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Triboranate Derivatives of Calcium and Strontium

Henry T. W. Shere, Michael S. Hill* and Mary F. Mahon

Department of Chemistry, University of Bath, Claverton Down, Bath, BA2 7AY, UK

Email: msh27@bath.ac.uk

Abstract

This contribution reports the alkaline earth-mediated formation of homonuclear sigma bonding between the metalloid element, boron. The resultant triborane anions result from the formal dismutation of bis(pinacolato)diboron (B_2pin_2) and the generation of putative heavier group 2 boryl intermediates. Initial reactions of the heavier alkaline earth bis-(trimethylsilyl)amides, $[Ae\{N(SiMe_3)_2\}_2]$ ($Ae = Ca$ or Sr), with an equimolar quantity of bis(pinacolato)diboron (B_2pin_2) provided the 4-coordinate group 2 silazide diborane adducts $[Ae(B_2pin_2)\{N(SiMe_3)_2\}_2]$ in which the diborane acts as a bidentate ligand via κ^2-O,O' coordination. Reaction of the calcium species at 60 °C with a further three molar equivalents of B_2pin_2 induced the elimination of $pinBN(SiMe_3)_2$ and the formation of the bis-triboranate derivative, $[Ca(B_3pin_3)_2]$, in which the 6-coordinate calcium centre is bound in a κ^3-O,O',O'' -coordination mode by the three contiguous pinacolate oxygen atoms of both *catena*- $B(sp^2)-B(sp^3)-B(sp^2)$ bonded anions. Although analogous treatment of $[Ae(B_2pin_2)\{N(SiMe_3)_2\}_2]$ provided similar triboranate anion formation, in this case two equivalents of the strontium silazide were retained within the structure of the trimetallic species, $[Sr(B_3pin_3)_2(Sr\{N(SiMe_3)_2\}_2)_2]$. Despite these contrasting outcomes both triboranate complexes provide rare examples of *catena*-boron species beyond the common diboranes, (R_2B-BR_2), in which the homologated unit is propagated by electron precise and otherwise unsupported B-B bonds.

Introduction

Whereas carbon's ability to catenate is perhaps the defining feature of organic chemistry, rational routes to homonuclear, sigma bonded chains of carbon's metalloid nearest neighbour, boron, are a rarity. The electronic structures of both elemental boron and deltahedral boron clusters generally invoke an element of B-B bonding.[1] These interactions are, however, generally augmented by bridging third-party atoms or comprise a component of a multicentre bond. Although diborane(4) molecules, R_2B-BR_2 (where $R = e.g.$ halide, alkyl, aryl, OR, NR_2), do provide electron precise B-B bonded structures with a loose analogy to ethane,[2] longer chain boron homologues propagated through 2 centre-2 electron sigma bonding are uncommon.[3-6] This scarcity may, at least in part, be traced to a lack of boron-centred synthetic methods comparable with those available to the organic synthetic chemist in which an electrophilic carbon reagent (e.g. an organic halide) is combined with a carbon-centred nucleophile. Boron's more metallic and electropositive character ensured that a historical majority of borane reagents are classified as sources of electrophilic boron, such that the development of complementary boron

nucleophiles is of more recent origin. Although predated by a variety of transition metal-boron bonded molecules,[7-9] Yamashita and co-workers' initial boryl (or boranyl) lithium species (e.g. **1**, Figure 1),[10, 11] therefore, provided the impetus for the development of a significant number of boryl species that display a direct interaction to an even more electropositive, generally alkali or alkaline earth metal, cation.[12-15] In common with most routes to diborane(4) molecules, synthetic approaches to boryl anions exemplified by the lithium species **1** require alkali metal reduction of a haloborane precursor, while the synthesis of the alkaline earth derivatives **2 - 5** exploited the nucleophilic behaviour of **1** via metathesis with (beryllium, magnesium) halide or (calcium, strontium) silazide reagents.[16-19]

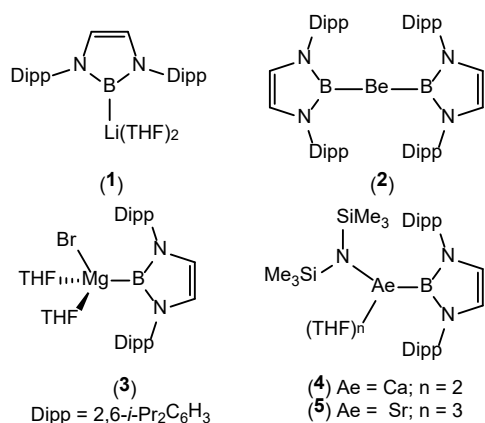
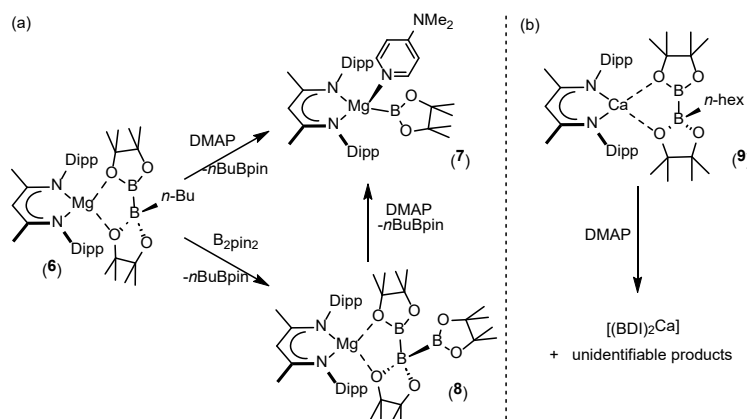


Figure 1: Examples of group 1 and group 2 boryl derivatives.

In parallel with the latter of these advances, we have pursued an alternative pathway in which B-B heterolysis and the generation of a terminal magnesium boryl is induced through the addition of an exogenous base such as 4-dimethylaminopyridine (DMAP) to an initially formed β -diketiminato (BDI) magnesium diboranate (**6**, Scheme 1).[20-22] Like compounds **1 - 5**, compound **7** has proved to be a potent source of nucleophilic boron toward both organic and inorganic electrophiles.[21, 23] Desymmetrised B(sp^2)-B(sp^3) diborane adducts have attracted recent attention as latent sources of nucleophilic boron [2, 24-31] and, in a similar manner, we have observed that the diboranate precursor to compound **7**, compound **6**, also acts as a surrogate source of the [Bpin]⁻ anion. Although this chemistry has facilitated a range of C-B bond forming reactions, any potential Mg-B bonded species are formed only as short-lived intermediates.[32] In common with these observations, however, we have demonstrated that treatment of **6** with borane and diborane electrophiles proves a facile and controllable route to B-B' bond formation and the isolation of unusual magnesium triboranate (or, alternatively, bis(boryl)borate) derivatives (e.g. **8**).[20, 33, 34] Although the boron anions are propagated by contiguous and electron precise (i.e. 2c-2e) B(sp^2)-B(sp^3)-B(sp^2) interactions, compounds such as **8** are similarly labile to heterolysis and the generation of nucleophilic boryl equivalents when treated either with a base (e.g. Scheme 1b) or an appropriate electrophile. Notably, these latter reactions ensue through the elimination of an intact equivalent of B₂pin₂. Although this latter feature is to the detriment of overall atom economy in a purely stoichiometric process, the subsequent

availability of the eliminated diborane may prove significant for the future elaboration of any onward reactivity to a catalytic regime.

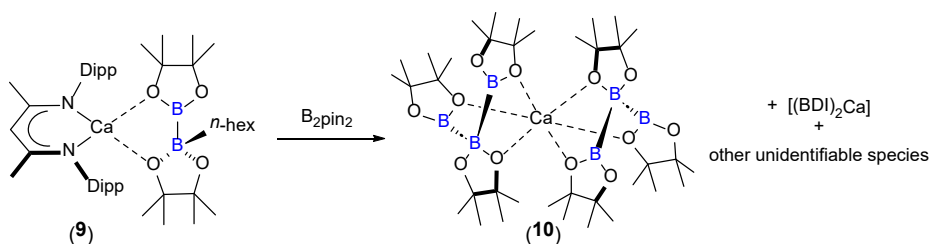


Scheme 1: (a) Synthesis of compounds **7** and **8**; (b) solution dismutation of compound **9**.

In a very recent contribution, we have described our initial attempts to translate the chemistry summarised in Scheme 1 to magnesium's heavier congener, calcium.[35] Although the calcium *n*-hexyl analogue of **6**, compound **9** (Scheme 1b), proved readily accessible, attempts to induce comparable behaviour as a source of boron nucleophile were thwarted by the larger Ca²⁺ radius and the consequent more labile behaviour of the β-diketiminato ligand, whereupon addition of bases such as DMAP induced Schlenk-type dismutation and the generation of [(BDI)₂Ca] as the only identifiable reaction product (Scheme 1b).[36, 37] With these issues in mind, we now report our attempts to extend this chemistry to the synthesis of calcium (and strontium) analogues of the magnesium triborate species **8**, in the anticipation that they might provide more kinetically robust surrogates for heavier alkaline earth boryl nucleophiles.

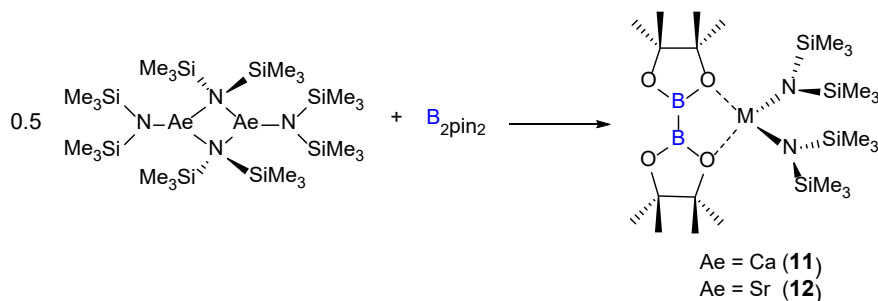
Results and Discussion

An initial equimolar reaction between compound **9** and bis(pinacolato)diboron (B₂pin₂) was monitored by ¹H NMR spectroscopy. Although any attempt to induce reaction by mild heating again evidenced the generation of multiple species including the homoleptic β-diketiminato derivative, [(BDI)₂Ca] (identified by the appearance of a diagnostic BDI γ-methine singlet at δ 4.75 ppm,[36] this reaction also deposited a small number of single crystals of a new calcium species, **10**. Compound **10** was identified by single crystal X-ray diffraction analysis (*vide infra*) as the bis-triborate derivative, [Ca(B₃pin₃)₂] (Scheme 2), which comprises a pair of catenated triborate anions that are effectively identical to the boron-based ligand that was previously identified as a constituent of compound **8**.[20]



Scheme 2: Reaction of **9** and B_2pin_2 leading to the isolation of compound **10**.

While the identification of compound **10** confirms the viability of triborate anion formation, the BDI ligand evidently provides insufficient kinetic stability to allow the isolation of the direct heteroleptic calcium analogue of compound **8**. With this observation in hand we, therefore, sought a more rational route to compound **10** via the similarly homoleptic, and readily available, bis(trimethylsilyl)amide derivatives, $[Ae\{N(SiMe_3)_2\}_2]$ ($Ae = Ca$ or Sr). Equimolar reactions between B_2pin_2 and both $[Ae\{N(SiMe_3)_2\}_2]$ reagents were, thus, monitored by NMR spectroscopy. The stoichiometric formation of two new compounds, **11** ($Ae = Ca$) and **12** (Sr) was identified by 1H NMR spectroscopy through a marginal downfield shift induced in the methyl proton resonances arising from the free diborane and unperturbed bis(trimethylsilyl)amide reagents (Scheme 3 and see Figure S4). Diagnostic 1H and ^{11}B NMR data for the bis(trimethylsilyl)amide starting materials and their respective diborane-adducted products (**11** and **12**) are summarised in Table 1, alongside those of the diborane starting material, (B_2pin_2).



Scheme 3. Syntheses of the alkaline earth complexes **11** and **12**.

Table 1: 1H and ^{11}B NMR data for B_2pin_2 , alkaline earth bis(trimethylsilyl)amides $[Ae\{N(SiMe_3)_2\}_2]$ ($Ae = Ca, Sr$) and compounds **11** and **12** (C_6D_6 , 298 K).

	$C-CH_3 \delta / ppm$	$Si-CH_3 \delta / ppm$	$B \delta / ppm$
B_2pin_2	1.02	-	31.3
$[Ca\{N(SiMe_3)_2\}_2]$	-	0.32	-
11	1.03	0.39	29.9
$[Sr\{N(SiMe_3)_2\}_2]$	-	0.27	-
12	1.05	0.35	31.7

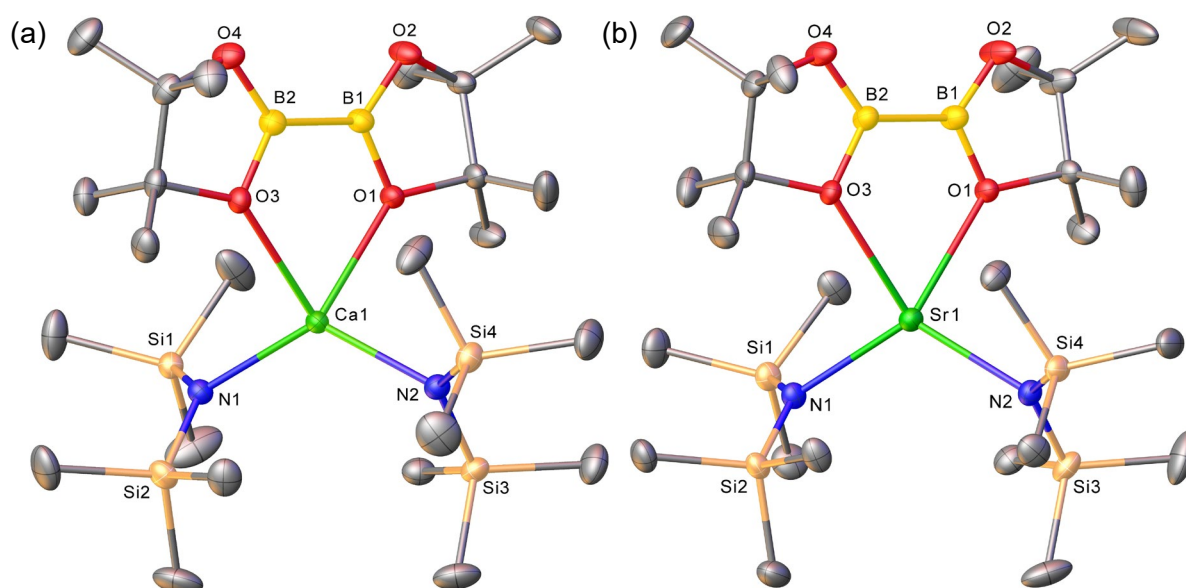


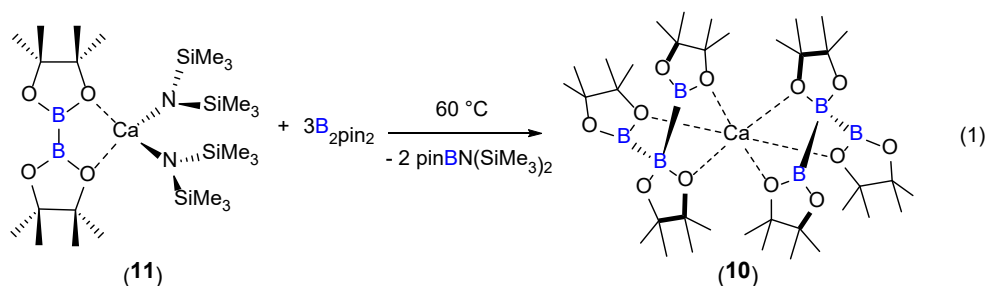
Figure 2: Displacement ellipsoid (30% probability) plots of (a) the Ca1 component of compound **11** and (b) compound **12**. All hydrogen and disordered atoms and co-crystallised solvent molecules have been removed for clarity.

Table 2: Selected bond distances (Å) and bond angles (°) for **11** (Ae = Ca), **12** (Ae = Sr) and the diborane derivative **9** for comparison.

	9	11	12
Ae(1)-N(1)	2.348(5)	2.2937(11)	2.407(3)
Ae(1)-N(2)	2.354(5)	2.2873(12)	2.413(3)
Ae(1)-O(1)	2.228(5)	2.4562(9)	2.592(2)
Ae(1)-O(3)	2.386(5)	2.4764(9)	2.599(2)
B(1)-B(2)	1.754(10)	1.701(2)	1.710(6)
N(1)-Ae(1)-N(2)	82.76(19)	124.62(4)	118.90(10)
N(1)-Ae(1)-O(3)	113.84(18)	98.61(4)	98.12(9)
N(2)-Ae(1)-O(1)	120.17(19)	96.64(4)	98.85(9)
O(1)-Ae(1)-O(3)	88.98(17)	75.26(3)	71.69(7)

The results of the subsequent X-ray diffraction analyses performed on compounds **11** and **12** (Figure 2 and Table 2) revealed both compounds to be four-coordinate bis(trimethylsilyl)amide derivatives in which the group 2 centres are each further ligated by a molecule of B₂pin₂. Distorted tetrahedral geometries in both adducts are enforced by the chelation of two pinacolato oxygen atoms from the diborane about the alkaline earth metal centres. The elongated M-O distances for the heavier congener [Ae(1)-O(1): Ae = Ca, 2.4562(9); Ae = Sr, 2.592(2) Å; Ae(1)-O(3): Ae = Ca, 2.4764(9); Ae = Sr,

2.599(2) Å] are consistent with the expected increase based on the respective Ae^{2+} atomic radii [Ca = 1.00; Sr = 1.18 Å].[38] The encapsulation of the calcium centre in **11** via κ^2-N,N' - and κ^2-O,O' -chelation is reminiscent of the β -diketiminato and bis(pinacolato) coordination observed in the calcium diborane **9** (Table 1). The shorter Ca-N bond distances between the silazide ligands of **11** in comparison to those provided by the β -diketiminato ligand of **9**, [Ca(1)-N(1/2): **11** = 2.2937(11) and 2.2873(12); **9** = 2.348(5) and 2.354(5) Å], however, is as expected for the respective mono- rather than bi-dentate mono-anions. The B(1)-B(2) bond lengths [**11**, 1.701(2); **12**, 1.710(6) Å] are closely comparable to that of free B_2pin_2 [1.704(2) Å],[32] but are significantly shorter than that reported for **9** [1.754(10)] due to the sp^3 -hybridised boron centre present in the $[(n-Hex)B_2pin_2]^-$ diborane anion.[35]



Addition of further equivalents of B_2pin_2 to **11** in d_8 -toluene at room temperature did not initiate any apparent reaction. Heating of the reaction mixture at 60 °C, however, induced the precipitation of colourless single crystals of compound **10** and the appearance of two new singlet signals at δ 1.03 and 0.39 ppm (See, Figure S4) in the resultant 1H NMR spectrum. The appearance of these latter resonances in a 2:3 ratio leads us to assign them to the respective pinacolato and silazido methyl environments of $pinBN(SiMe_3)_2$, which is formed as a by-product of the formation of **10**. [39] Although compound **10** itself displayed sufficient solubility in aromatic solvents to allow its subsequent characterisation by 1H NMR spectroscopy, these data were largely uninformative, presenting a single pinacolato methyl signal at δ 1.02 ppm as the sole observable resonance at all temperatures. Similarly, the corresponding $^{13}C\{^1H\}$ NMR spectrum comprised solely of the resonances attributable to the pinacolato chelate, while its ^{11}B NMR spectrum manifested as a single resonance at δ 31.3 ppm as the only identifiable environment consistent with 3-coordinate boron. Although these observations were not further investigated, the solid-state structure of **10** leads us to suggest that they are a likely consequence of an as yet undefined dynamic process.

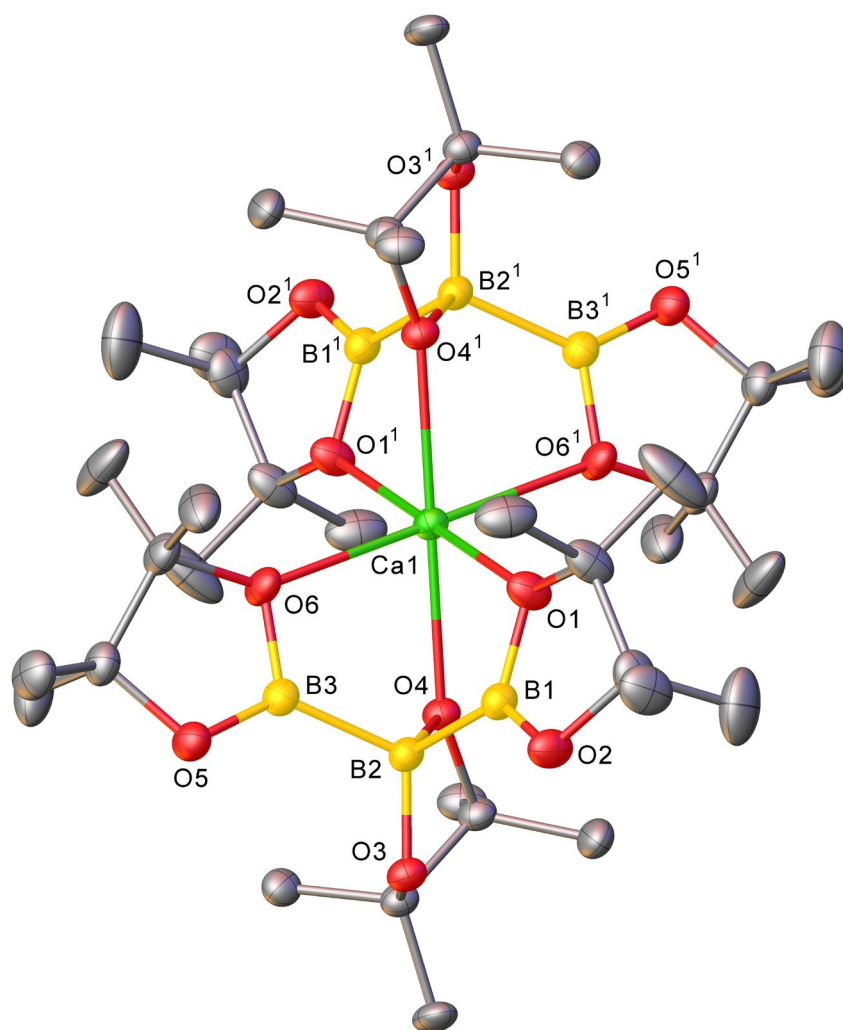


Figure 3: Displacement ellipsoid (30% probability) plot of the Ca1-containing molecule of compound **10**. All hydrogen atoms, disordered atoms and co-crystallised solvent molecules have been removed for clarity. Symmetry operation to generate equivalent atoms: 1-x, 2-y, 1-z.

Single crystal X-ray diffraction analysis allowed the identification of compound **10** as a homoleptic species comprising two effectively identical molecules. Discussion is, thus, limited to the Ca(1)-containing unit. The six-coordinate geometry of each calcium centre in **10** is enforced by two-fold κ^3 -*O*-chelation through three pinacolatoborate oxygen atom, as part of a centrosymmetric calcium bis-triborane complex, $[\text{Ca}(\text{B}_3\text{pin}_3)_2]$ (Figure 3, Table 3). In common with the magnesium derivative, **8**,^[20] the triborane anions of compound **10** bear a superficial similarity to several neutral *catena*-triboranes comprising linear chains propagated by unsupported B-B-B chains and described by Braunschweig and co-workers.^[40] Whereas these latter triborane molecules were prepared *via* hydroboration of B=B double bonds of base-stabilised diborenes, the formation of the homoleptic compound **10** is better rationalised as resulting from the displacement of two neutral molecules of pinBN(SiMe₃)₂ and the formal addition of a $[\text{Bpin}]^-$ anion to a further equivalent bis(pinacolato)diboron

(Eq.1). The elongation of the B(1)-B(2) [1.720(2) Å] and B(2)-B(3) [1.721(2) Å] bonds of **10** in comparison to the B-B bond of **11** [1.701(2) Å] is consistent with the now 4-coordinate geometry of the B(2) centre in the triborate anion and are closely comparable to those observed in the identically formulated anion characterised in the magnesium derivative, compound **8**.^[20] Despite the formal anionic charge borne by this latter unit and the now six-coordinate geometry of the Ca(1) atom, the Ca(1)-O bond distances are only marginally contracted in comparison to those of the 4-coordinate B₂pin₂ adduct [**11**: range 2.4562(9) - 2.4764(9); **10**: range 2.3780(10) - 2.4619(11) Å].

Table 3. Selected bond distances (Å) and bond angles (°) for **10** and **13**.

	10 ^a	13 ^b
Ae(1)-O(1)	2.4619(11)	2.6126(16)
Ae(1)-O(3)	-	2.5343(14)
Ae(1)-O5	-	2.5452(15)
Ae(1)-O(4)	2.3780(10)	2.5069(14) ^c
Ae(1)-O(6)	2.4237(11)	2.6706(16) ^d
Ae(2)-N(1)	-	2.451(2)
Ae(2)-N(2)	-	2.2291(19)
B(1)-B(2)	1.720(2)	1.720(3)
B(2)-B(3)	1.721(2)	1.742(3)
O(1)-Ae(1)-O(4)	78.59(4)	77.69(5) ^e
O(1)-Ae(1)-O(6)	87.83(4)	82.82(5) ^f
O(4)-Ae(1)-O(6)	79.50(4)	73.84(5) ^g
B(1)-B(2)-B(3)	107.84(12)	104.91(16)

^a Ae = Ca; ^b Ae = Sr; ^c Sr(2)-O(4); ^d Sr(2)-O(2); ^e O(1)-Sr(1)-O(3); ^f O(1)-Sr(1)-O(5); ^g O(3)-Ae(1)-O(5).

Similar treatment of the strontium compound **12** with excess B₂pin₂ also required a temperature of 60 °C to stimulate the generation of a new species, **13** (Eq. 2). As was observed in the calcium-derived reaction, the precipitation of X-ray diffraction quality single crystals occurred during the 12 hour period of heating, though redissolution of these crystals in C₆D₆ allowed their analysis by NMR spectroscopy. Although the resultant data were somewhat reminiscent of those provided by compound **10**, the ¹H and ¹³C{¹H} NMR spectra were notable in continuing to display signals attributable to silazide methyl residues (δ_H 0.38; δ_C 5.9 ppm), which in the ¹H spectrum exhibited an identical integral intensity as the pinacolate methyl resonances (δ_H 1.02 ppm).

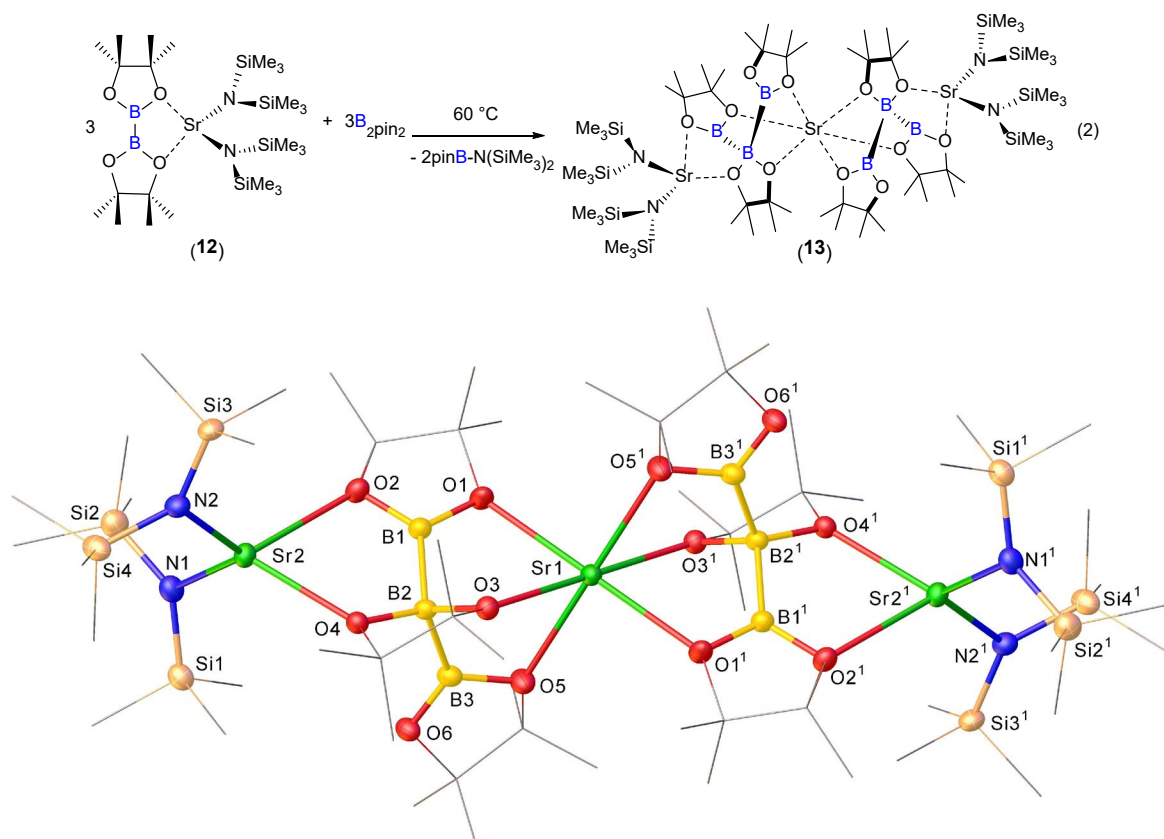


Figure 4: Displacement ellipsoid (30% probability) plot of compound **13**. For purposes of clarity, all hydrogen and disordered atoms have been removed and pinacolate and silazide methyl substituents are shown as wireframe for clarity. Symmetry operation to generate equivalent atoms: $\frac{3}{2}-x$, $\frac{1}{2}-y$, $1-z$.

A further single crystal X-ray diffraction analysis revealed the origin of these observations and allowed the identification of compound **13** as the tris-strontium complex, $[Sr(B_3pin_3)_2(Sr\{N(SiMe_3)_2\}_2)_2]$ (Figure 4, Table 2). As observed in compound **10**, the central alkaline earth metal centre in **13** presents as a homoleptic octahedral derivative in which Sr(1) is bonded to six pinacolate oxygen atoms of two triboranate units [Sr(1)-O(1/3/5), 2.6126(16), 2.5343(14) and 2.5452(15) Å]. In contrast to compound **10**, the strontium derivative has retained two $[Sr\{N(SiMe_3)_2\}_2]$ moieties, in which Sr(2)/Sr(2)ⁱ are κ^2-O, O' bound via two pinacolate oxygen donors, O(4)/O(4)ⁱ and O(2)/O(2)ⁱ, which, respectively comprise the central Bpin and a single peripheral Bpin units of each triboranate anion. Somewhat surprisingly, although the B(1)-B(2) bond of **13** is a component of the 5-membered Sr(2) chelate, its bond length [1.720(3) Å] is identical to that observed in the calcium bis-triboranate derivative, **10**, whereas the B(2)-B(3) bond distance is longer [1.742(3) Å]. This elongation suggests that the structures of such tri-boron anions may be further perturbed toward the *in-situ* $[Bpin]^-$ anion equivalents through the deliberate incorporation of additional Lewis acidic metal centres. We will, thus, continue to examine this supposition and to explore the reactivity of compounds **10**, **13** and related species.

Acknowledgements

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Conflict of interest

The authors declare no conflict of interest.

Appendix A. Supplementary data

Experimental details, NMR spectra and details of X-ray data are presented in the Supporting Information to this paper. CCDC 2271666-2271669 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; or by e-mail deposit@ccdc.cam.ac.uk.

References

- [1] P. D. Pancharatna, S. H. Dar, U. D. Chowdhury, M. M. Balakrishnarajan, *J. Phys. Chem. A*, 126 (2022) 3219-3228.
- [2] E. C. Neeve, S. J. Geier, I. A. I. Mkhalid, S. A. Westcott, T. B. Marder, *Chem. Rev.*, 116 (2016) 9091-9161.
- [3] H. Braunschweig, R. D. Dewhurst, *Angew. Chem. Int. Ed.*, 52 (2013) 3574-3583.
- [4] G. Linti, D. Loderer, H. Noth, K. Polborn, W. Rattay, *Chem. Ber.*, 127 (1994) 1909-1922.
- [5] J.C. Jeffery, N.C. Norman, J.A.J. Pardoe, P.L. Timms, *Chem. Commun.*, (2000) 2367-2368.
- [6] Y. Hayashi, Y. Segawa, M. Yamashita, K. Nozaki, *Chem. Commun.*, 47 (2011) 5888-5890.
- [7] L. Dang, Z. Y. Lin, T. B. Marder, *Chem. Commun.*, (2009) 3987-3995.
- [8] J. F. Hartwig, K. S. Cook, M. Hapke, C. D. Incarvito, Y. B. Fan, C. E. Webster, M. B. Hall, *J. Am. Chem. Soc.*, 127 (2005) 2538-2552.
- [9] I. A. I. Mkhalid, J. H. Barnard, T. B. Marder, J. M. Murphy, J. F. Hartwig, *Chem. Rev.*, 110 (2010) 890-931.
- [10] Y. Segawa, M. Yamashita, K. Nozaki, *Science*, 314 (2006) 113-115.
- [11] Y. Segawa, Y. Suzuki, M. Yamashita, K. Nozaki, *J. Am. Chem. Soc.*, 130 (2008) 16069-16079.
- [12] M. Yamashita, Y. Suzuki, Y. Segawa, K. Nozaki, *Chem. Lett.*, 37 (2008) 802-803.
- [13] S. Robinson, J. McMaster, W. Lewis, A. J. Blake, S. T. Liddle, *Chem. Commun.*, 48 (2012) 5769-5771.
- [14] W. Lu, H. T. Hu, Y. X. Li, R. Ganguly, R. Kinjo, *J. Am. Chem. Soc.*, 138 (2016) 6650-6661.

- [15] T. Ohsato, Y. Okuno, S. Ishida, T. Iwamoto, K.-H. Lee, Z. Lin, M. Yamashita, K. Nozaki, *Angew. Chem. Int. Ed.*, 55 (2016) 5.
- [16] M. Yamashita, Y. Suzuki, Y. Segawa, K. Nozaki, *J. Am. Chem. Soc.*, 129 (2007) 9570-9571.
- [17] T. Arnold, H. Braunschweig, W. C. Ewing, T. Kramer, J. Mies, J. K. Schuster, *Chem. Commun.*, 51 (2015) 737-740.
- [18] J. K. Schuster, D. K. Roy, C. Lenczyk, J. Mies, H. Braunschweig, *Inorg. Chem.*, 58 (2019) 2652-2658.
- [19] A. V. Protchenko, P. Vasko, M. A. Fuentes, J. Hicks, D. Vidovic, S. Aldridge, *Angew. Chem. Int. Ed.*, 60 (2021) 2064-2068.
- [20] A. F. Pécharman, A. L. Colebatch, M. S. Hill, C. L. McMullin, M. F. Mahon, C. Weetman, *Nature Commun.*, 8 (2017), 15022.
- [21] A.-F. Pécharman, M. S. Hill, G. McMullon, C. L. McMullin, M. F. Mahon, *Chem. Sci.*, 10 (2019) 6672-6682.
- [22] A.-F. Pécharman, M. S. Hill, M. F. Mahon, *Dalton Trans.*, 47 (2018) 7300-7305.
- [23] A.-F. Pécharman, M. S. Hill, C. L. McMullin, M. F. Mahon, *Organometallics*, 37 (2018) 4457-4464.
- [24] M. Gao, S. B. Thorpe, W. L. Santos, *Org. Lett.*, 11 (2009) 3478-3481.
- [25] S. B. Thorpe, X. Guo, W. L. Santos, *Chem. Commun.*, 47 (2011) 424-426.
- [26] M. Gao, S. B. Thorpe, C. Kleeberg, C. Sledobnick, T. B. Marder, W. L. Santos, *J. Org. Chem.*, 76 (2011) 3997-4007.
- [27] A. Bonet, C. Pubill-Ulldemolins, C. Bo, H. Gulyas, E. Fernández, *Angew. Chem. Int. Ed.*, 50 (2011) 7158-7161.
- [28] H. Gulyas, A. Bonet, C. Pubill-Ulldemolins, C. Sole, J. Cid, E. Fernández, *Pure Appl. Chem.*, 84 (2012) 2219-2231.
- [29] J. Cid, H. Gulyas, J. J. Carbó, E. Fernández, *Chem. Soc. Rev.*, 41 (2012) 3558-3570.
- [30] R. D. Dewhurst, E. C. Neeve, H. Braunschweig, T. B. Marder, *Chem. Commun.*, 51 (2015) 9594-9607.
- [31] S. Pietsch, E. C. Neeve, D. C. Apperley, R. Bertermann, F. Y. Mo, D. Qiu, M. S. Cheung, L. Dang, J. B. Wang, U. Radius, Z. Y. Lin, C. Kleeberg, T. B. Marder, *Chem. Eur. J.*, 21 (2015) 7082-7098.
- [32] H. Shere, M. S. Hill, A.-F. Pécharman, M. F. Mahon, *Dalton Trans.*, 50 (2021) 1283-1292.
- [33] A.-F. Pécharman, M. S. Hill, C. L. McMullin, M. F. Mahon, *Angew. Chem. Int. Ed.*, 56 (2017) 16363-16366.
- [34] A.-F. Pécharman, M. S. Hill, M. F. Mahon, *Angew. Chem. Int. Ed.*, 57, (2018) 10688-10691.
- [35] H. T. W. Shere, M. S. Hill, S. E. Neale, M. F. Mahon, C. L. McMullin, A. S. S. Wilson, *Z. Anorg. Allg. Chem.*, 649 (2023) e202200376.
- [36] S. Harder, *Organometallics*, 21 (2002) 3782-3787.

- [37] A. G. Avent, M. R. Crimmin, M. S. Hill, P. B. Hitchcock, *Dalton Trans.*, (2005) 278-284.
- [38] R. D. Shannon, *Acta Cryst. Sect. A*, 32 (1976) 751-767.
- [39] While pinBN(SiMe₃)₂ has been characterized previously by NMR spectroscopy, none of these reports have utilized *d*₈-toluene as the solvent. Although the identity of the aminoborane by-product was not further corroborated, the similarity of the current spectra to those previously reported in C₆D₆ (see, for example, the recently described data in J. Bykowski, J. Sinclair, J. Trach, M. J. Ferguson, E. Rivard, *Dalton Trans.*, 52 (2023)1602–1607), alongside the constitution of compound **10**, instil a high level of confidence in the likely veracity of this assignment.
- [40] H. Braunschweig, R. D. Dewhurst, C. Horl, A. K. Phukan, F. Pinzner, S. Ullrich, *Angew. Chem. Int. Ed.*, 53 (2014) 3241-3244.