Dalton Transactions

PAPER

Check for updates

Cite this: Dalton Trans., 2018, 47, 5850

Received 13th February 2018 Accepted 16th March 2018 DOI: 10.1039/c8dt00610e rsc.li/dalton

Introduction

Decaborane plays a central role in polyhedral boron chemistry. The preparation of this ten-vertex cluster involves the pyrolysis of diborane-6 at temperatures near 373 K, a reaction discovered by Alfred Stock and co-workers.¹ Decaborane is now commercially available, and this versatile molecule can be functionalized with organic and organometallic groups, either by incorporation into the framework or by attachment to the cluster surface, affording a completely new realm of possibilities to these conventional areas.²⁻⁵ An example of this rich functional chemistry is the reaction with Lewis bases, L, to give 6,9-(L)₂arachno-B₁₀H₁₂, and the subsequent insertion of acetylenic carbon atoms into the cage. This is of considerable importance in polyhedral boron chemistry because it affords the formation of dicarbadodecaboranes, namely, 1,2-(R¹)(R²)-closo-1,2-C₂B₁₀H₁₀, which form an extensive family of compounds with applications in diverse areas such as medicine, nanoscale engineering, catalysis, etc.6-9

Decaborane anion tautomerism: ion pairing and proton transfer control[†]

Sandra Pérez, Pablo J. Sanz Miguel 问 and Ramón Macías 问 *

The reaction of 1,8-bis(dimethylamino)naphthalene-which is often referred by the trade name Proton-Sponge (PS)—with decaborane in hexane afforded [HPS][$B_{10}H_{13}$] (1) salt as a pale-yellow precipitate. Variable-temperature NMR studies allowed the full assignment of ¹H and ¹¹B spectra for this familiar ten-vertex polyhedral anion. In addition, this work reveals that an increase in the temperature leads to the intramolecular exchange of three B-H-B hydrogen atoms around the hexagonal face of the boat-shaped cluster. This previously unrecognised H-tautomerism complements the long-known lowenergy proton exchange of only one of the bridging hydrogen atoms. The temperature dependent proton fluxional behaviour controls the molecular environment of the polyhedral cage, averaging the negative charge of the anion. The result is a debilitation of the cation-anion interactions in solution, favouring the transfer of the proton from the organic aromatic cation, $[HPS]^+$, to the polyhedral anion, $[B_{10}H_{13}]^-$. This proton transfer affords Proton-Sponge and decaborane, increasing the entropy of the system and sustaining an equilibrium which at high temperatures shifts toward the neutral reactants and at low temperatures moves toward the ionic products. A single X-ray diffraction analysis of 1 is discussed.

> The capacity of decaborane to accommodate atoms is not limited to carbon, and this ten-vertex boat-shaped molecule can incorporate a large number of elements throughout the Periodic Table.^{10,11} For example, reactions with inorganic reagents such as NaCN, NaNO₂, Na₂SeO₃, Na₂(S_x) or AsI₃ result in insertion or degradation-insertion of heteroatoms into the borane skeleton, affording 7-NH3-7-CB10H12, 6-NB9H12, 7,8-Se₂B₉H₉, 6-SB₉H₁₁ or $[AsB_{10}H_{12}]^{-12-15}$ These heteroboranes can be further functionalized by reactions with Lewis bases, organic molecules and organometallic fragments.^{16,17} In fact, the reactions between decaborane and its heteroboron derivatives with transition element complexes are a general route for the synthesis of metallaboranes and metallaheteroboranes.^{11,18–23} The latter group includes metallacarboranes, which, as indicated above, are ubiquitous in polyhedral boron chemistry.⁶⁻⁹

> Decaborane(14) exhibits a dual Lewis/Brønsted nature: (i) with good σ -donor ligands, it forms L-boron ligated adducts (eqn (1)); and (ii) with strong bases, B, it transfers a proton to give the $[nido-B_{10}H_{13}]^-$ anion (eqn (2)).^{2,3} This ambivalent reactivity is controlled by a balance between the nucleophilic and basic character of the entering ligand, L; and, in some cases, both reactions (adduct formation and cluster deprotonation) can occur in a stepwise manner. For example, in organic-water mixtures, decaborane behaves as a strong Lewis acid, forming a H₂O-ligated adduct, 6-(H₂O)-nido-B₁₀H₁₄, which subsequently dissociates a proton, becoming a Brønsted acid which depend-



View Article Online

Departamento de Química Inorgánica, Instituto de Síntesis Química y Catálisis Homogénea (ISQCH), Universidad de Zaragoza-CSIC, 50009 Zaragoza, Spain. E-mail: rmacias@unizar.es

[†]Electronic supplementary information (ESI) available: Additional NMR data, including diffusion experiments; Cartesian coordinates for the optimized geometries. CCDC 1583013. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c8dt00610e

ing on the water content can span from moderately strong to very strong acid (eqn (3)).^{24,25} The dual Lewis/Brønsted acidic behaviour of decaborane should play an important role in the reactions with inorganic salts (mentioned above) in the presence of water, triggering adduct formation/deprotonation processes that result in insertion/degradation-insertion of heteroatoms; whereas the simple deprotonation of decaborane with various bases has previously utilized to synthesize $[nido-B_{10}H_{13}]^{-2,3}$

$$nido-B_{10}H_{14} + 2 L \rightarrow 6, 9-(L)_2-B_{10}H_{12} + H_2 (g)$$
 (1)

$$nido-B_{10}H_{14} + B \rightarrow [nido-B_{10}H_{13}]^{-} + [HB]^{+}$$
 (2)

$$nido-B_{10}H_{14} \stackrel{H_{2}O}{\longleftrightarrow} 6-(H_{2}O)-B_{10}H_{14} \stackrel{H_{2}O}{\longleftarrow} [6-(HO)-B_{10}H_{14}]^{-} + H_{3}O^{+}$$
(3)

Similar to its neutral conjugated acid, $B_{10}H_{14}$, the $[B_{10}H_{13}]^$ anion reacts with σ -donor ligands to give [6-(L)-*nido*- $B_{10}H_{13}]^$ anions that resemble the neutral bis-adducts, $6.9-(L)_2$ -*arachno*- $B_{10}H_{12}$, in which a hydride ion replaces one ligand, L.² Interestingly, this 10-vertex polyhedral anion is capable of reacting with alkynes to give *ortho*-dicarbadodecaboranes,²⁶ suggesting that this anionic cluster may also play a role in the classical carbon insertion reactions that take place between bis-decaborane adducts and alkynes. More recently, it has been demonstrated that the decaborane cluster anion can enhance the ignition delay in hypergolic ionic liquids and it can also induce hypergolicity to otherwise inactive molecular solvents.²⁷

Clearly, neutral *nido*-B₁₀H₁₄ and anionic [nido-B₁₀H₁₃]⁻ are useful, well-known starting materials in polyhedral boron chemistry. Both clusters have been characterized in the solid state and solution by means of X-ray diffraction, NMR spectroscopy, IR, *etc.* However, the available NMR data are rather old, being largely based on low-dispersion spectroscopy with little assignment work.^{2,3,28} This is particularly evident in the case of the $[B_{10}H_{13}]^-$ anion for which, to the best of our knowledge, a full assignment of the ¹¹B and ¹H NMR spectra has not been published yet.²⁹ Moreover, a fluxional process involving one of the B–H–B bridging hydrogen atoms was identified early, but, so far, there have been no ¹H variable temperature (VT) studies providing experimental data for the non-rigid behavior of the [nido-B₁₀H₁₃]⁻ anion.^{2,3,30}

The formation of the decaborane anion in the salt $[HPS][B_{10}H_{13}]$, where PS = Proton-Sponge (1,8-bis(dimethylamino)naphthalene), was reported in 1979. The work focused on the reactivity of PS with different boranes, demonstrating that this strong aromatic base can abstract a proton from *nido*- $B_{10}H_{14}$, producing quantitatively [*nido*- $B_{10}H_{13}]^-$; but this paper did not offer further experiments dealing with, for example, the assignment of previous NMR data, fluxional behavior or structural studies of the PS salt.³¹

Here we report on the synthesis and characterization of $[HPS][B_{10}H_{13}]$ (1), including the X-ray crystallographic analysis

of this salt and a full assignment of the NMR data.[‡] We complete this research with VT experiments that give further evidence for the previously reported low-energy proton tautomerism, together with the discovery of an unknown fluxional process. Overall, this work provides a comprehensive characterization of the chemical non-rigidity of the decaborane cluster anion. We also discuss that **1** exhibits a protonation/ deprotonation equilibrium.

Results and discussion

The addition of Proton-Sponge to decaborane (both reactants dissolved in hexane) immediately affords a pale-yellow precipitate. This solid is conveniently crystallized from dichloromethane/hexane to give yellow needle-like crystals, which were characterized as the salt $[HPS][B_{10}H_{13}](1)$.

In this reaction, Proton-Sponge abstracts a proton from the 10-vertex *nido*-decaborane, with the subsequent formation of the anion $[nido-B_{10}H_{13}]^-$ (Scheme 1). The resulting yellow crystalline salt, 1, is stable in air at room temperature, and soluble in chlorinated solvents such as chloroform and dichloromethane.

X-ray diffraction analysis

The ten-vertex polyhedral anion $[B_{10}H_{13}]^-$ has been characterized by X-ray diffraction in the salts $[NMe_3(CH_2Ph)][B_{10}H_{13}]$ (2) and $[NEt_4][B_{10}H_{13}]$.^{32,33} Table 1 shows selected distances for the salts 1 and 2, together with those for decaborane.^{34,35}

Salt 1 crystallized in the space group $P\bar{1}$ (Fig. 1). The distances and angles are within the ranges found for the previously reported *nido*- $[B_{10}H_{13}]^-$ anion in salt 2 and for *nido*- $B_{10}H_{14}$ (Table 1).^{32–35} It is worth mentioning that in the neutral decaborane molecule, the B5–B6 and B5–B10 distances at 1.789(2) and 1.989(2) Å, respectively, are significantly longer



Scheme 1 Reaction of decaborane with Proton Sponge.

[‡] Crystal data for 1: [C₁₄H₃₂B₁₀N₂], triclinic, *P*Ī, *a* = 8.1280(5) Å, *b* = 10.5661(6) Å, *c* = 13.3633(8) Å, *α* = 67.7860(10)°, *β* = 83.6620(10)°, *γ* = 73.8830(10)°, *Z* = 2, *M*_r = 336.51, *V* = 1020.70(11) Å³, *D*_{calcd} = 1.095 g cm⁻³, λ (Mo Kα) = 0.71073 Å, *T* = 100 K, *μ* = 0.056 mm⁻¹, 15 216 reflections collected, 4858 unique (*R*_{int} = 0.0642), 3215 observed, *R*₁(*F*_o) = 0.0568 [*I* > 2*σ*(*I*)], w*R*₂ (*F*_o²) = 0.1659 (all data), GOF = 1.025. CCDC 1583013.†

Table 1 Selected B-B interatomic distances (Å) for nido-B₁₀H₁₄, $[HPS][B_{10}H_{13}]$ (1) and $[NMe_2(CH_2Ph_3)][B_{10}H_{13}]$ (2) with estimated standard uncertainties (s.u.) in parentheses. Calculated values for the DFT-optimized energy minimum of salt 1 are enclosed [in brackets]

	nido-B ₁₀ H ₁₄ ^a	1	2^b
B1-B2	1.787(2)	1.763(3) [1.747]	1.745(5)
B1-B3	1.779(3)	1.789(3) [1.783]	1.780(5)
B1-B4	1.783(3)	1.794(3) [1.790]	1.783(5)
B1-B5	1.749(2)	1.744(3) [1.735]	1.731(5)
B1-B10	1.751(2)	1.785(3) [1.786]	1.780(4)
B2-B3	1.783(3)	1.766(3) [1.761]	1.756(5)
B2-B5	1.792(3)	1.787(3) [1.735]	1.785(5)
B2-B6	1.731(2)	1.752(3) [1.755]	1.735(5)
B2-B7	1.787(3)	1.760(3) [1.771]	1.754(5)
B3-B4	1.787(2)	1.774(3) [1.776]	1.765(5)
B3-B7	1.751(2)	1.765(3) [1.769]	1.758(5)
B3-B8	1.749(2)	1.734(3) [1.737]	1.734(5)
B4-B8	1.792(2)	1.777(3) [1.773]	1.767(5)
B4-B9	1.731(2)	1.715(3) [1.708]	1.707(5)
B4-B10	1.787(3)	1.803(3) [1.815]	1.798(5)
B5-B6	1.790(3)	1.688(3) [1.663] ^c	1.657(6)
B5-B10	1.988(2)	1.870(3) [1.845]	1.848(4)
B6-B7	1.782(3)	1.793(3) [1.773]	1.788(5)
B7-B8	1.988(2)	$2.021(3)$ $[2.008]^d$	2.003(5)
B8-B9	1.790(2)	1.798(3) [1.774]	1.768(5)
B9-B10	1.782(3)	1.826(3) [1.784]	1.783(4)

^a Data from ref. 35. ^b Data from ref. 32. ^c Shortest B-B distance. ^d Longest B–B distance.



Fig. 1 Crystallographically determined molecular structures of the $[HPS]^+$ cation (left) and of the $[nido-B_{10}H_{13}]^-$ anion (right) in the salt, [HPS][B₁₀H₁₃] (1). Ellipsoids are shown at 50% probability levels.

than those in the anions of the salts 1 and 2 [1.673(6)] and 1.859(4) Å, averaged between the two anions]; and that the B5-B6–B7 angle of the anionic cluster is $ca. 9^{\circ}$ smaller than the neutral decaborane cage. These structural changes are the response that the cluster undergoes upon the liberation of a proton that in neutral decaborane lies along the B5-B6 edge.

The polyhedral ten-vertex nido-anions pack by forming chains along the crystallographic a direction; the shortest interatomic distance within the anionic chains is 2.61(3) Å, which corresponds to the B2-H2···H9-B9 contact (Fig. 2). In addition, two antiparallel chains connect via their B7(H) sites (2.61(4) Å) forming ribbons (Fig. S1, ESI[†]). These intra- and inter-chain distances are significantly longer than the van der Waals radii of two hydrogen atoms (2.4 Å),36 and we cannot definitely propose a dihydrogen interaction. Thus, the main forces that govern the crystal structure of salt 1 should be ionic



Fig. 2 View of the B-H···H-B contacts along the *a* axis in the crystal lattice of 1

in nature; although, we could also invoke, to some degree, hydrophophic interactions between the polyhedral $[nido-B_{10}H_{13}]^{-}$ anions as a reason for the close proximity of the clusters within the chains. The aromatic cations, [HPS]⁺, are embedded within the cavities of the lattice.

NMR spectroscopy: characterization and cluster fluxionality

In 1959, Lipscomb proposed two possible structures related by hydrogen tautomerism for [nido-B₁₀H₁₃]⁻.³⁷ Twelve years later, Todd and co-workers reported the characterization of this tenvertex polyhedral anion by NMR spectroscopy, providing experimental data that supported a fast intramolecular exchange of one of the three B-H-B bridging hydrogen atoms that renders a molecule with a $C_{\rm s}$ symmetry in solution.²⁹ The same fast H-tautomerism was suggested by Heřmánek and Plešek to take place when decaborane, B₁₀H₁₄, is dissolved in water/ethanol (eqn (3)).²⁵ These spectroscopic results were further rationalized by computational studies that provided a good agreement with the experimentally observed ¹¹B NMR spectrum.38

The above mentioned studies focused on the ¹¹B NMR spectroscopic features of the tridecahydro-decaborate(1-) anion; and, as far as we know, a full ¹H NMR characterization of the anion $[B_{10}H_{13}]^-$ has not been published yet.

Herein we fill this gap; Table 2 shows a complete assignment of the ¹¹B and ¹H NMR spectra at 243 K for this paradigmatic polyhedral anion; and to facilitate the comparison, we include NMR data of nido-B10H14 and its pyridine adduct, $6,9-(py)_2$ -arachno- $B_{10}H_{12}$.

In CDCl₃, the ¹¹B NMR spectrum of **1** at –30 °C exhibits five peaks with a 2:1:4:1:2 relative intensity ratio. The peak with relative intensity four at $\delta(^{11}B)$ –4.4 ppm corresponds to the resonances of B(5,10) and B(7,8) which in the ¹¹B spectrum are accidentally coincident. Selective ¹H-{¹¹B} decoupling experiments correlated this boron resonance with the proton signals of relative intensity two at +2.43 and +2.91 ppm. Thus, the six proton resonances of 2:2:1:1:2:2 relative intensity in the positive region of the ${}^{1}H - {}^{11}B$ spectrum at -30 °C are assigned to the B-H terminal hydrogen atoms; whereas the two resonances of 1:2 relative intensity ratio at -2.70 and -3.54 ppm are due to the B-H-B bridging hydrogen atoms on

Table 2 ^{11}B and ^{1}H NMR data of [HPS][B₁₀H₁₃] (1), <code>nido-B₁₀H₁₄</code> and 6,9-(py)₂-arachno-B₁₀H₁₂. In brackets, the corresponding DFT/GIAO-calculated ^{11}B -nuclear shielding values for 1

[HPS][B ₁₀ H ₁₃] ^{<i>a,b</i>}	$\delta(^{11}\text{B})$	$\delta(^{1}H)$
B(6,9) B3 B(5,10) B(7,8) B1 B(2,4) B-H-B	+7.3 [-9.9, +20.7] +2.9 [-0.1] -4.4 (4B) [-12.3, -6.1, -0.6, -8.9] -5.3 [-7.8] -35.2 [-44.5, -30.1]	+3.46 (2H) +2.86 (1H) +2.91 (2H) +2.43 (2H) +2.53 (1H) +0.23 (2H) -2.70 (1H), -3.54 (2H)
B ₁₀ H ₁₄ ^c	$\delta(^{11}B)$	$\delta(^{1}H)$
B(1,3) B(6,9) B(5,7,8,10) B(2,4) B-H-B	+12.2 +10.3 +0.7 -36.0	+3.85 (2H) +3.68 (2H) +3.12 (4H) +0.65 (2H) -2.16 (4H)
$6,9-(py)_2-B_{10}H_{12}^{d}$	$\delta(^{11}\mathrm{B})$	$\delta(^{1}H)$
B(2,4) B(6,9) B(5,7,8,10) B(1,3) B-H-B	-3.7 -15.5 -17.7 -39.4	+2.07 (2H) +0.66 (2H) +1.64 (4H) +0.26 (2H) -4.38 (2H)

^{*a*} Measured at 243 K in CDCl₃. ^{*b*} Assignments based on ¹H–{¹¹B} selective experiments, the H-tautomerism that equilibrates B–H positions in pairs and DFT/GIAO calculated ¹¹B chemical shielding data. ^{*c*} Measured at 298 K in CDCl₃. ^{*d*} Measured at 298 K in CD₂Cl₂.

the hexagonal face of boat-shaped ten-vertex $[nido-B_{10}H_{13}]^-$ (Fig. 3).

It is empirically known that boron atoms that lie trans to B-H-B bridging hydrogen atoms on the open faces of polyhedral boron-containing compounds show significantly lower chemical shifts than boron vertices in opposite edges that do not have μ H bridges.³⁹ This effect explains the crossing of the B(1,3) and B(2,4) resonances when the decaborane, *nido*-



Fig. 4 Stick diagrams representing the chemical shifts and relative intensities in the ¹¹B NMR spectra of *nido*-B₁₀H₁₄ (lowest trace), *nido*-[B₁₀H₁₃]⁻ (middle) and 6,9-(py)₂-*arachno*-B₁₀H₁₂ (top). Hatched lines connect equivalent positions.

 $B_{10}H_{14}$, becomes the pyridine adduct, 6,9-(py)₂-*arachno*- $B_{10}H_{12}$. This ¹¹B NMR pattern is diagnostic of a *nido*-to-*arachno* transformation that implies reorganization of the B–H–B bridging hydrogen atoms on the hexagonal open face (Fig. 4).

Compared to neutral decaborane, the ¹¹B NMR spectrum of the anion exhibits an overall shielding. The largest change corresponds to the B1 resonance that suffers a 17.5 ppm shift toward low frequency. This boron atom lies trans to the B5–B10 edge, and the low energy B–H–B bridging hydrogen exchange on the B6–B5–B10–B9 side has a strong influence on its ¹¹B chemical shift. Thus, from the point of view of the empirical " μ H rule", it is clear that the ¹¹B resonance corresponding to the B1 nucleus should undergo a significant low-frequency shift.

The $^1H\text{-}\{^{11}B\}$ spectrum at 178 K (Fig. S2, ESI†) demonstrates that the exchange of the bridging hydrogen atom



Fig. 3 Variable-temperature ${}^{1}H - {}^{11}B$ NMR spectra of [HPS][$B_{10}H_{13}$] (1) in CDCl₃. The peaks marked with blue squares correspond to decaborane, $B_{10}H_{14}$, whereas those marked with red triangles are due to 1.

between the B5–B6 and B9–B10 edges is still fast on the NMR time-scale, implying that the interconversion of the two enantiomeric forms of the anion has a ΔG^{\ddagger} value lower than 7 kcal mol⁻¹.⁴⁰ This result sets an experimental upper limit on the differences in energy among the ground state, transition state, and intermediates involved in this H-tautomerism.

At higher temperatures, the ¹H–{¹¹B} NMR spectra show that the resonances corresponding to the terminal hydrogen atoms, H(5,10), H1, H3 and H(7,8) coalesce at 303 K, whereas the signals of the B–H–B bridging hydrogen atoms broaden significantly, and finally coalesce at 315 K (Fig. 3). This spectroscopic behaviour is consistent with a second H-tautomerism that involves the exchange of the three bridging hydrogen atoms on the open face of the *nido*-anion. The activation energy, $\Delta G_{318}^{\ddagger}$, is 14.2 kcal mol⁻¹, and this value is reproduced in the energy profile calculated for the pathway that leads to the exchange of the three hydrogen atoms (*vide infra*).

For the low energy H-tautomerism, DFT-calculations give a transition state (TS), in which the fluxional hydrogen atom occupies an *endo* position on either B5 or B10 and which lies higher in energy than the C_1 static anion in a range between 5.3 and 7.8 kcal mol⁻¹ (depending on the computational method).^{30,38} The exchange of this hydrogen atom can be regarded to take place (formally) through an intermediate in which the mobile hydrogen stays along the B5–B10 edge (compare the discussion above dealing with the low frequency chemical shift of B1); this C_s cluster is a true minimum in the potential energy surface that lies 4.1 to 6.4 kcal mol⁻¹ above the parent C_1 static tautomer (Fig. 5).^{30,38}

In this work, we provide new computational data obtained with the M11L functional and the 6-311++G(d,p) basis set. The excellent agreement between experimental and computed data for the geometry of small molecules supports this combination as a useful predictive tool.^{41,42} In our DFT calculations, we included the organic cation in order to account for anion–cation interactions (*vide infra*). Thus, in agreement with the DFT studies mentioned above, together with our low temperature ¹H NMR measurements, the transition state for the fast

movement of one bridging hydrogen atom on the B6–B5–B10– B9 side of the anion lies about 6.7 kcal mol⁻¹ above the C_1 static structure, with the C_s tautomer at 5.4 kcal mol⁻¹ (Fig. 5).

For the full hydrogen rearrangement, we envision that the low energy proton exchange along the B6–B5–B10–B9 lateral is followed by a proton flip from side to side through a transition state of the $C_{\rm s}$ symmetry that exhibits an *endo*-hydrogen atom at the BH(6) vertex. This TS is 14.0 kcal mol⁻¹ higher in energy than the C_1 tautomer, matching the experimentally determined activation energy for this H-tautomerism of 14.2 kcal mol⁻¹ (Fig. 6).

The combination of these proton shifts (Fig. 5 and 6) provides a rationale for the full exchange of the three B–H–B hydrogen atoms on the hexagonal face of $[B_{10}H_{13}]^-$. The proposed mechanism that combines these low- and high-energy proton tautomerisms is depicted in Scheme 2.

Deprotonation/protonation equilibrium

In the previous section, the discussion focuses on the spectroscopic NMR characterization of the polyhedral anion in the hybrid salt **1**, and on its fluxional behaviour in solution; but the VT NMR spectra also reveal that the ions, $[B_{10}H_{13}]^-$ and $[HPS]^+$, are present in solution as major products together with neutral decaborane, $B_{10}H_{14}$, and Proton-Sponge as minor components (see Fig. 3 above and Fig. S3 and S4 in the ESI[†]).

The existence of well-resolved signals corresponding to the neutral and ionic species in the ¹H NMR spectra implies that the proton transfer is slow in the time-scale of the experiment. This is clearly demonstrated by the presence of the high frequency signal at $\delta_{\rm H}$ +19.16 ppm that corresponds to the N–H proton of the organic cation, together with the fact that this resonance does not change significantly with the temperature (see Fig. S3, ESI†). At low temperatures, the intensity of the ¹H NMR signals that correspond to the neutral molecules, B₁₀H₁₄



Fig. 5 Calculated Gibbs energy profile (in kcal mol⁻¹) in CH₂Cl₂ at 298.15 K for the fluxional hydrogen rearrangement that interconverts the two enantiomeric forms of the anion in [HPS][B₁₀H₁₃] (1). The [HPS]⁺ cation was included in the DFT-optimized structures ($1C_{1-a}$ and $1C_{s-a}$ in Fig. 8) and in the transition states, but this is omitted for clarity.

Fig. 6 Calculated Gibbs energy profile (in kcal mol⁻¹) in CH₂Cl₂ at 298.15 K for the side-to-side proton shift on the boat-like hexagonal face of $[B_{10}H_{13}]^-$ in **1**. The [HPS] cation was included in the DFT-optimized structures (**1**C₁**...a** in Fig. 8) and in the transition state but this is omitted for clarity.



Scheme 2 Low- and high-energy hydrogen rearrangements, leading to the exchange of the three B–H–B bridging hydrogen atoms in [*nido*- $B_{10}H_{13}$]⁻.

and PS, decreases and eventually the peaks disappear. Conversely, at higher temperatures, the concentration of the neutral species increases (see, Fig. 3, S3 and S4 in the ESI†). This behaviour reveals an equilibrium between reactants and products, as illustrated in Scheme 1.

The equilibrium ratio of the anionic *versus* the neutral species was measured by ¹H–{¹¹B} NMR at 273, 294, 303, 313 and 320 K. As shown in Fig. 7, a straight-line fit to a plot of ln K_{eq} *versus* 1/T is obtained giving $\Delta H = -13.85 \pm 0.25$ kcal mol⁻¹ and $\Delta S = -36.33 \pm 0.25$ cal K⁻¹ mol⁻¹.

The exothermicity of this equilibrium shows that the N–H bond in PS is stronger than the B–H–B bond in decaborane. The negative value of ΔS was *a priori* unexpected since the transfer of a proton between decaborane and PS does not involve a change in the total number of molecules in the system. This entropy change demonstrates, therefore, that the protonated base, [HPS]⁺, and the polyhedral anion, [*nido*-B₁₀H₁₃]⁻, form ion pairs in solution. This fact is independently supported by diffusion experiments that we describe in the following paragraphs.

Diffusion experiments

Table 3 shows the diffusion data obtained by NMR spectroscopy.⁴³ In dichloromethane, the *D*-values for both the poly-



Fig. 7 Plot of $\ln K_{eq}$ vs. 1/T derived from ¹H NMR intensities signals in CDCl₃.

Table 3 Diffusion data of the ions $[\mathsf{HPS}]^+$ and $[\mathsf{B}_{10}\mathsf{H}_{13}]^-$ in 1, free decaborane and PS

	CD_2Cl_2		CH_3CN	
	D	$r_{\rm H}$ (Å)	D	$r_{ m H}$ (Å)
[HPS] ⁺	1.13	4.9	1.70	3.8
$[B_{10}H_{13}]^{-}$	1.05	5.3	1.95	3.3
$B_{10}H_{14}$	2.12	2.6	2.18	2.9
PS	1.78	3.1	2.19	2.9

 $D \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$, 0.07 M solutions at 300 K. Estimated radius in the solid state: [HPS]⁺/[B₁₀H₁₃]⁻ ion pair in 1, $r_{X\text{-}ray} = 6.8$ Å; decaborane, $r_{X\text{-}ray} = 3.0$ Å; PS: $r_{X\text{-}ray} = 3.9$ Å.

hedral anion, $[nido-B_{10}H_{13}]^-$, and the protonated base, $[HPS]^+$ are identical within the experimental error, demonstrating strong ion pairing and entropy lowering in the system upon deprotonation of decaborane by PS.

In CD_3CN , the diffusion coefficients of the polyhedral anion and the organic cation are not identical, indicating that the ion pairs are broken in this polar, coordinating solvent. It is interesting to note, however, that the *D*-values of both ions are slightly smaller than those found for the free neutral species in the same concentration. This behaviour suggests that the ions may interact to a certain level in acetonitrile, leading to a weak pairing.

Ion pairing and proton transfer

The negative entropy and the diffusion experiments demonstrate that the ions in the hybrid salt 1 form pairs when dissolved in CH_2Cl_2 and $CHCl_3$.

An approach of the $[\text{HPS}]^+$ cation towards the B6–B5–B10– B9 side of the $[nido-B_{10}H_{13}]^-$ anion, from which the proton has been abstracted, should be, *a priori*, favoured by electrostatic forces. In this regard, the values of natural atomic charges (NBO) show, as expected, an asymmetric distribution in the C_1 anion versus the C_{2v} neutral decaborane (see Fig. S16, ESI†). The charge in the anion is polarized on the hexagonal boatshaped face of the ten-vertex *nido*-cluster. The B5 vertex carries the largest negative charge in the static C_1 structure of the anion, being higher than the charge calculated for the parent decaborane. Interestingly, the butterfly-like belt, B1–B2–B3–B4, exhibits a low level of polarization with charge values that resemble those of the neutral decaborane.

We also carried out DFT-energy optimizations of several ion pairs, trying to provide a glimpse of the potential energy surface that results from $[HPS]^+$ -to- $[B_{10}H_{13}]^-$ interactions. The calculations, as indicated in the Experimental section, were carried out using a polarizable continuum model in order to consider the solvent effects. Fig. 8 illustrates four energy-optimized minima, $1C_{1-a}$, $1C_{1-b}$, $1C_{s-a}$, and $1C_{s-b}$, together with the ion pairs, $1C_{1-c}$ and $1C_{s-c}$, that correspond to transition states (TS's) involving slight cation/anion rocking. We tried to find true minima around these two TS's by changing the coordinates, but the calculations afforded systematically transition states.



Fig. 8 Calculated Gibbs energy profile (in kcal mol⁻¹) in CH₂Cl₂ at 298.15 K for different cation-anion interactions simulating the formation of ion pairs.

The ion pairs, $1C_{1_a}$ and $1C_{1_b}$, show the same energy, but the $1C_{1_c}$ TS lies 4.0 kcal mol⁻¹ higher in energy. These differences are in agreement with the above mentioned charge distribution of the C_1 tautomer in which the butterfly-like B1–B2– B3–B4 belt is much less polarized than the upper hexagonal face. Thus, a change of the ion interaction from B1–H1…H–PS in $1C_{1_a}$ to B3–H3…H–PS in $1C_{1_b}$ does not have an energy cost; whereas the interaction at the B7–H7 upper-belt vertex affords an unstable TS, $1C_{1_c}$.

However, the highest energy penalty as illustrated in Fig. 8 involves the C_1 to C_s H-tautomerism. The simple shift of the B9–H–B10 bridging hydrogen atom in $1C_{1_}a$ to the B5–B6 edge in $1C_{s_}a$ rises 5.4 kcal mol⁻¹ the energy of the system. In contrast to the ion pairs involving the C_1 tautomer, a change of the cation–anion interaction from the B1(H) vertex to the B3(H) vertex has an energy penalty of 1.2 kcal mol⁻¹. Moreover, the system becomes more unstable when the anionic C_s tautomer and the [HPS]⁺ cation interact around the B7(H) vertex, affording a TS, $1C_{s_}c$ that lies 10.2 kcal mol⁻¹ above the lowest energy pairs, $1C_{1_}a$ and $1C_{1_}b$.

The energy trend found in this small mapping agrees well with cation–anion interactions that depend, to an important extent, on changes in the charge distribution of the cluster. In this regard, the hydrogen shift between the enantiomeric forms of the $[nido-B_{10}H_{13}]^-$ anion should result in an averaging of the negative charge around the B6–B5–B10–B9 side, maintaining the polarity of the cage with respect to the plane that contains the B6–B9–B2–B4 vertices (see Fig. S16, ESI†). Since this low energy H-tautomerism prevails at low temperatures, it is reasonable to expect a higher number of N–H…H–B interactions between the ion pairs involving the B1, B5 and B10 vertices as the temperature decreases.

At higher temperatures, the full proton exchange on the hexagonal face starts to play an important role; and, under the fast regime of the three-proton tautomerism, the charges should average over the cage framework, approaching the situation found in the C_{2v} decaborane vertices (see Fig. S16†). This scenario should weaken the ion pairs, facilitating the formation of the neutral parent reactants, $B_{10}H_{14}$ and PS.

In other words, the H-tautomerism in the $[B_{10}H_{13}]^-$ anion regulates the charge distribution at the BH vertices, tuning the cation–anion interactions in solution. At low temperatures, the negative charge is polarized favouring ion pairing; but as the temperature increases, the negative charge averages around the cluster, debilitating the interactions and promoting the proton transfer to give the neutral species. This reverse reaction is, as discussed above, sustained by an increase in the entropy of the system.

Conclusions

The salt $[HPS][B_{10}H_{13}]$ (1) has been synthesised followed by a full assignment of the ¹H and ¹¹B NMR spectra for the classical polyhedral anion $[nido-B_{10}H_{13}]^-$. Variable-temperature ¹H-{¹¹B} NMR experiments in the poorly coordinating solvents CD_2Cl_2 and $CDCl_3$ demonstrated that the ions, $[HPS]^+$ and $[B_{10}H_{13}]^{-}$, form pairs that are in equilibrium with the neutral reagents, PS and decaborane via a proton transfer between the polyhedral cage and the organic aromatic base. Additionally, these studies reveal a previously unrecognized H-tautomerism that involves the exchange of the three B-H-B bridging hydrogen atoms around the hexagonal face of the $[B_{10}H_{13}]^{-}$ anion, complementing the long-known low-energy fluxional process of a single hydrogen atom. At high temperatures, the fast intramolecular rearrangement of the three hydrogen atoms results in a delocalization of the negative charge around the cage; and the polyhedral anions reduce their charge anisotropy, debilitating the cation-anion interactions in solution. This weakening favors the proton transfer to give the neutral molecules. As a result, the entropy of the system increases. In other words, a variation in temperature changes the H-tautomerism rate controlling the ion-pair formation/proton transfer equilibrium.

Experimental

General procedures

We carried out the reactions under an argon atmosphere using standard Schlenk-line techniques. Dried solvents were obtained from a Solvent Purification System from Innovative Technology Inc. Decaborane was sublimed prior to use (45 °C under *vacuum*). 1,8-Bis(dimethylamino)-naphthalene (referred throughout the paper by its trade name Proton-Sponge, and abbreviated as PS) was purchased from Sigma-Aldrich and used as received. The deuterated solvents CDCl₃, CD₂Cl₂ and CD₃CN were deaerated, following freeze-pump-thaw methods, and dried over 3 Å molecular sieves.

Infrared spectra were recorded on a PerkinElmer 100 spectrometer, using a Universal ATR Sampling Accessory. NMR spectra were recorded on Brüker Avance 300 MHz, AV 400 MHz and AV 500 MHz spectrometers, using ¹¹B, ¹¹B–{¹H}, ¹H, ¹H–{¹¹B} and ¹H–{¹¹B(selective)} techniques (see Fig. S5–S7†). The diffusion experiments were carried out using a standard pulse sequence for 2D DOSY spectroscopy on a Brüker AV 400 MHz spectrometer;⁴³ and the data were processed using the *SimFit (T1/T2 Analysis)* of the *TopSpin* software (see Fig. S7–S15†). The ¹H NMR chemical shifts were measured relative to the partially deuterated solvent peaks but are reported in ppm relative to [BF₃(OEt)₂]. Elemental analyses C/H/N were carried out in a PerkinElmer 2400 CHNS/O analyzer.

X-ray analysis of [HPS][**B**₁₀**H**₁₃] (1). Crystal data, data collection and refinement parameters were recorded at 100(2) K with a Bruker APEX DUO diffractometer equipped with an area detector and graphite monochromated MoK_{α} radiation (0.71073 Å) using narrow ω rotation (0.3°). Data reduction was done with the APEX2 software.⁴⁴ The structure was solved by direct methods and refined by full-matrix least squares methods based on F^2 using the SHELXL-97 and WinGX programs.^{45,46} Hydrogen atoms were located in the Fourier difference maps.

Calculations. All calculations were performed using the Gaussian 09 package.47 Structures were initially optimized using standard methods with the STO-3G* basis-sets. The final optimizations, including frequency analyses to confirm the true minima, together with GIAO nuclear-shielding calculations, were performed using M11L methodology,48 with the 6-311++G(d,p) basis-set. The effect of the solvent employed in experiments (CH₂Cl₂, ε = 8.93) was introduced through singlepoint calculations at the optimized geometries under vacuum, using the polarizable continuum model that corresponds to scrf=(smd,solvent=dichloromethane) at 298.15 K.49 GIAO nuclear shielding calculations were performed on the final optimized geometries, and computed ¹¹B shielding values were related to chemical shifts by comparison with the computed value for B_2H_6 , which was taken to be $\delta(^{11}B)$ +16.6 ppm relative to the $BF_3(OEt_2) = 0.0$ ppm standard.

Synthesis of [HPS][*nido*-B₁₀H₁₃] (1). 0.9691 g of $B_{10}H_{14}$ (7.928 mmol) was placed in a Schlenk tube under an argon atmosphere, and dissolved in 25 mL of hexane, which was injected and the system was then deaerated. In a second Schlenk tube, 2.0389 g (9.515 mmol) of Proton-Sponge (PS) was dissolved in 10 mL of hexane, the system was deaerated, and, then, the PS solution was added *via* cannula to the decaborane solution. Upon addition of the base, a pale-yellow precipitate was formed. The mixture was stirred for thirty minutes, and the solid was collected by filtration through a glass frit in air. Yellow crystals were obtained from dichloromethane/pentane. Yield: 2.4 g, 7.132 mmol, 80%. Table 2 lists ¹¹B and ¹H NMR data of salt 1 at 243 K, with a focus on the polyhedral anion. In this section, we included additional NMR data at different temperatures.

Anal. calcd for $B_{10}C_{14}H_{32}N_2$: C, 49.97; H, 9.58; N, 8.32; found: C, 49.36; H, 9.07; N, 8.36. IR (ATR): ν_{max}/cm^{-1} 2500–2458 s (BH). ¹¹B–{¹H} NMR (160.46 MHz, CDCl₃, 313 K): δ +7.10 (2B, s, BH), +2.80 (1B, s, BH), -4.81 (5B, s, BH), -35.23 (2B, s, BH). ¹¹B NMR (160.46 MHz, CDCl₃, 213 K): δ +7.64 (2B, pseudo-singlet, BH), +2.93 (1B, d, ${}^{1}J({}^{11}B^{-1}H) = 114$ Hz, BH), -4.43 (5B, d, ${}^{1}J({}^{11}B^{-1}H) = 112$ Hz, BH), -35.20 (2B, d, ${}^{1}J({}^{11}B^{-1}H) = 136$ Hz, BH). ¹¹B NMR (160.46 MHz, CDCl₃, 298 K): δ +7.16 (2B, d, ${}^{1}J({}^{11}B^{-1}H) = 137$ Hz, BH), +2.78 (1B, d, ${}^{1}J({}^{11}B^{-1}H) = 127$ Hz, BH), -4.49 (5B, s, ${}^{1}J({}^{11}B^{-1}H) = 118$ Hz, BH), -35.25 (2B, d, ${}^{1}J({}^{11}B^{-1}H) = 139$ Hz, BH). ${}^{11}H^{-1}H^{3}$ NMR (500 MHz, CDCl₃, 243 K): δ +19.36 (1H, s, [H–N–PS]⁺), +7.97 (2H, d, ${}^{2}J({}^{1}H^{-1}H) = 8.2$ Hz, CH), +7.79 (2H, d, ${}^{2}J({}^{1}H^{-1}H) = 7.5$ Hz, CH), +7.68 (2H, t, ${}^{2}J({}^{1}H^{-1}H) = 7.9$ Hz, CH), +3.18 (12H, s, CH). ${}^{1}H^{-113}$ NMR (500 MHz, CDCl₃, 313 K): δ +18.94 (1H, s, CH).

$$\begin{split} & [\mathrm{H-N-PS}]^+), \ +7.97\ (2\mathrm{H},\ \mathrm{d},\ {}^2J(^1\mathrm{H-}^1\mathrm{H}) = 8.2\ \mathrm{Hz},\ \mathrm{CH}), \ +7.78\ (2\mathrm{H},\ \mathrm{d},\ {}^2J(^1\mathrm{H-}^1\mathrm{H}) = 7.6\ \mathrm{Hz},\ \mathrm{CH}), \ +7.68\ (2\mathrm{H},\ \mathrm{d},\ {}^2J(^1\mathrm{H-}^1\mathrm{H}) = 7.9\ \mathrm{Hz},\ \mathrm{CH}), \ +3.44\ (2\mathrm{H},\ \mathrm{s},\ \mathrm{BH}), \ +3.22\ (12\mathrm{H},\ \mathrm{s},\ \mathrm{CH}), \ +2.70\ (6\mathrm{H},\ \mathrm{s},\ \mathrm{BH}), \ +0.24\ (2\mathrm{H},\ \mathrm{s},\ \mathrm{BH}), \ -2.75\ (1\mathrm{H},\ \mathrm{s},\ \mathrm{BHB}), \ -3.50\ (2\mathrm{H},\ \mathrm{s},\ \mathrm{BHB}). \ {}^{1}\mathrm{H-}^{\{11}\mathrm{B}\}\ \mathrm{NMR}\ (500\ \mathrm{MHz},\ \mathrm{CDC}_{3},\ 318\ \mathrm{K}):\ \delta\ +18.91\ (1\mathrm{H},\ \mathrm{s},\ [\mathrm{H-N-PS}]^+), \ +7.97\ (2\mathrm{H},\ \mathrm{d},\ {}^2J(^1\mathrm{H-}^1\mathrm{H}) = 8.2\ \mathrm{Hz},\ \mathrm{CH}), \ +7.78\ (2\mathrm{H},\ \mathrm{d},\ {}^2J(^1\mathrm{H-}^1\mathrm{H}) = 7.9\ \mathrm{Hz},\ \mathrm{CH}), \ +7.78\ (2\mathrm{H},\ \mathrm{d},\ {}^2J(^1\mathrm{H-}^1\mathrm{H}) = 7.9\ \mathrm{Hz},\ \mathrm{CH}), \ +3.44\ (2\mathrm{H},\ \mathrm{s},\ \mathrm{BH}), \ +3.22\ (12\mathrm{H},\ \mathrm{s},\ \mathrm{CH}),\ +2.70\ (6\mathrm{H},\ \mathrm{s},\ \mathrm{BH}), \ +3.24\ (2\mathrm{H},\ \mathrm{s},\ \mathrm{BH}), \ +3.22\ (12\mathrm{H},\ \mathrm{s},\ \mathrm{CH}), \ +2.70\ (6\mathrm{H},\ \mathrm{s},\ \mathrm{BH}), \ +0.25\ (2\mathrm{H},\ \mathrm{s},\ \mathrm{BH}),\ -3.47\ (3\mathrm{H},\ \mathrm{s},\ \mathrm{BHB}). \end{split}$$

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

We acknowledge the University of Zaragoza (UZ2017-188-43, UZ2015-CIE-09) for financial support.

Notes and references

- 1 A. Stock, *Hydrides of Boron and Silicon*, Cornell University, Ithaca, NY, 1933.
- 2 M. F. Hawthorne, in *Adv. Inorg. Chem. Radiochem*, ed. H. J. Emeléus and A. G. Sharpe, Academic Press, 1963, vol. 5, pp. 307–345.
- 3 V. I. Stanko, A. C. Yu, V. A. Brattsev and I. Z. Leonid, *Russ. Chem. Rev.*, 1965, **34**, 424.
- 4 T. Onak, in *Comprehensive Organometallic Chemistry*, ed.
 G. Wilkinson, F. G. A. Stone and E. W. Abel, Pergamon Press, Ltd., Oxford, 1982, vol. 1, pp. 411–457.
- 5 L. Barton, T. P. Onak, R. J. Remmel and S. G. Shore, in *Gmelin Handbuchder Anorganischen Chemie*, Erg-Werk, 1979, vol. 54, "Borverbindungen 20", pp. 122–209.
- 6 N. S. Hosmane, *Boron Science: New Technologies and Applications*, CRC Press, Boca Raton, FL, 2012.
- 7 N. S. Hosmane and J. A. Maguire, in *Comprehensive* Organometallic Chemistry III, ed. D. Michael, P. Mingos and R. H. Crabtree, Elsevier, Oxford, 2007, pp. 175–264.
- 8 R. N. Grimes, *Carboranes*, Academic Press, Elsevier Inc., Amsterdam, 2nd edn, 2011.
- 9 T. Onak, in *Comprehensive Organometallic Chemistry*, ed.
 E. W. Abel, F. G. A. Stone and G. Wilkinson, Elsevier Science Ltd., Oxford, 1995, vol. 1, pp. 217–255.
- L. T. Todd, in *Comprehensive Organometallic Chemistry*, ed.
 G. Wilkinson, F. G. A. Stone and E. W. Abel, Pergamon Press Ltd., Oxford, 1982, vol. 1, pp. 534–553.
- 11 L. Wesemann, in *Comprehensive Organometallic Chemistry*, ed. D. M. P. Mingos and R. H. Crabtree, Elsevier, Oxford, 2007, vol. 3, pp. 113–131.
- 12 K. Baše, Collect. Czech. Chem. Commun., 1983, 48, 2593.
- 13 R. W. Rudolph and W. R. Pretzer, *Inorg. Synth.*, 1983, 22, 226–228.

- 14 P. Paetzold, Eur. J. Inorg. Chem., 1998, 1998, 143– 153.
- J. L. Little, S. S. Pao and K. K. Sugathan, *Inorg. Chem.*, 1974, 13, 1752–1756.
- 16 K. Baše, M. G. H. Wallbridge, X. L. R. Fontaine, N. N. Greenwood, J. H. Jones, J. D. Kennedy and B. Stibr, *Polyhedron*, 1989, 8, 2089–2090.
- 17 B. Stibr, K. Base, J. Plešek, S. Heřmánek, J. Dolansky and Z. Janousek, *Pure Appl. Chem.*, 1977, 49, 803–811.
- 18 L. Barton and D. K. Strivastava, in *Comprehensive Organometallic Chemistry II*, ed. E. W. Abel, F. G. A. Stone and G. Wilkinson, Pergamon, New York, 1995, vol. 1, pp. 275–372.
- 19 J. D. Kennedy, Prog. Inorg. Chem., 1986, 34, 211-434.
- 20 A. S. Weller, in *Comprehensive Organometallic Chemistry III*, ed. R. H. Crabtree and D. M. P. Mingos, Elsevier, Oxford, 2007, vol. 3, pp. 133–174.
- 21 A. K. Saxena, J. A. Maguire and N. S. Hosmane, *Chem. Rev.*, 1997, **97**, 2421–2462.
- 22 J. Bould, V. Passarelli, L. A. Oro and R. Macías, *Eur. J. Inorg. Chem.*, 2017, 2017, 4599–4617.
- 23 R. Macías, J. Bould, J. Holub, B. Štíbr and J. D. Kennedy, *Dalton Trans.*, 2008, 4776–4783.
- 24 G. A. Guter and G. W. Schaeffer, J. Am. Chem. Soc., 1956, 78, 3546–3546.
- 25 S. Heřmánek, H. Plotová and J. Plešek, *Collect. Czech. Chem. Commun.*, 1975, **40**, 3593–3601.
- 26 Y. Li, P. J. Carroll and L. G. Sneddon, *Inorg. Chem.*, 2008, 47, 9193–9202.
- 27 P. D. McCrary, P. S. Barber, S. P. Kelley and R. D. Rogers, *Inorg. Chem.*, 2014, 53, 4770–4776.
- 28 G. M. Bodner and L. G. Sneddon, *Inorg. Chem.*, 1970, 9, 1421-1423.
- 29 A. R. Siedle, G. M. Bodner and L. J. Todd, J. Inorg. Nucl. Chem., 1971, 33, 3671–3676.
- 30 C. W. Yoon, U. Kusari and L. G. Sneddon, *Inorg. Chem.*, 2008, 47, 9216–9227.
- 31 T. Onak, H. Rosendo, G. Siwapinyoyos, R. Kubo and L. Liauw, *Inorg. Chem.*, 1979, 18, 2943–2945.
- 32 A. J. Wynd and A. J. Welch, Acta Crystallogr., Sect. C: Cryst. Struct. Commun., 1989, 45, 615–617.
- 33 L. G. Sneddon, J. C. Huffman, R. O. Schaeffer and W. E. Streib, *J. Chem. Soc., Chem. Commun.*, 1972, 474– 475.
- 34 E. B. Moore Jr., R. E. Dickerson and W. N. Lipscomb, J. Chem. Phys., 1957, 27, 209–211.
- 35 R. Brill, H. Dietrich and H. Dierks, Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem., 1971, 27, 2003– 2018.
- 36 R. S. Rowland and R. Taylor, *J. Phys. Chem.*, 1996, **100**, 7384-7391.
- 37 W. N. Lipscomb, Adv. Inorg. Chem. Radiochem., 1959, 1, 117–156.
- 38 M. Hofmann and P. v. R. Schleyer, *Inorg. Chem.*, 1998, 37, 5557–5565.
- 39 S. Hermánek, Chem. Rev., 1992, 92, 325-362.

- 40 J. D. Kennedy and B. Stíbr, in *Current Topics in the Chemistry of Boron*, ed. G. Kabalka, The Royal Society of Chemistry, Cambridge, 1994, pp. 285–292.
- 41 A. Vellé, A. Cebollada, S. Ruiz, C. Fonseca Guerra and P. J. Sanz Miguel, *Cryst. Growth Des.*, 2015, **15**, 5873–5878.
- 42 A. Vellé, A. Cebollada, R. Macías, M. Iglesias, M. Gil-Moles and P. J. Sanz Miguel, *ACS Omega*, 2017, **2**, 1392–1399.
- 43 P. S. Pregosin, P. G. A. Kumar and I. Fernández, *Chem. Rev.*, 2005, **105**, 2977–2998.
- 44 APEX2, Bruker-AXS, Madison, Wisconsin, 2011.
- 45 G. M. Sheldrick, *SHELXS-97 AND SHELXL-97*, University of Göttingen, Germany, 1997.
- 46 L. J. Farrugia, J. Appl. Crystallogr., 1999, 32, 837-838.
- 47 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. Marenich, J. Bloino, B. G. Janesko, R. Gomperts,
 - B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov,

J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman and D. J. Fox, *Gaussian 09, Revision A.02*, Gaussian, Inc., Wallingford CT, 2016.

- 48 R. Peverati and D. G. Truhlar, J. Phys. Chem. Lett., 2012, 3, 117–124.
- 49 A. V. Marenich, C. J. Cramer and D. G. Truhlar, *J. Phys. Chem. B*, 2009, **113**, 6378–6396.