The Lewis acidity of borylcarboranes

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The Lewis Acidity of Borylcarboranes

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In celebration of the 120th birthday anniversary of A.N. Nesmeyanov and dedicated to the memory of Professor I.T. Chizhevsky (1952-2016).

Abstract

The dimesitylborylcarborane [1-$BMes_2$-2-Me-*closo*-1,2-$C_2B_{10}H_{10}$] (**1**) has been prepared. The Lewis acidity of **1** has been assessed by the Gutmann-Beckett method and found to be effectively identical to that of the previously reported 2-H and 2-Ph analogues. Similarly, the new catecholylborylcarboranes [1-Bcat-*closo*-1,2-$C_2B_{10}H_{11}$] (**2**) and [1-Bcat-2-Me-*closo*-1,2-$C_2B_{10}H_{10}$] (**3**), although more strongly Lewis acidic than the dimesitylborylcarboranes, were found to have Acceptor Numbers very close to that of the known 2-Ph analogue. [μ-2,2′-BPh-(1-1′-*closo*-1′,2′-$C_2B_{10}H_{10}$)-*closo*-1,2-$C_2B_{10}H_{10}$] (**4**), a compound with a boryl fragment attached to two carboranyl units [in the form of bis(*ortho*-carborane)] has been prepared and found to be highly Lewis acidic, reflecting the strongly electron-withdrawing property of *C*-bound carboranyl groups. The first example of a compound in which both Lewis acidic and Lewis basic substituents are appended to a single carborane cage, [1-Bcat-7-PPh_2-*closo*-1,7-$C_2B_{10}H_{10}$] (**5**), is reported. In **5** the Acceptor Number of the Bcat substituent is very close to those of **2** and **3** and the basicity of the PPh_2 substituent, assessed by measurement of the $^1J_{PSe}$ NMR coupling constant of the related selenide [1-Bcat-7-P(Se)Ph_2-*closo*-1,7-$C_2B_{10}H_{10}$] (**5Se**), is very close to that of [1-PPh_2-*closo*-1,7-$C_2B_{10}H_{11}$], suggesting that the properties of both substituents in **5** are effectively unaffected by the presence of the other.

Keywords

Lewis acid; Borylcarborane; Acceptor Number; Synthesis; NMR spectroscopy; Crystal structure

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1. Introduction

Boron science is an exceedingly active field of research with a unique and diverse array of real and potential applications.[1] We are interested in using carboranyl cages as scaffolds for Lewis acid and/or Lewis base units because the tremendous variability inherent in these clusters means that, at least in principle, it should be possible to tune the acidity or basicity of the appended unit for particular applications, for example as components of Frustrated Lewis Pairs (FLPs). Carboranes are known with between 5 and 14 vertices, can have between 1 and 6 carbon atoms, can be neutral or anionic and can be functionalised with a wide variety of substituents with varying steric and/or electronic properties at both carbon and boron vertices.[2] Thus the potential range of carboranyl scaffolds is vast and it is instructive to attempt systematically to understand how each of these variables affects the properties of an appended acid or base function.

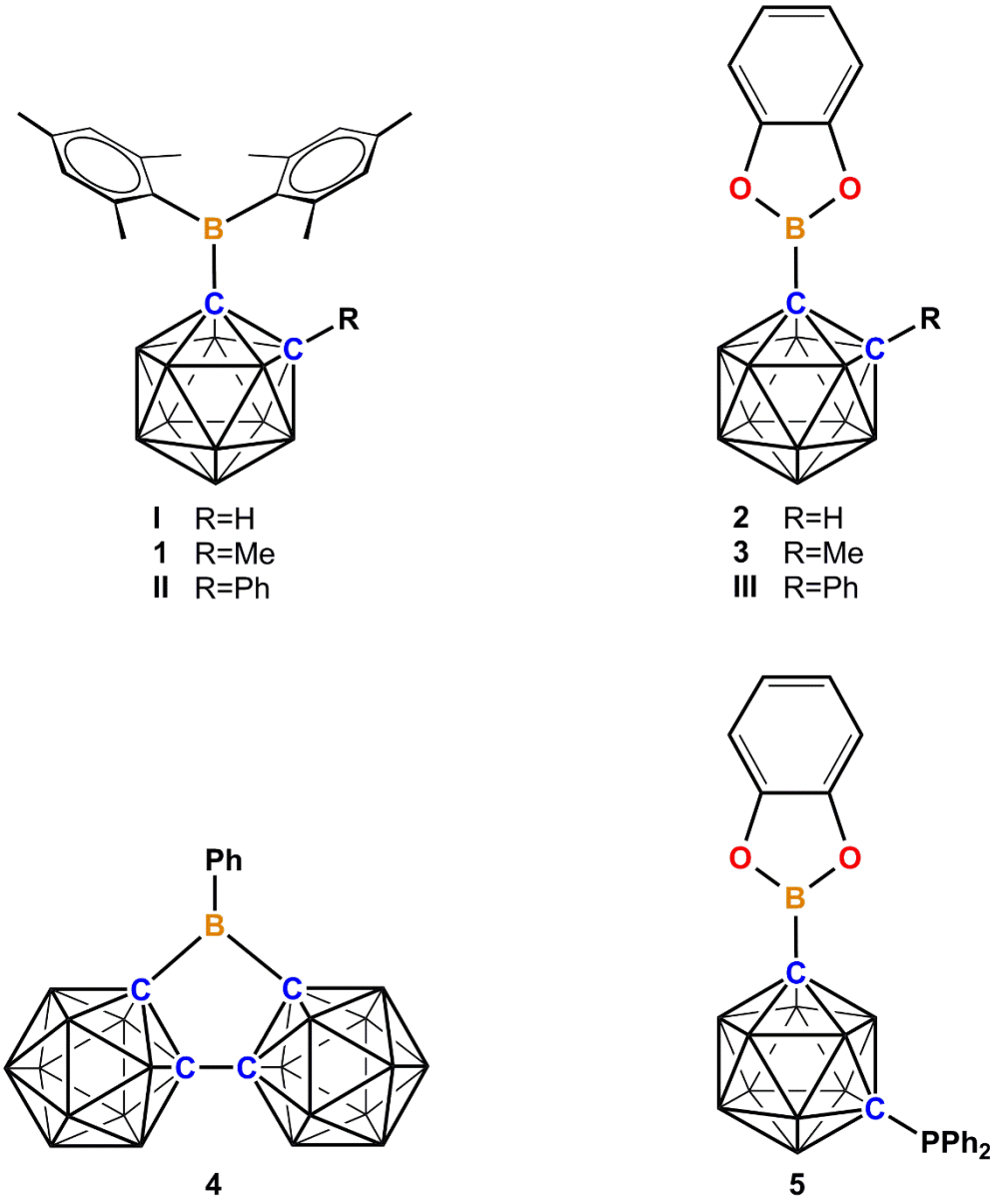
We recently reported a study of the various factors affecting the basicity of carboranylphosphines, rank-ordering the basicities both by DFT calculation of proton affinities and by measurement of the $^{1}J_{PSe}$ NMR coupling constant of the carboranylphosphine selenide.[3b] An important (and somewhat surprising) conclusion of this study was that, for a given carborane isomer, the basicity of a {PPh_2} fragment appended to one cage C atom was essentially insensitive to the nature of the substituent on the other cage C atom.

In the present work we explore the effects of variation of the second substituent on the Lewis acidity of dimesitylborylcarboranes and catecholylborylcarboranes, assessing Lewis acidity in terms of the Acceptor Number (AN) derived from $^{31}P\{^{1}H\}$ NMR spectroscopy using the modified Gutmann-Beckett method.[4,5] We also describe a strongly Lewis acidic borylcarborane derived from 1,1'-bis(*ortho*-carborane) and the first example of an intramolecular FLP with a carborane scaffold.

2. Results and Discussion

Line diagrams of all the compounds discussed in this work are provided in Scheme 1. The compounds [1-$BMes_2$-*closo*-1,2-$C_2B_{10}H_{11}$] (**I**) and [1-$BMes_2$-2-Ph-*closo*-1,2-$C_2B_{10}H_{10}$] (**II**) have been described by Weber, Fox and co-workers,[6l] and are two examples of the relatively small number of compounds in which a trigonal B atom is directly bonded to a carborane cage without an additional link between substituent and cage.[6] Our first objective was the preparation of the 2-Me analogue, achieved following a similar route to that used for **I** and **II**. The compound [1-$BMes_2$-2-Me-*closo*-1,2-$C_2B_{10}H_{10}$] (**1**) was isolated in good yield and initially characterised by elemental analysis and mass spectrometry. In the ^{1}H NMR spectrum the four *ortho*-Me groups of the $BMes_2$ unit are equivalent as are the four aromatic H atoms, implying free rotation about the B–C_{Mes} bonds and at least significant libration about the B–C_{cage} bond in solution at room temperature. The $^{11}B\{^{1}H\}$ NMR spectrum is consistent with a molecule with time-averaged C_s symmetry assuming that the resonance at δ -8.2 is a 2+2+1 coincidence.

A crystallographic study of compound **1** revealed the structure shown in Fig. 1, which includes important molecular parameters. The length of the C1–C2 connectivity, 1.715(3) Å, is intermediate between that in **I** [1.677(3) Å] and **II** [1.762(2) Å] but the C1–B1, B1–C101 and B1–C110 bond lengths are in good agreement with those in the analogous species. As was the case in both **I** and **II** the C101–B1–C110 angle, 124.2(2)°, in **1** is the widest of those at the trigonal B atom. The trigonal plane at B1 is twisted with respect to C2 with a C110–B1–C1–C2 torsion angle of 30.2(3)°.



Scheme 1. The borylcarboranes considered in this contribution. Compounds in Roman numerals are literature species whilst those in Arabic numerals are reported for the first time.

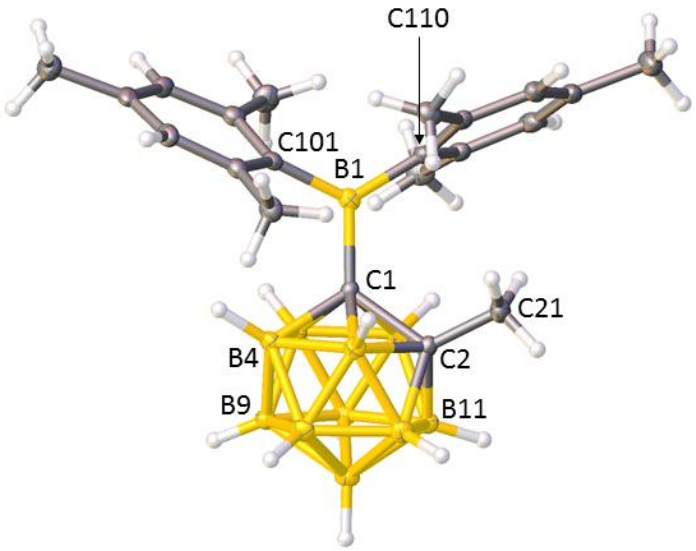


Fig. 1. Perspective view of [1-$BMes_2$-2-Me-*closo*-1,2-$C_2B_{10}H_{10}$] (**1**). Displacement ellipsoids are drawn at the 50% probability level except for H atoms. Selected molecular parameters (Å; °): C1−C2 1.715(3), C1−B1 1.637(4), C2−C21 1.510(4), B1−C101 1.584(4), B1−C110 1.589(4), C1−B1−C101 116.9(2), C1−B1−C110 118.9(2), C101−B1−C110 124.2(2).

Compounds **I**, **1** and **II** constitute a series of analogues in which the substituent at the C2 vertex of the carborane cage is varied from H to Me to Ph, respectively, and we are interested to discover how the formally electron-donating and electron-withdrawing Me and Ph substituents affect the Lewis acidity of the $BMes_2$ unit at the C1 vertex. To assess this we have used the Gutmann-Beckett method [4] in which 1 equivalent of Et_3PO is added to 3 equivalents of the Lewis acid [5] and the Acceptor Number (AN) of the resulting adduct determined from its $^{31}P\{^1H\}$ NMR chemical shift. Full details are provided in the Experimental section.

Table 1 Acceptor numbers for borylcarboranes and related species.

Compound	Acceptor Number
I	28.4
1	27.7
II	27.9
$FBMes_2$	10.0
2	82.6
3	81.1
III	80.6
4	86.4
5	79.0
5Se	-
$B(C_6F_5)_3$	76.1

The results are presented in Table 1 and to provide a reference for Lewis acidity we also determined the AN of $FBMes_2$. In comparison with this (AN = 10.0) the borylcarboranes **I**, **1** and **II** are all relatively Lewis acidic, consistent with the finding of Weber, Fox and co-workers that in these compounds the

carborane cage is electron withdrawing, and the Mes groups electron-donating, to the boron centre [6l] (in $FBMes_2$ the Lewis acidity will be compromised by F → B π bonding). However, for the series **I**, **1** and **II** the value of AN, 28±0.4, hardly varies, suggesting that changing the substituent at the second cage C atom has little or no effect on the Lewis acidity of the group bound to C1. We very recently reported equivalent findings with regards to the Lewis basicity of a PPh_2 at C1 in a series of carboranylphosphines with H, Me and Ph substituents at C2.[3b]

Seeking a second series of borylcarboranes with which to test these conclusions we turned to catecholylborylcarboranes. The compound [1-Bcat-2-Ph-*closo*-1,2-$C_2B_{10}H_{10}$] (**III**) was recently reported [6n] and so to complement this we have synthesised and characterised the 2-H and 2-Me analogues [1-Bcat-*closo*-1,2-$C_2B_{10}H_{11}$] and [1-Bcat-2-Me-*closo*-1,2-$C_2B_{10}H_{10}$].

The compound [1-Bcat-*closo*-1,2-$C_2B_{10}H_{11}$] (**2**) was prepared in 49% isolated yield from the reaction between BcatBr and lithiated *ortho*-carborane, and characterised by microanalysis, mass spectrometry, and ^1H and $^{11}B\{^1H\}$ NMR spectroscopies, the latter implying a molecule with C_s symmetry in solution at room temperature on the NMR timescale. Compound **2** was also studied crystallographically, and Fig. 2 provides a perspective view of a single molecule.

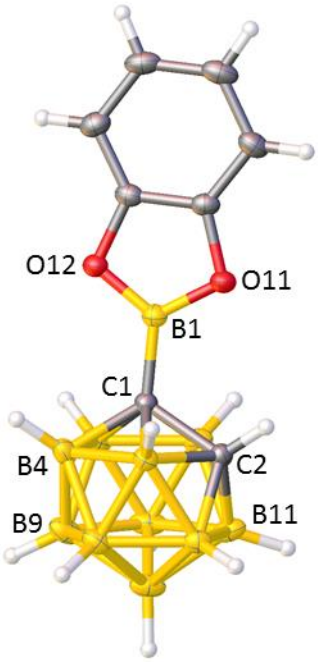


Fig. 2. Perspective view of [1-Bcat-*closo*-1,2-$C_2B_{10}H_{11}$] (**2**). Displacement ellipsoids as in Fig. 1. Selected molecular parameters (Å; °): C1−C2 1.6405(15), C1−B1 1.5632(17), B1−O11 1.3764(16), B1−O12 1.3716(16), C1−B1−O11 122.72(11), C1−B1−O12 123.47(11), O11−B1−O12 113.80(10).

Similarly, the methyl-substituted compound [1-Bcat-2-Me-*closo*-1,2-$C_2B_{10}H_{10}$] (**3**) was prepared in good yield starting from [1-Me-*closo*-1,2-$C_2B_{10}H_{11}$]. Characterisation by mass spectrometry and ^1H and $^{11}B\{^1H\}$ NMR spectroscopies was complemented by a crystallographic study (Fig. 3) which revealed two crystallographically-independent molecules in the asymmetric fraction of the unit cell.

The C1−B_{cat} and B−O distances in **2** and **3** are very similar to those in **III**, and in all three Bcat species the internal angle at the trigonal B atom, O11−B1−O12, is the narrowest. The length of the C1−C2

connectivity in the carborane cage reflects the steric bulk of the substituent on C2, changing from 1.6405(15) Å for H to 1.6692(19)/1.666(2) Å for Me to 1.6840(15) Å for Ph. Similarly, even though the twist of the Bcat substituent with respect to C2 is quite different for the two crystallographically-independent molecules of **3**, it also increases along this series, with acute O−B−C1−C2 torsion angles of 7.67(13)° in **2**, 28.9(2) and 57.6(2)° for the unprimed and primed molecules, respectively, in **3**, and 74.57(16)° in **III**.

The AN values for the catecholylborylcarboranes (Table 1) are substantially higher than those for the dimesitylborylcarboranes, as would be anticipated for the change from $BMes_2$ to Bcat, but again we see little or no variation in AN as we change the substituent on C2 from H to Me to Ph, confirming the insensitivity of the AN to substitution at the second cage carbon atom.

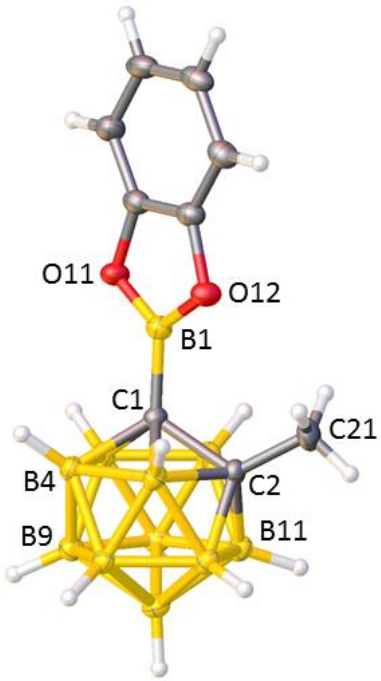


Fig. 3. Perspective view of one of the two crystallographically-independent molecules of [1-Bcat-2-Me-*closo*-1,2-$C_2B_{10}H_{10}$] (**3**). Displacement ellipsoids as in Fig. 1. Selected molecular parameters (Å; °): unprimed molecule; C1−C2 1.6692(19), C1−B1 1.565(2), C2−C21 1.516(2), B1−O11 1.3803(19), B1−O12 1.371(2), C1−B1−O11 123.38(13), C1−B1−O12 123.58(14), O11−B1−O12 113.04(14): primed molecule; C1−C2 1.666(2), C1−B1 1.568(2), C2−C21 1.518(2), B1−O11 1.3753(19), B1−O12 1.3784(19), C1−B1−O11 123.40(13), C1−B1−O12 123.35(13), O11−B1−O12 113.25(13).

Thus these studies on borylcarboranes support the conclusions of our earlier report on carboranylphosphines;[3b] changing the substituent on C2 in an *ortho*-carborane cluster does not influence the Lewis acidity (borylcarboranes) or Lewis basicity (carboranylphosphines) of a substituent on C1.

In the context of Lewis acidity it is well established that a functional group attached to the carbon atom of a carborane scaffold experiences a strong electron-withdrawing effect.[7] We have previously shown that in carboranylphosphines of the type [μ-2,2′-PR-(1-1′-*closo*-1′,2′-$C_2B_{10}H_{10}$)-*closo*-1,2-$C_2B_{10}H_{10}$] (in which the P atom is directly bonded to the C atoms of *two* carborane cages) this results

in compounds which are amongst the weakest carboranylphosphine Lewis bases known.[8] Thus it was of interest to explore the Lewis acidity of a {BR} fragment similarly attached to a bis(*ortho*-carborane) unit.

The double deprotonation of 1,1′-bis(*ortho*-carborane), formally [1-(1′-*closo*-1′,2′-$C_2B_{10}H_{11}$)-*closo*-1,2-$C_2B_{10}H_{11}$], followed by reaction with $BPhCl_2$ affords, following workup, a reasonable yield of a yellow solid subsequently identified as [μ-2,2′-BPh-(1-1′-*closo*-1′,2′-$C_2B_{10}H_{10}$)-*closo*-1,2-$C_2B_{10}H_{10}$] (**4**) (see Scheme 1 for a line diagram) by a combination of mass spectrometry and ^1H and $^{11}B\{^1H\}$ NMR spectroscopies. The strong Lewis acidity of the trigonal boron centre was implied by the relatively high-frequency ^1H NMR chemical shifts of the phenyl protons (δ 6.89-8.29) and confirmed by a Gutmann-Beckett analysis yielding an AN of 86.4 (Table 1), greater than that of the catecholylborylcarboranes. Thus, overall, the combination of bis(*ortho*-carboranyl) and phenyl (compound **4**) is more electron-withdrawing than the combination of carboranyl and catecholyl (compound **2**, **3** and **III**).

As noted in the Introduction, one of the reasons for our interest in carboranes with Lewis acid or Lewis base substituents is their possible use in the burgeoning field of FLP chemistry.[9] Thus we recently demonstrated that compound **III** acted as the Lewis acid component of an intermolecular FLP in catalysing a Michael addition reaction, whilst the carboranylphosphine [1-PPh_2-*closo*-1,2-$C_2B_{10}H_{11}$] acted as the Lewis base component of an intermolecular FLP in catalysing hydrosilylation.[6n] It was therefore of considerable interest to establish if we could combine both Lewis acidic and Lewis basic substituents on a single carborane scaffold, potentially producing an intramolecular FLP.

The logical route to such species is to install the Lewis base function first and the more reactive Lewis acid function second, and we have chosen to work with the *meta*-carborane scaffold, [1,7-*closo*-$C_2B_{10}H_{12}$], substituting the acid and base groups on the non-adjacent carbon atoms to avoid possible steric congestion. However, starting from the known compound [1-PPh_2-1,7-*closo*-$C_2B_{10}H_{11}$] all attempts to deprotonate (a necessary precursor to installing the Lewis acid group) using *n*-BuLi led to cleavage of the P−C1 bond as evidenced by $^{31}P\{^1H\}$ NMR spectroscopy, even if a BH_3 "cap" was used to protect the P lone pair (see Supplementary Material for details of the synthesis and characterisation of [1-P(BH_3)Ph_2-1,7-*closo*-$C_2B_{10}H_{11}$]).

Use of the non-nucleophilic base Li[TMP], however, proved to be successful. Deprotonation of [1-PPh_2-1,7-*closo*-$C_2B_{10}H_{11}$] with Li[TMP] followed by reaction with BcatBr afforded the compound [1-Bcat-7-PPh_2-*closo*-1,7-$C_2B_{10}H_{10}$] (**5**) in 40% isolated yield after workup. This product, the first example of an intramolecular FLP on a carborane scaffold, was characterised by mass spectrometry, ^1H, $^{11}B\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectroscopies and by *X*-ray diffraction.

A single molecule of **5** is shown in Fig. 4, which also includes important molecular parameters. Dimensions within the {C1Bcat} fragment are fully comparable with those in **2**, **3** and **III**.[6n] Similarly, the C_{cage}–P distance in **5**, 1.8822(11) Å, bears excellent comparison with those in [1-PPh_2-1,7-*closo*-$C_2B_{10}H_{11}$], 1.8770(13) Å,[3b] and [1,7-$(PPh_2)_2$-1,7-*closo*-$C_2B_{10}H_{10}$], 1.889(3) and 1.882(3) Å.[10]

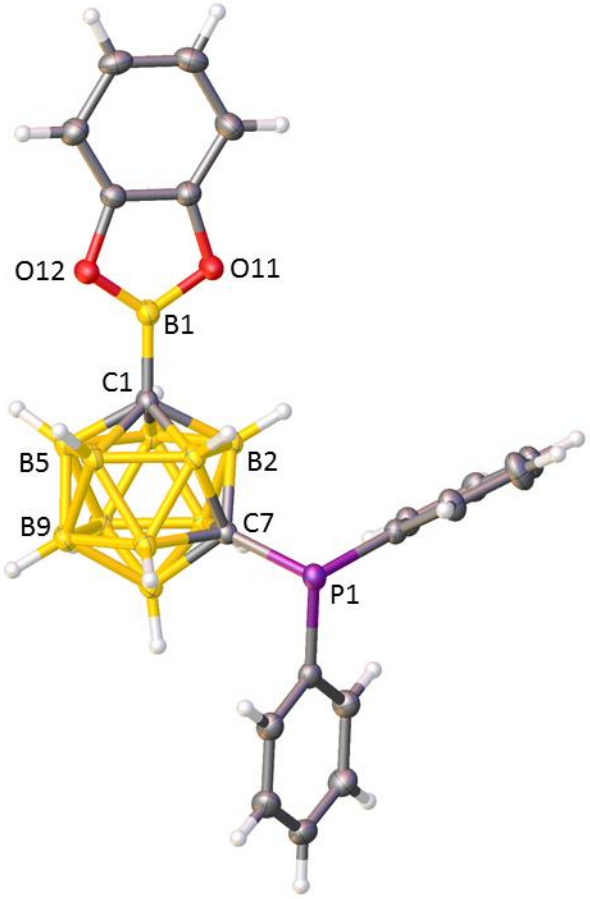


Fig. 4. Perspective view of [1-Bcat-7-PPh_2-*closo*-1,7-$C_2B_{10}H_{10}$] (**5**). Displacement ellipsoids as in Fig. 1. Selected molecular parameters (Å; °): C1−B1 1.5594(16), C7−P1 1.8822(11), B1−O11 1.3743(15), B1−O12 1.3739(14), C1−B1−O11 123.10(10), C1−B1−O12 123.91(10), O11−B1−O12 112.98(10).

Spectroscopically, compound **5** also appears to closely resemble its constituent parts. In the $^{31}P\{^1H\}$ NMR spectrum of **5** in C_6D_6 the P atom resonates at δ 20.3 ppm, whilst in [1-PPh_2-1,7-*closo*-$C_2B_{10}H_{11}$] in $CDCl_3$ the signal is at δ 19.3,[3a] and although [1-Bcat-1,7-*closo*-$C_2B_{10}H_{11}$] is currently unknown the closely related species **2** has the resonance for the trigonal B atom in the ^{11}B NMR spectrum at δ 29.4 ppm, whilst for **5** it is barely different, δ 30.3 ppm. This suggests minimal influence of the Lewis acid and Lewis base functions on each other. This finding is reinforced by determination of the AN for **5**, 79.0, close to the values in **2**, **3** and **III**, and by measurement of the $^1J_{PSe}$ coupling constant for **5Se**, the selenide derivative of **5**, of 817 Hz, close to that (797 Hz) in [1-P(Se)Ph_2-1,7-*closo*-$C_2B_{10}H_{11}$].[3b] Note that compound **5Se** was prepared on a 0.01 mmol scale in a J. Young NMR tube and although it was characterised by multinuclear NMR spectroscopy no attempt at isolation was made.

These results demonstrate that both Lewis acid and Lewis base functions can be installed on a single carborane cage without loss of activity and suggest that intramolecular FLPs supported by carborane scaffolds could be useful future compounds for catalysis. Note that based on Acceptor Numbers (Table 1) the borylcarboranes **2**, **3**, **4**, **5** and **III** are all somewhat more Lewis acidic than $B(C_6F_5)_3$, the archetypal Lewis acid used in FLP chemistry.

In conclusion, we have demonstrated that the Lewis acidity of a dimesitylboryl or catecholylboryl group appended to C1 of an *ortho*-carborane scaffold is unaffected by changes to the substituent (H, Me, Ph) at C2. These results are fully consistent with those described in our recent study of the Lewis basicity of carboranylphosphines, in which the basicity of a PPh_2 unit bound to a C1 was similarly insensitive to the nature of the substituent at C2.[3b] We have further shown that, in the first example of a compound in which both Lewis acidic and Lewis basic units are bonded to a single carborane cage, these units have acidities and basicities, respectively, that appear to be unaffected by the presence of the other group. Research which capitalises on the consequences of these conclusions is ongoing in our laboratory.

3. Experimental

3.1. Synthesis

Experiments were performed under dry, oxygen-free, N_2 using standard Schlenk techniques, although subsequent manipulations were performed in the open laboratory in the case of compound **1**. 40-60 Petroleum ether (petrol) was freshly distilled under nitrogen from sodium wire and degassed (3×freeze-pump-thaw cycles) before use. Toluene and fluorobenzene were stored over 4 Å molecular sieves and degassed before use. Deuterated solvents for NMR spectroscopy ($CDCl_3$ and C_6D_6) were stored over 4 Å molecular sieves and C_6D_6 was additionally distilled under nitrogen from molten potassium prior to use. Elemental analyses were conducted using an Exeter CE-440 elemental analyser. NMR spectra at 400.1 MHz (^{1}H), 162.0 MHz (^{31}P) and 128.4 MHz (^{11}B) were recorded on a Bruker AVIII-400 spectrometer from appropriate deuterated solutions at 298 K. Electron ionisation mass spectrometry (EIMS) was carried out using a Thermo MAT900XP-Trap mass spectrometer at the University of Edinburgh. Compounds **I**,[6l] **II** [6l] and **III** [6n] were re-synthesised according to the literature. The starting materials [1-Me-*closo*-1,2-$C_2B_{10}H_{11}$],[11] 1,1'-bis(*ortho*-carborane),[12] [1-PPh_2-*closo*-1,7-$C_2B_{10}H_{11}$] [3] and Li[TMP] [13] were prepared according to, or using local adaptions of, literature procedures. All other reagents were purchased from commercial sources (Fluorochem, Sigma Aldrich, Across Organics, Katchem) and used without further purification.

*3.1.1. [1-$BMes_2$-2-Me-closo-1,2-$C_2B_{10}H_{10}$] (**1**)*

A toluene solution (15 mL) of [1-Me-*closo*-1,2-$C_2B_{10}H_{11}$] (150 mg, 0.95 mmol) was cooled to 0 °C before *n*-BuLi (0.76 mL of a 1.39 M solution in hexanes, 1.04 mmol) was added dropwise. The solution was warmed to room temperature and stirred for 1 h. A toluene solution (5 mL) of $FBMes_2$ (280 mg, 1.04 mmol) was added dropwise to the stirring solution which was then heated to reflux overnight during which time the white suspension gave way to a pale yellow solution. The product mixture was washed with water (2×5 mL) and saturated sodium chloride solution (10 mL) and the combined organic phases dried over sodium sulfate. Solvent was removed and the residue washed with petrol and dried to afford the product as a white solid (308 mg, 80%). $C_{21}H_{35}B_{11}$ requires C: 62.1, H: 8.68; found: C: 62.0, H: 8.61%. ^{1}H NMR ($CDCl_3$): δ 6.79 (s, 4H, Mes), 2.47 (s, 12H, Mes), 2.24 (s, 6H, Mes), 1.46 (s, 3H, C*H*$_3$). ^{11}B{^{1}H} NMR (C_6D_6): δ 81.4 (1B, *B*Mes_2), 3.2 (1B), -4.9 (2B), -8.2 (5B), -9.7 (2B). EIMS: envelope centred on *m/z* 406.4 (M^+). Crystals suitable for SCXRD were grown from slow evaporation of a concentrated fluorobenzene solution.

*3.1.2. [1-Bcat-closo-1,2-$C_2B_{10}H_{11}$] (**2**)*

A toluene solution (25 mL) of [*closo*-1,2-$C_2B_{10}H_{12}$] (0.36 g, 2.5 mmol) was cooled to 0 °C before *n*-BuLi (1.79 mL of a 1.54 M solution, 2.75 mmol) was added dropwise. The solution was allowed to warm to room temperature and stirred for 16 h causing a white suspension to form. The solution was frozen at -196 °C and BcatBr (0.547 g, 2.75 mmol) was added in one portion to the frozen mixture. The reagents were allowed to warm to room temperature and stir for 15 mins before being heated to reflux for 16 h. The suspension was cooled to room temperature and the toluene-soluble materials were transferred *via* cannula and evaporated to dryness. The toluene-insoluble materials were washed with petrol (2×20 mL) and the solution combined with the toluene-soluble materials and evaporated to a colourless residue. This was then extracted with petrol (3×10 mL) and the solution transferred *via* cannula and evaporated to a white solid. The product was then sublimed under vacuum, washed from the cold finger with petrol and evaporated to dryness to yield a white solid (490 mg, 49%). $C_8H_{15}B_{11}O_2$ requires C: 36.6, H: 5.77; found: C: 36.3, H: 6.00%. ^{1}H NMR (C_6D_6): δ 6.80-6.77 (m, 2H, C_6H_4), 6.72-6.69 (m, 2H, C_6H_4), 2.93 (br. s, 1H, CH_{cage}). $^{11}B\{^1H\}$ NMR (C_6D_6): δ 29.4 (1B, *B*cat), 0.8 (1B), -1.0 (1B), -7.0 (2B), -11.3 (2B), -12.3 (4B). EIMS: envelope centred on *m/z* 262.2 (M^+). Crystals suitable for SCXRD were grown from the slow evaporation of a concentrated petrol solution.

*3.1.3. [1-Bcat-2-Me-closo-1,2-$C_2B_{10}H_{10}$] (**3**)*

A toluene solution (50 mL) of [1-Me-*closo*-1,2-$C_2B_{10}H_{11}$] (0.80 g, 5.06 mmol) was cooled to 0 °C before *n*-BuLi (3.89 mL of a 1.54 M solution, 5.99 mmol) was added dropwise. The solution was allowed to warm to room temperature and stir for 10 mins before being heated to 65 °C for 1 h resulting in the formation of a white suspension. This was frozen at -196 °C and BcatBr (1.09 g, 5.40 mmol) was added in one portion. The reagents were allowed to warm to room temperature before being heated to reflux for 16 h. The suspension was cooled to room temperature and toluene-soluble materials were transferred *via* cannula and evaporated to dryness. The residue was then extracted with cold petrol (0 °C, 3×5 mL) and the petrol-soluble materials were transferred *via* cannula and evaporated to afford a white solid. Impurities were then removed *via* vacuum sublimation and the product was isolated as the residual white solid (980 mg, 70%). ^{1}H NMR (C_6D_6): δ 6.82-6.79 (m, 2H, C_6H_4), 6.69-6.67 (m, 2H, C_6H_4), 1.52 (s, 3H, CH_3). $^{11}B\{^1H\}$ NMR (C_6D_6): δ 29.2 (1B, *B*cat), 2.1 (1B), -4.7 (1B), -7.2 (2B), -7.8 to -10.8 (6B). EIMS: envelope centred on *m/z* 276.2 (M^+). Crystals suitable for SCXRD were grown from the slow evaporation of a concentrated petrol solution.

*3.1.4. [μ-2,2'-BPh-(1-1'-closo-1',2'-$C_2B_{10}H_{10}$)-closo-1,2-$C_2B_{10}H_{10}$] (**4**)*

A fluorobenzene (15 mL) solution of 1,1'-bis(*ortho*-carborane) (250 mg, 0.93 mmol) was cooled to 0 °C before the dropwise addition of *n*-BuLi (1.27 mL of a 1.54 M solution, 1.95 mmol). The colourless solution was warmed to room temperature and stirred for 1 h. The pale yellow solution was cooled to 0 °C and $BPhCl_2$ (0.12 mL, 0.93 mmol) was added dropwise, after which the reagents were heated to reflux for 2 h. The yellow solution was cooled and separated from a white solid by filtration. The fluorobenzene-soluble materials were then evaporated to dryness *in vacuo* to yield a dark yellow solid (150 mg, 44%). ^{1}H NMR (C_6D_6): δ 8.29-8.26 (m, 1H, C_6H_5), 7.98-7.96 (m, 2H, C_6H_5), 6.93-6.89 (m, 2H, C_6H_5). $^{11}B\{^1H\}$ NMR (C_6D_6): δ 58.5 (1B, *B*Ph), 3.4 (2B), -2.4 (2B), -6.0 (8B), -7.5 (4B), -11.3 (4B). EIMS: envelope centred on *m/z* 372.4 (M^+).

*3.1.5. [1-Bcat-7-PPh_2-closo-1,7-$C_2B_{10}H_{10}$] (**5**)*

A toluene solution (25 mL) of [1-PPh_2-*closo*-1,7-$C_2B_{10}H_{11}$] (0.44 g, 1.35 mmol) was cooled to 0 °C before a toluene solution (10 mL) of Li[TMP] (0.218 g, 1.49 mmol) was added dropwise. The solution was warmed to room temperature and stirred for 6 h. The solution was then evaporated to dryness

to afford a white solid which was washed with petrol (3×15 mL). The insoluble materials were then dissolved in toluene (25 mL) and frozen at -196 °C. To the frozen mixture BcatBr (0.29 g, 1.49 mmol) was added in one portion following which the reagents were allowed to warm to room temperature and stir for 15 mins. The solution was then heated to reflux for 18 h. The white suspension was cooled to room temperature and the reaction mixture was evaporated to dryness. The residue was extracted with petrol (3×15 mL) and the soluble materials transferred *via* cannula and evaporated to dryness. The residue was extracted with cold petrol (-5 °C, 3×10 mL) and the petrol-soluble materials transferred *via* cannula and evaporated to dryness. Excess [1-PPh_2-*closo*-1,7-$C_2B_{10}H_{11}$] was removed from the residue *via* vacuum sublimation and the product was isolated as a white solid (240 mg, 40%). ^{1}H NMR (C_6D_6): δ 7.84-7.67 (br. m, 4H, C_6H_5), 7.11-6.97 (br. m, 6H, C_6H_5), 6.79-6.68 (br. m, 2H, C_6H_4), 6.68-658 (br. m, 2H, C_6H_4). ^{11}B{^{1}H} NMR (C_6D_6): δ 30.3 (1B, *B*cat), -0.7 (1B), -3.8 (1B), -6.7 to -10.5 (6B), -12.8 (2B). ^{31}P{^{1}H} NMR (C_6D_6): δ 20.3 (s). EIMS: envelope centred on *m/z* 446.2 (M^+). Crystals suitable for SCXRD were grown from a cooled (-20 °C), concentrated petrol solution.

*3.1.6. [1-Bcat-7-P(Se)Ph_2-closo-1,7-$C_2B_{10}H_{10}$] (**5Se**)*

Compound **5** (5 mg, 0.01 mmol) was dissolved in C_6D_6 (0.7 mL) in a J. Young NMR tube. Elemental selenium (26 mg, 0.3 mmol) was then added and the mixture shaken and left at room temperature for 7 d. The reaction was monitored *via* ^{31}P{^{1}H} NMR spectroscopy until full conversion to the selenide was observed. No isolation of **5Se** was attempted. ^{1}H NMR (C_6D_6): δ 8.36-8.31 (m, 4H, C_6H_5), 6.98-6.93 (m, 6H, C_6H_5), 6.74-6.72 (m, 2H, C_6H_4), 6.64-6.61 (m, 2H, C_6H_4). ^{11}B{^{1}H} NMR (C_6D_6): δ 30.0 (1B, *B*cat), 0.7 to -4.1 (2B), -5.5 to -11.2 (6B), -11.2 to -16.1 (2B). ^{31}P{^{1}H} NMR (C_6D_6): δ 45.1 (s + Se satellites, $^1J_{PSe}$ = 817 Hz).

3.2. Gutmann-Beckett Method for Acceptor Number Determination

A modified Gutmann-Beckett method [5] was employed to obtain Acceptor Numbers (ANs) for the Lewis acids. The Lewis acid (0.11 mmol) was dissolved in C_6D_6 (1 mL), triethylphosphine oxide (5.0 mg, 0.037 mmol) was added and the solution transferred to a J. Young NMR tube. From the ^{31}P{^{1}H} NMR spectrum the AN was calculated using the equation below, where δ(1) = 41.0 ppm (Et_3PO in hexane), δ(2) = 86.1 ppm (Et_3PO-$SbCl_5$) and δ(complex) = the chemical shift of the adduct between the Lewis acid and Et_3PO.[4]

$$\mathrm{AN} = \frac{\delta(\mathrm{complex}) - \delta(1)}{\delta(2) - \delta(1)} \mathrm{x}\, 100$$

3.3. Crystallography

Diffraction data from **1** were collected on a Bruker X8 APEXII diffractometer operating at 100 K (Mo-K_α *X*-radiation), from **2** and **3** on a Rigaku Oxford Diffraction SuperNova diffractometer at 120 K (Cu-K_α), and from **5** on a Bruker D8 Venture diffractometer at 100 K (Mo-K_α) from crystals mounted in inert oil on a cryoloop and cooled in a stream of cold N_2. Using OLEX2 [14] structures were solved using the SHELXS [15] or SHELXT [16] programme and refined by full-matrix least-squares using SHELXL [15]. In the case of **2** the cage C was unambiguously distinguished from B atoms by application of the VCD and BHD methods [17]. All crystals were single and the structures fully ordered with no solvate molecules. H atoms bound to cage B atoms were allowed to refine positionally whilst other H atoms were constrained to idealised geometries with C_{aryl}–H 0.95 Å and C_{methyl}–H 0.98 Å. All H displacement parameters were constrained to be 1.2×U_{eq} (bound B or C) except Me H atoms 1.5×U_{eq} (C_{methyl}). Table 2 contains further experimental details. Structures have been deposited with the Cambridge Crystallographic Data Centre, CCDC 1959431-1959434 and 1959463.

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Appendix A. Supplementary Material

Supplementary material related to this article can be found at https://doi.org/10.1016/…

Table 2 Crystallographic data.

	1	**2**	**3**	**5**
CCDC	1959431	1959432	1959433	1959463
Formula	$C_{21}H_{35}B_{11}$	$C_8H_{15}B_{11}O_2$	$C_9H_{17}B_{11}O_2$	$C_{20}H_{24}B_{11}O_2P$
M	406.40	262.11	276.13	446.27
Crystal system	monoclinic	monoclinic	monoclinic	triclinic
Space group	*Cc*	$P2_1/n$	$P2_1/c$	$P\bar{1}$
a/Å	14.7894(8)	6.9222(2)	12.4743(2)	9.8187(2)
b/Å	17.9813(9)	19.8493(7)	12.30460(10)	11.1387(3)
c/Å	9.7695(5)	10.4990(5)	20.3392(3)	12.5639(3)
α/°	90	90	90	71.5900(10)
β/°	111.132(3)	96.171(3)	106.7030(10)	72.5500(10)
γ/°	90	90	90	67.4950(10)
U/Å^3	2423.3(2)	1427.39(9)	2990.17(7)	1179.09(5)
Z, *Z*′	4, 1	4, 1	8, 2	2, 1
F(000)/e	864	536	1136	460
D_{calc}/Mg m^{-3}	1.114	1.220	1.227	1.257
X-radiation	Mo-K_α	Cu-K_α	Cu-K_α	Mo-K_α
λ/Å	0.71073	1.54178	1.54178	0.71073
μ/mm^{-1}	0.055	0.503	0.504	0.134
θ_{max}/°	28.96	75.86	75.90	28.28
Data measured	22579	20543	23137	48251
Unique data	6285	2965	6113	5840
R_{int}	0.0560	0.0963	0.0719	0.0345
R, wR_2 (obs. data)	0.0469, 0.0990	0.0467, 0.1283	0.0528, 0.1366	0.0331, 0.0831
S	1.010	1.071	1.037	1.050
Variables	326	223	459	337
E_{max}, E_{min}/e Å^{-3}	0.17, −0.21	0.29, −0.23	0.28, −0.30	0.35, −0.26
Flack parameter	-0.4(10)	-	-	-

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