb^{DiPP}}Ba(H₂-9BBN).Et₂O] (3.Et₂O**). A solution of [H-9BBN]₂ (77 mg, 0.16 mmol) in petroleum ether (10 mL) was added dropwise to a suspension of [{Carb^{DiPP}}Ba(N{SiMe₃)₂]₂] (**1**; 300 mg, 0.32 mmol) in petroleum ether (20 mL), resulting in a yellow solution. After 16 h, the solution was**

concentrated to 5 mL and layered with 5 drops of diethyl ether. After 3 days at room temperature, the title compound was isolated as large yellow blocks suitable for an X-ray diffraction study. Recrystallisation of the mother liquor gave a second crop of crystals. Yield (combined crops): 112 mg + 78 mg = 190 mg (57%). The crystals are extremely reactive and quickly decompose in crystal mineral oil with the evolution of (presumably hydrogen) gas.

^1H NMR (400.16 MHz, benzene- d_6 , 25 °C): δ 8.70 (d, $^4J_{\text{HH}} = 2.0$ Hz, 2H, Ar-*H*), 8.35 (s, 2H, CH=N), 7.60 (d, $^4J_{\text{HH}} = 1.9$ Hz, 2H, Ar-*H*), 7.18 (m, 6H, Ar-*H*); 3.18 (q, $^3J_{\text{HH}} = 6.9$ Hz, 8H, OCH₂), 3.03 (hept, $^3J_{\text{HH}} = 6.9$ Hz, 2H, CH(CH₃)₂), 2.05 (m, 2H, 9BBN), 1.77 (m, 4H, 9BBN), 1.63 (m, 2H, 9BBN), 1.46 (s, 18H, C(CH₃)₃), 1.40 (d, $^3J_{\text{HH}} = 6.8$ Hz, 12H, CH(CH₃)₂), 1.38 (m, 6H, 9BBN, obscured by CH(CH₃)₂ resonance), 1.12 (d, $^3J_{\text{HH}} = 6.8$ Hz, 12H, CH(CH₃)₂), 1.00 (t, $^3J_{\text{HH}} = 7.0$ Hz, 12H, OCH₂CH₃), 0.54 (br s, 2H, H₂B) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (100.63 MHz, benzene- d_6 , 25 °C): δ 171.70 (CH=N), 148.94 (Ar-C), 147.94 (Ar-C), 139.81 (Ar-C), 138.76 (Ar-C), 132.27 (Ar-C), 128.18 (Ar-C), 126.49 (Ar-C), 124.39 (Ar-C), 122.49 (Ar-C), 119.96 (Ar-C), 65.70 (OCH₂), 34.96 (BCHCH₂CH₂), 34.50 (C(CH₃)₃), 32.17 (C(CH₃)₃), 29.47 (CH(CH₃)₂), 26.70 (BCHCH₂CH₂), 25.91 (br, BCHCH₂CH₂), 25.46 (CH(CH₃)₂), 23.18 (CH(CH₃)₂), 15.33 (OCH₂CH₃) ppm.

^{11}B NMR (160.46 MHz, benzene- d_6 , 27 °C): δ -6.76 (t, $^1J_{\text{BH}} = 74.5$ Hz) ppm.

[{Carb^{Dipp}Ba.(Et₂O)₂}⁺[H₂N{B(C₆F₅)₃]₂}⁻ (4). In a glovebox, a Schlenk flask was loaded with [{Carb^{Dipp}Ba(N{SiMe₃})₂]}₂ (**1**; 300 mg, 0.32 mmol) and [H.(Et₂O)₂]⁺[H₂N{B(C₆F₅)₃]₂}⁻ (378 mg, 0.32 mmol). The flask was removed from the glovebox and attached to a Schlenk line. The contents of the vessel were dissolved in toluene (30 mL) and left to stir overnight at room temperature. The volatiles were removed under reduced pressure, and the residue was redissolved in a mixture of toluene (5 mL) and CH₂Cl₂ (10 drops). The resulting yellow-orange suspension was then filtered to eliminate insoluble impurities, the solution was concentrated to 2 mL and a drop of diethyl ether was added. The solution was then stored at -30 °C in a freezer. A few orange crystals suitable for an X-ray diffraction study were yielded after several weeks. As the compound is difficult to crystallise, presumably due to its extreme solubility in CH₂Cl₂, the mother liquor was also worked up. Removal of the volatiles from the liquor results in an orange powder, that after being washed with petroleum ether (10 mL) is suitable for further synthesis. Yield (crystals + powder) of **[{Carb^{Dipp}Ba.(Et₂O)_{0.25}}⁺[H₂N{B(C₆F₅)₃]₂}⁻**: 445 mg (75%)

^1H NMR (400.16 MHz, benzene- d_6 , 25 °C): δ 8.70 (d, $^4J_{\text{HH}} = 2.0$ Hz, 2H, CH-Carb), 8.13 (s, 2H, CH=N), 7.59 (d, $^4J_{\text{HH}} = 2.0$ Hz, 2H, CH-Carb), 7.18 (br s, 6H, Ar-*H*), 6.35 (br s, 2H, NH₂), 3.18 (q, 8H, OCH₂), 2.52 (hept, $^3J_{\text{HH}} = 6.8$ Hz, 4H, CH(CH₃)₂), 1.45 (s, 18H, C(CH₃)₃), 1.19 (d, $^3J_{\text{HH}} = 6.8$ Hz, 12H, CH(CH₃)₂), 1.00 (t, 12H, OCH₂CH₃), 0.98 (d, $^3J_{\text{HH}} = 6.7$ Hz, 12H, CH(CH₃)₂) ppm.

^{13}C NMR (100.63 MHz, benzene- d_6 , 25 °C): δ 173.21 (CH=N), 148.76 (dm, $^1J_{\text{CF}} = 240.6$ Hz, C₆F₅), 148.25 (Ar-C), 146.33 (Ar-C), 140.93 (Ar-C), 139.85 (dm, $^1J_{\text{CF}} = 230.7$ Hz, C₆F₅), 139.53 (Ar-C), 137.33 (dm, $^1J_{\text{CF}} = 241.0$ Hz, C₆F₅), 132.87 (Ar-C), 129.3 (Ar-C, obscured by solvent); 124.90 (Ar-C),

123.90 (Ar-C), 121.53 (ipso-C₆F₅), 118.91 (Ar-C), 65.43 (OCH₂), 34.55 (C(CH₃)₃), 31.87 (C(CH₃)₃), 29.42 (CH(CH₃)₂), 25.01 (CH(CH₃)₂), 22.88 (CH(CH₃)₂), 15.04 (OCH₂CH₃) ppm.

¹¹B NMR (128.38 MHz, benzene-*d*₆, 25 °C): δ -7.62 (br s, B(C₆F₅)₃) ppm.

¹⁹F NMR (376.37 MHz, benzene-*d*₆, 25 °C): δ -132.22 (d, ³J_{FF} = 21.0 Hz, 6F, ortho-*F*), -158.88 (t, ³J_{FF} = 20.7 Hz, 12F, para-*F*), -164.52 (t, ³J_{FF} = 21.3 Hz, 12F, meta-*F*) ppm.

[Ba.(thf)₇]²⁺[H₂N{B(C₆F₅)₃]₂]⁻² (5). In a glovebox, a Schlenk vessel was loaded with [{Carb^{Dipp}}Ba(N{SiMe₃})₂] (**1**; 300 mg, 0.32 mmol) and [H.(Et₂O)₂]⁺[H₂N{B(C₆F₅)₃]₂]⁻ (378 mg, 0.32 mmol). The flask was removed from the glovebox and attached to a Schlenk line. The contents of the Schlenk flask were dissolved in toluene (20 mL), and thf (1 mL) was added before the solution was left to stir overnight at room temperature. The volatiles were removed under reduced pressure and the yellow-orange solid was washed with petroleum ether. Recrystallisation attempts in mixtures of toluene and thf yielded a few colourless blocks of the title compound after several months which were isolated by cannula filtration, and dried under reduced pressure.

¹H NMR (500.13 MHz, dichloromethane-*d*₂, 27 °C): δ 5.68 (br s, 4H, NH₂), 3.80 (m, 28H, OCH₂), 2.01 (m, 28H, OCH₂CH₂) ppm.

¹³C{¹H} NMR (125.77 MHz, dichloromethane-*d*₂, 27 °C): δ 148.33 (dm, ¹J_{CF} = 240.4 Hz, C₆F₅), 139.55 (dm, ¹J_{CF} = 250.3 Hz, C₆F₅), 137.24 (dm, ¹J_{CF} = 246.5 Hz, C₆F₅), 120.72 (br, ipso-C₆F₅), 69.38 (OCH₂), 25.85 (OCH₂CH₂) ppm.

¹¹B NMR (160.46 MHz, dichloromethane-*d*₂, 27 °C): δ -8.38 (br s, B(C₆F₅)₃) ppm.

¹⁹F NMR (470.52 MHz, dichloromethane-*d*₂, 27 °C): δ -132.82 (d, ³J_{FF} = 20.8 Hz, 6F, ortho-*F*), -161.11 (t, ³J_{FF} = 20.3 Hz, 12F, para-*F*), -165.64 (t, ³J_{FF} = 21.3 Hz, 12F, meta-*F*) ppm.

Credit authorship contribution statement

P. M. Chapple carried out all synthetic work and participated to the design of experiments, analysis of results and preparation of the manuscript. T. Roisnel and M. Cordier solved the X-ray structures of all complexes described herein. J.-F. Carpentier participated to the investigations and data analysis. Y. Sarazin was the lead investigator for the project.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

P.M.C thank the French *Agence Nationale de la Recherche* for the provision of a research grant (ANR-17-CE07-0017-01).

Appendix A. Supplementary data

CCDC 2127024-2127026 and 2127168 contains the supplementary crystallographic data for compounds 2-5. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

References

- [1] M. Westerhausen, Heavy Grignard reagents – Synthesis and reactivity of organocalcium compounds, *Coord. Chem. Rev.* 252 (2008) 1516–1531.
- [2] S. Harder, From Limestone to Catalysis: Application of Calcium Compounds as Homogeneous Catalysts, *Chem. Rev.* 110 (2010) 3852–3876.
- [3] A. G. M. Barrett, M. R. Crimmin, M. S. Hill, P. A. Procopiou, Heterofunctionalization catalysis with organometallic complexes of calcium, strontium and barium, *Proc. R. Soc. A* (2010) 466, 927–963.
- [4] S. Kobayashi, Y. Yamashita, Alkaline Earth Metal Catalysts for Asymmetric Reactions, *Acc. Chem. Res.* 44 (2011) 58–71.
- [5] M. R. Crimmin, M. S. Hill, Homogeneous Catalysis with Organometallic Complexes of Group 2. In *Alkaline-Earth Metal Compounds: Oddities and Applications*; S. Harder, Ed.; 2013; *Top. Organomet. Catal.* 45 (2013) 191–241.
- [6] J.-F. Carpentier, Y. Sarazin, Alkaline-Earth Metal Complexes in Homogeneous Polymerization Catalysis. In *Alkaline-Earth Metal Compounds: Oddities and Applications*; S. Harder, Ed.; 2013; *Top. Organomet. Catal.* 45 (2013) 141–190.
- [7] M. Arrowsmith, M. S. Hill, Alkaline Earth Chemistry: Applications in Catalysis. In *Comprehensive Inorganic Chemistry II, Second Edition* (2013) 1189–1216.
- [8] M. S. Hill, D. J. Liptrot, C. Weetman, Alkaline earths as main group reagents in molecular catalysis, *Chem. Soc. Rev.*, 45 (2016) 972–988.
- [9] M. Westerhausen, A. Koch, H. Görls, S. Kriek, Heavy Grignard Reagents: Synthesis, Physical and Structural Properties, Chemical Behavior, and Reactivity, *Chem. Eur. J.* 23 (2017) 1456–1483.
- [10] D. Mukherjee, D. Schuhknecht, J. Okuda, Hydrido Complexes of Calcium: A New Family of Molecular Alkaline-Earth-Metal Compounds, *Angew. Chem. Int. Ed.* 57 (2018) 9590–9602.
- [11] B. Rösch, S. Harder, New horizons in low oxidation state group 2 metal chemistry, *Chem. Commun.*, 57 (2021) 9354–9365.
- [12] A. S. S. Wilson, M. S. Hill, M. F. Mahon, C. Dinoi, L. Maron, *Science* 358 (2017) 1168–1171.
- [13] B. Rösch, T. X. Gentner, J. Langer, C. Färber, J. Eysel, L. Zhao, C. Ding, G. Frenking, S. Harder, Dinitrogen complexation and reduction at low-valent calcium, *Science* 371 (2021) 1125–1128.

- [14] P. M. Chapple, Y. Sarazin, Contemporary Molecular Barium Chemistry, *Eur. J. Inorg. Chem.*, (2020) 3321–3346.
- [15] S. Harder, J. Brettar, Rational Design of a Well-Defined Soluble Calcium Hydride Complex, *Angew. Chem. Int. Ed.* 45 (2006) 3474–3478.
- [16] A. G. Avent, M. R. Crimmin, M. S. Hill, P. B. Hitchcock, Kinetic stability of heteroleptic (β -diketiminato) heavier alkaline-earth (Ca, Sr, Ba) amides, *Dalton Trans.* (2004) 278–284.
- [17] X. Shi, C. Hou, C. Zhou, Y. Song, J. Cheng, A Molecular Barium Hydrido Complex Stabilized by a Super-Bulky Hydrotris(pyrazolyl)borate Ligand, *Angew. Chem. Int. Ed.* 56 (2017) 16650–16653.
- [18] M. Wiesinger, B. Maitland, C. Färber, G. Ballmann, C. Fischer, H. Elsen, S. Harder, Simple Access to the Heaviest Alkaline Earth Metal Hydride: A Strongly Reducing Hydrocarbon-Soluble Barium Hydride Cluster, *Angew. Chem. Int. Ed.* 56 (2017) 16654–16659.
- [19] X. Shi, G. Qin, Y. Wang, L. Zhao, Z. Liu, J. Cheng, Super-Bulky Penta-arylcyclopentadienyl Ligands: Isolation of the Full Range of Half-Sandwich Heavy Alkaline-Earth Metal Hydrides, *Angew. Chem. Int. Ed.* 58 (2019) 4356–4360.
- [20] P. M. Chapple, S. Kahlal, J. Cartron, T. Roisnel, V. Dorcet, M. Cordier, J.-Y. Saillard, J.-F. Carpentier, Yann Sarazin, Bis(imino)carbazolate: A Master Key for Barium Chemistry, *Angew. Chem. Int. Ed.* 59 (2020) 9120–9126.
- [21] P. M. Chapple, M. Cordier, V. Dorcet, T. Roisnel, J.-F. Carpentier, Y. Sarazin, A versatile nitrogen ligand for alkaline-earth chemistry, *Dalton Trans.* 49 (2020) 11878–11889.
- [22] M. Bremer, H. Noth, M. Thomann, M. Schmidt, Preparation and Molecular Structures of Tetrahydrofuran, Diethylene Diglycol Dimethyl Ether and 18-Crown-6 Complexes of Strontium and Barium Tetrahydridoborate, *Chem. Ber.* 128 (1995) 455–460.
- [23] M. D. Anker, M. Arrowsmith, R. L. Arrowsmith, M. S. Hill, M. F. Mahon, Alkaline-Earth Derivatives of the Reactive $[\text{HB}(\text{C}_6\text{F}_5)_3]^-$ Anion, *Inorg. Chem.* 56 (2017) 5976–5983.
- [24] Mark J. Saly, Charles H. Winter, Highly Distorted $\kappa^3\text{-N,N,H}$ Bonding of Bis(3,5-di-*tert*-butylpyrazolyl)borate Ligands to the Heavier Group 2 Elements, *Organometallics* 29 (2010) 5472–5480.
- [25] K. Izod, C. Wills, S. El-Hamruni, R. W. Harrington, P. G. Waddell, M. R. Probert, Structural Diversity in Alkaline Earth Metal Complexes of a Phosphine-Borane-Stabilized 1,3-Dicarbocation, *Organometallics* 34 (2015) 2406–2414.
- [26] K. Izod, C. Wills, W. Clegg, R. W. Harrington, Alkaline Earth Metal Complexes of a Phosphine-Borane-Stabilized Carbanion: Synthesis, Structures, and Stabilities, *Inorg. Chem.* 46 (2007) 4320–4325.
- [27] R. K. Kottalanka, A. Harinath, Tarun K. Panda, Chiral alkaline earth metal complexes with M–Se direct bond (M = Mg, Ca, Sr, Ba): syntheses, structures and ϵ -caprolactone polymerization, *RSC Adv.* 5 (2015) 37755–37767.

- [28] J. Bhattacharjee, A. Harinath, A. Sarkar, T. K. Panda, Polymerization of ϵ -Caprolactam to Nylon-6 Catalyzed by Barium σ -Borane Complex under Mild Condition, *ChemCatChem* 11 (2019) 3366–3370.
- [29] Matthias Westerhausen, Christian Gückel, Stefan Schneiderbauer, Heinrich Nöth, Narayan S. Hosmane, The First Barium-Carborate Complex: Synthesis and Structural Investigation, *Angew. Chem. Int. Ed.* 40 (2001) 1902–1904.
- [30] Bo Liu, Vincent Dorcet, Laurent Maron, Jean-François Carpentier, Yann Sarazin, β -Diketiminato–Alkaline Earth Cationic Complexes: Synthesis, Structures, Lactide Polymerization and Unusual Oxidative Reactivity of the Ancillary Ligand, *Eur. J. Inorg. Chem.* (2012) 3023–3031.
- [31] P. Jochmann, J. P. Davin, T. P. Spaniol, L. Maron, J. Okuda, A Cationic Calcium Hydride Cluster Stabilized by Cyclen-Derived Macrocyclic N,N,N,N Ligands, *Angew. Chem. Int. Ed.* 51 (2012) 4452–4455.
- [32] V. Leich, T. P. Spaniol, L. Maron, J. Okuda, Molecular Calcium Hydride: Dicalcium Trihydride Cation Stabilized by a Neutral NNNN-Type Macrocyclic Ligand, *Angew. Chem. Int. Ed.* 55 (2016) 4794–4797.
- [33] D. Schuhknecht, C. Lhotzky, T. P. Spaniol, L. Maron, J. Okuda, Calcium Hydride Cation $[\text{CaH}]^+$ Stabilized by an NNNN-type Macrocyclic Ligand: A Selective Catalyst for Olefin Hydrogenation, *Angew. Chem. Int. Ed.* 56 (2017) 12367–12371.
- [34] D. Mukherjee, T. Höllerhage, V. Leich, T. P. Spaniol, U. Englert, L. Maron, J. Okuda, The Nature of the Heavy Alkaline Earth Metal–Hydrogen Bond: Synthesis, Structure, and Reactivity of a Cationic Strontium Hydride Cluster, *J. Am. Chem. Soc.* 140 (2018) 3403–3411.
- [35] J. Pahl, S. Brand, H. Elsen, S. Harder, Highly Lewis acidic cationic alkaline earth metal complexes, *Chem. Commun.* 54 (2018) 8685–8688.
- [36] L. Garcia, M. D. Anker, M. F. Mahon, L. Maron, M. S. Hill, Coordination of arenes and phosphines by charge separated alkaline earth cations, *Dalton Trans.* 47 (2018) 12684–12693.
- [37] L. Garcia, M. F. Mahon, M. S. Hill, Multimetallic Alkaline-Earth Hydride Cations, *Organometallics* 38 (2019) 3778–3785.
- [38] Philipp Dabringhaus, Marcel Schorpp, Harald Scherer, and Ingo Krossing, A Highly Lewis Acidic Strontium *ansa*-Arene Complex for Lewis Acid Catalysis and Isobutylene Polymerization, *Angew. Chem. Int. Ed.* 59 (2020) 22023–22027.
- [39] K. Thum, J. Martin, H. Elsen, J. Eyselein, L. Stiegler, J. Langer, S. Harder, Lewis Acidic Cationic Strontium and Barium Complexes, *Eur. J. Inorg. Chem.* (2021) 2643–2653.
- [40] T. Höllerhage, A. Carpentier, T. P. Spaniol, L. Maron, U. Englert, J. Okuda, Cationic strontium hydride complexes supported by an NNNN-type macrocycle, *Chem. Commun.* 57 (2021) 6316–6319.

- [41] S. Itoh, H. Kumei, S. Nagatomo, T. Kitagawa, S. Fukuzumi, *J. Am. Chem. Soc.* 123 (2001) 2165–2175.
- [42] Y. Sarazin, V. Poirier, T. Roisnel, J.-F. Carpentier, Discrete, Base-Free, Cationic Alkaline-Earth Complexes – Access and Catalytic Activity in the Polymerization of Lactide, *Eur. J. Inorg. Chem.* (2010) 3423–3428.
- [43] Y. Sarazin, B. Liu, T. Roisnel, L. Maron, J.-F. Carpentier, Discrete, Solvent-Free Alkaline-Earth Metal Cations: Metal···Fluorine Interactions and ROP Catalytic Activity, *J. Am. Chem. Soc.* 133 (2011) 9069–9087.
- [44] B. Liu, T. Roisnel, Y. Sarazin, Well-defined, solvent-free cationic barium complexes: Synthetic strategies and catalytic activity in the ring-opening polymerization of lactide, *Inorg. Chim. Acta* 380 (2012) 2–13.
- [45] A. G. M. Barrett, M. R. Crimmin, M. S. Hill, P. B. Hitchcock, P. A. Procopiou, Reactions of β -Diketiminato-Stabilized Calcium Amides with 9-Borabicyclo[3.3.1]nonane (9-BBN), *Organometallics* 26 (2007) 4076–4079.
- [46] S. Harder, J. Spielmann, Calcium-mediated hydroboration of alkenes: “Trojan horse” or “true” catalysis?, *J. Organomet. Chem.* 698 (2012) 7–14.
- [47] D. J. Liptrot, M. S. Hill, M. F. Mahon, A. S. S. Wilson, Alkaline-Earth-Catalyzed Dehydrocoupling of Amines and Boranes, *Angew. Chem. Int. Ed.* 54 (2015) 13362–13365.
- [48] M. Bochmann, Highly electrophilic main group compounds: Ether and arene thallium and zinc complexes, *Coord. Chem. Rev.* 253 (2009) 2000–2014.
- [49] Y. Sarazin, J.-F. Carpentier, Discrete Cationic Complexes for Ring-Opening Polymerization Catalysis of Cyclic Esters and Epoxides, *Chem. Rev.* 115 (2015) 3564–3614.
- [50] I. M. Riddlestone, A. Kraft, J. Schaefer, I. Krossing, Taming the Cationic Beast: Novel Developments in the Synthesis and Application of Weakly Coordinating Anions, *Angew. Chem. Int. Ed.* 57 (2018) 13982-14024.
- [51] S. J. Lancaster, A. Rodriguez, A. Lara-Sanchez, M. D. Hannant, D. A. Walker, D. H. Hughes, M. Bochmann, $[\text{H}_2\text{N}\{\text{B}(\text{C}_6\text{F}_5)_3\}_2]^-$: A New, Remarkably Stable Diborate Anion for Metallocene Polymerization Catalysts, *Organometallics* 21 (2002) 451-453.
- [52] K. Fromm, Structural Evolution from the Solid State to the Molecule for BaI_2 : Synthesis and Crystal Structures of $[\text{BaI}_2(\mu_2\text{-OH}_2)_2]_{3/\infty}$, $[\text{BaI}_2(\mu_2\text{-OH}_2)_2(\text{OC}_3\text{H}_6)]_{2/\infty}$, $[\text{BaI}_2(\text{thf})_3]_{1/\infty}$ and $[\text{BaI}_2(\text{thf})_5]\cdot\text{THF}$, *Angew. Chem. Int. Ed.* 36 (1997) 2799-2801.
- [53] M. Gartner, H. Görls, M. Westerhausen, Arylphosphanide Complexes of the Heavy Alkaline Earth Metals Calcium, Strontium and Barium of the Formula $(\text{thf})_n\text{M}[\text{P}(\text{R})\text{Aryl}]_2$, *Z. Anorg. Allg. Chem.* 633 (2007) 2025-2031.
- [54] O. Michel, H. Kaneko, H. Tsurugi, K. Yamamoto, K. W. Törnroos, R. Anwänder, K. Mashima, Diene Dissolution of the Heavier Alkaline Earth Metals, *Eur. J. Inorg. Chem.* (2012) 998-1003.