Access to cationic polyhedral carboranes via dynamic cage surgery with N-heterocyclic carbenes

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Polyhedral boranes and heteroboranes appear almost exclusively as neutral or anionic species, while the cationic ones are protonated at exoskeletal heteroatoms or they are instable. Here we report the reactivity of 10-vertex closo-dicarbadecaboranes with one or two equivalents of N-heterocyclic carbene to 10-vertex nido mono- and/or bis-carbene adducts, respectively. These complexes easily undergo a reaction with HCl to give cages of stable and water soluble 10-vertex nido-type cations with protonation in the form of a BHB bridge or 10-vertex closo-type cations containing one carbene ligand when originating from closo-1,10-dicarbadecaborane. The reaction of a 10-vertex nido mono-carbene adduct with phosphorus trichloride gives nido-11-vertex 2-phospha-7,8-dicarbaundecaborane, which undergoes an oxidation of the phosphorus atom to P=O, while the product of a bis-carbene adduct reaction is best described as a distorted C2B6H8 fragment bridged by the (BH)2PCl2+ moiety.
n the hundred-year-history of boron hydrides and their successors (polyhedral boranes, carboranes and other heteroboranes) and derivatives, the number, molecular shape, reactivity and applications of these species have become enormous, thus establishing a self-consistent field of chemistry. Examples in synthetic organic chemistry and catalysis include the early use of diborane in organic chemistry as a reducing agent; ionic closo-carboranes as weakly-coordinating anions, transfer agents or recently as a supporting scaffold for the stabilization of low-valent main-group elements by silylenes and low-coordinate boron species for the one-pot reduction of dinitrogen to ammonium chloride. Especially the last case, based on Robinson’s idea, further developed by Braunschweig, of the use of supporting N-heterocyclic carbene (NHC) ligands, could open avenues for synthetic applications. There are also a number of applications in multidisciplinary areas such as energy storage and conversion, materials science, nuclear-waste treatment, and medicine, which contribute to the broad scope of this area of chemistry.

Some of the most successful tools for the description and prediction of the structure of these mostly deltahedral species are structural relationships and the related Wade–Mingos rules, which are based on the electron count around the cluster or the number of skeletal electron pairs (SEPs). In general, the species with the same number of SEPs \( n - 1 \) are related if one or two vertices are removed from the neutral or anionic parent closo cluster – e.g. closo \( n \) vertices, nido \( n - 1 \) vertices, arachno \( n - 2 \) vertices and hypso \( n - 3 \) vertices. In other words, for a series of clusters with the same number of vertices \( n \), each step requires one extra SEP, hence \( n + 1 \) for closo up to \( n + 4 \) for hypso. This is only achievable by an increase in the negative charge or the addition of bridging hydrogen atoms. At the same time, the number of the SEPs for monocentric clusters is likely to be different, \( n + 0.5 \) for closo up to \( n + 3.5 \) for hypso, but the cationic clusters are still elusive, except for \( \text{closo-C}_2\text{B}_9\text{H}_{12} \) (3-methylbutyl) radical cation published very recently by Spokony. There is a big number of cationic boronics, however, the positive charge is predominantly located on a functional group connected to the parent borane \( \text{Me}_2\text{S} \), phosphonium \( \text{I} \), and ammonium \( \text{NH} \), not in the borane cage itself.

Taking these considerations into account, one could expect that the addition of a strong \( \sigma \)-donor such as NHCs would increase the electron density on those traditionally taken electron-deficient skeletons and stabilise them like in the many cases of low-valent or cationic main-group elements, described specifically for boron compounds by Braunschweig. Surprisingly enough, the number of studies dealing with the reactivity of polyhedral boranes and heteroboranes with NHCs is limited to 12-vertex \( \text{closo-heteroboranes} \) (\( \text{o-carborane} – 1,2\)-dicarbadodecaborane(12) and \( \text{1-thiadecaborane(12)} \)) and \( \text{13-vertex heteroboranes} \). The reactions of \( \text{o-carborane} \) and \( \text{Xie’s 13-vertex dicarbaboranes mostly lead to deprotonated or deboronated species with one less vertex; in the reactions of thiaborane, however, also cage distortion and the rearrangement of one hydrogen atom from terminal to bridging position have been observed. Such a transformation should formally lead to a \( \text{nido-arrangement} \), but the count of SEPs varies depending on the nature of the bond between the borane cluster and carbene. In addition, the \( \text{o-carborane} \) reacts with two equivalents of \( \text{Os}_2\text{(CO)}_9\text{(NCMe)}_2 \) upon opening the carbobane cage by \( \text{C-B} \) and \( \text{B-B} \) bonds cleavage, while the reduction of main-group element compounds containing the redox- noninnocent bis(silylenyl)-o-carboranyl ligand led to the breaking of \( \text{C-C} \) bond upon formation of radical anions.

Based on the fact that decaborane(14) is the most prominent starting compound in the chemistry of boranes and heteroboranes, we started our exploration of the reactivity of NHCs with compounds in ten-vertex series in order to find access to elusive compounds and structural patterns.

In this work, we report the reactions of one of the most sterically demanding NHCs with \( \text{closo-dicarbadecaborane} \) series, as smaller congeners of the most frequently used 12-vertex \( \text{closo} \) compounds, which yields the ten-vertex \( \text{nido} \) mono- or bis-carbene adducts, respectively. Upon reaction with HCl, thermally stable and water-soluble positively charged derivatives are obtained.

**Results and discussion**

Three particular pathways (Fig. 1) of selected NHC (\( \text{iPr} \), 1,3-(2,6-\text{iPr}-\text{C}_6\text{H}_4)\text{-imidazole-2-ylidene} \)) reactivity with three different ten-vertex \( \text{closo-dicarbadecaboranes} \), \( \text{closo-1,2-dicarbadecaborane} \) in the trivial nomenclature referred to as \( \text{ortho} \) (red trace); \( \text{closo-1,6-dicarbadecaborane} \) – \( \text{meta} \) (blue trace); and \( \text{closo-1,10-dicarbadecaborane} \) – \( \text{para} \) (green trace) have been investigated. First, \( \text{o-carborane} \) reacts vigorously with one equivalent of \( \text{iPr} \), producing \( \text{nido-o-1} \), which is in accordance with the reactivity of 12-vertex heteroboranes \( \text{closo-C}_2\text{B}_{10}\text{H}_{12} \) or \( \text{closo-12-X-1SB}_{11}\text{H}_{10} \) (\( R = \text{H}, \text{I} \)). The \( ^{11} \text{B} \) NMR spectrum exhibits eight different signals of equal intensity. Despite the neutral charge of \( \text{closo-o-1} \), its pattern is remarkably similar to that of its structural analogue, \( \text{nido-5-C}_6\text{B}_{11}\text{H}_{12} \). The solid-state structure of \( \text{closo-o-1} \) has been determined by scXRD methods (Fig. 2). The \( \text{o-carborane} \) crystallises in the acyclic group \( \text{H}_4\text{OC} \) with distorted decaborane(14)-like structure containing one bridging hydrogen located between \( \text{B9} \) and \( \text{B10} \) atoms. The separations of \( \text{C11} \) atom from carbene and \( \text{B8} \) \( 1.583(3) \) Å are close to the values found for the reported adducts of a carbene and boranes, carbones or thiaboranes, respectively.

Interestingly, the distances from the upper vertex \( \text{C6} \) to \( \text{C7} \) \( 1.474(4) \) Å and \( \text{B5} \) \( 1.503(4) \) Å and from the upper vertex \( \text{B9} \) to \( \text{B8} \) \( 1.672(4) \) Å are significantly shorter than the separations of the respective elements found in related compounds. On the other hand, the \( \text{B5-B10} \) bond is much longer \( 1.969(4) \) Å than the rest of such \( \text{B-B} \) bonds and is reminiscent of the upper-rim \( \text{B-B} \) bonds in pseudo-\( \text{nido} \) thiaborane–carbene adducts.

Remarkably, \( \text{o-carborane} \) (\( \text{o-1} \)) reacts solidly with two (one) equivalents of \( \text{iPr} \) (Fig. 1), producing borane \( \text{o-2} \). This is in contrast with the published reactivity of 12-vertex heteroboranes, which undergo deprotonation or boron-atom extrusion with the addition of the second equivalent of the carbene. The \( \text{o-carborane} \) and \( \text{Xie’s 13-vertex dicarbaboranes mostly lead to deprotonated or deboronated species with one less vertex; in the reactions of thiaborane, however, also cage distortion and the rearrangement of one hydrogen atom from terminal to bridging position have been observed. Such a transformation should formally lead to a \( \text{nido-arrangement} \), but the count of SEPs varies depending on the nature of the bond between the borane cluster and carbene. In addition, the \( \text{o-carborane} \) reacts with two equivalents of \( \text{Os}_2\text{(CO)}_9\text{(NCMe)}_2 \) upon opening the carbobane cage by \( \text{C-B} \) and \( \text{B-B} \) bonds cleavage, while the reduction of main-group element compounds containing the redox noninnocent bis(silylenyl)-o-carboranyl ligand led to the breaking of \( \text{C-C} \) bond upon formation of radical anions.

Based on the fact that decaborane(14) is the most prominent starting compound in the chemistry of boranes and heteroboranes, we started our exploration of the reactivity of NHCs
asymmetrical behaviour of \( m-2 \). In this molecule, the upper vertex B6 enters the virtual centre of the cage more closely than the B9 one, which is reflected in the magnitudes of the interatomic angles B4-B2-B6 \[90.44(11)°\] vs. B2-B4-B9 \[97.50(9)°\] and C11-B6-B9 \[175.81(13)°\] vs. C38-B9-B6 \[159.83(11)°\]. The lengths of the bonds between the upper vertex B atom and the carbene as well as the respective lower vertex are significantly different – B9-C38 1.577(3) Å; B2-B6 1.863(3) Å, whereas the other skeletal B–B and C–B bonds are similar to those of \( o-1 \). In the case of \( p-2 \), the alternating but symmetrical positions of the carbon atoms inside the cluster predetermine the averaging of the respective separations, such as 1.604(7) and 1.622(6) Å for the B-carbene ones. In fact, these structures evoke the structure suggested for the transition state of the isomerisation of ten-vertex clusters by Z-mechanism\(^{43}\).

**Fig. 1** Reactivity of 10-vertex closo-dicarbadecaboranes. All the ten-vertex carboranes show different reactivity towards the carbene and subsequently hydrogen chloride or phosphorus trichloride. closo-1,2-dicarbadecaborane is referred to as ortho \((o, \text{red trace})\); closo-1,6-dicarbadecaborane is referred to as meta \((m, \text{blue race})\); closo-1,10-dicarbadecaborane is referred to as para \((p, \text{green trace})\).  

**Fig. 2** The molecular structures of \( o-1 \) (left), \( m-2 \) (centre) and \( p-2 \) (right). ORTEP-type plots, 40% probability level. The 2,6-diisopropylphenyl groups are displayed as wireframes for clarity.
noteworthy that such isomerisation of parent carboranes \( o \) and \( m \) to the thermodynamically most stable \( p \) requires very harsh conditions (temperature above 350 °C).\(^{44}\)

Compounds \( o-1 \), \( o-2 \), \( m-2 \) and \( p-2 \) were treated by hydrogen chloride in order to cleave the boron–carbene bond(s) and presumably obtain neutral open-cage \( nido \) or \( arachno \) compounds. Surprisingly, \( o-1 \) did not even react with an over-stoichiometric amount of hydrogen chloride—only a slow decomposition into several undefined compounds was observed after 1 week. On the contrary, \( o-2 \) and \( m-2 \) were unexpectedly converted into their corresponding hydrochlorides \( o-2a \) and \( m-2a \), which is, to the best of our knowledge, the first example of a proton capture by a neutral borane cage leading to the formation of a cation without any changes in the functional groups. Such a reactivity is known for of amino, sulfido or phosphino based exoskeletal functional groups protonation or quaternionization\(^{30-32}\). In this respect, there is only one example of the substitution of sulfide groups in bis-dialkylsulfido-dodecahydrododecaborane with hydrogen halogenides.\(^{45}\) Both carboranes \( o-2a \) and \( m-2a \) are very stable—there was no decomposition observed after 1-month exposure to air and they do not react with the hydrogen chloride or even with the excess of triethylamine. The \( ^{11}B \) NMR spectra of compounds \( o-2a \) and \( m-2a \) exhibit the same pattern as their precursors with only a few chemical-shift changes. This fact indicates only slight changes in the overall structure of the carborane cage, which was also confirmed by scXRD methods (Fig. 3).

The structures of both \( o-2a \) and \( m-2a \) cage parts closely resemble the neutral parent compound \( m-2 \), with the only exception being the elongation of the \( B7–B8 \) and \( B9–B10 \) bonds to \( \approx 1.84 \text{ Å} \), which is characteristic of boron atoms, bridged by the hydrogen atom originating from HCl. The difference between the position of that bridge in \( o-2a \) and \( m-2a \) is a result of the mutual distribution in prepared compounds. The central borane cluster \( C_{2}B_{8}H_{10} \) in \( o-1 \) and \( o/m/p-2 \) revealed slightly negative charge \((−0.023 − (−0.044) \text{ e}) \), for more details see Supplementary Table 11), while the carbene moieties showed slightly positive values \((0.006–0.041 \text{ e}) \) with the exception of \( m-2 \) \((+0.088 \text{ and } −0.061 \text{ e}) \), which is not surprising considering its unsymmetrical structure. The situation changes dramatically in the cationic series \( o/m/p-2a \). The positive charge is predominantly localised in the boron cluster (0.692–0.713 \text{ e}) however, the carbene groups still preserved the slightly positive charges \((0.071–0.123 \text{ e}) \).

The cationic character of the cages is also reflected in the fact that the compounds are sensitively detected in the positive ion mode. In contrast, electrospray-based mass spectrometry studies of the majority of borane and carborane compounds reveal the molecular peaks in the negative-ion mode.\(^{46}\)

Having the cationic borane clusters in hand and bearing the fact that several boranes or carboranes exhibit promising biological activity in mind, we tested the solubility and stability of \( o-2a \) and \( p-2 \) in water solution. Both compounds showed satisfactory solubility and appropriate NMR spectral patterns in \( D_{2}O \) with no decomposition, and they had the same traces of ESI-MS spectra before and after a day in a water solution.

A logical way to investigate the reactivity of open heteroborane clusters is to increase the number of vertices by the incorporation of a new boron atom or a heteroatom. Therefore, we treated the carboranes \( o-1 \) and \( o-2 \), \( m-2 \) and \( p-2 \) with phosphorus trichloride (Fig. 1). Both \( o-1 \) and \( o-2 \) were able to accommodate the phosphorus atom forming the heteroboranes \( o-1a \) and \( o-2b \), whereas \( m-2 \) and \( p-2 \) gave only mixtures of various products, predominantly their hydrochlorides \( m-2a \) and \( p-2a \). Several isomers and its derivatives of phosphadecaborane \( P_{3}C_{3}B_{11} \) have already been published in the literature\(^{37,48}\) but there is no evidence of a cluster bearing the phosphorus atom inside the cage (positions 1–6). It is usually located in the upper five-membered ring. This might also be one of the reasons for the reactivity of \( o-1a \) with oxygen, because it reacts even with traces of air to the oxidised form \( o-1b \) with the phosphorus atom already situated in

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**Fig. 3** The molecular structures of \( o-2a \) (left), \( m-2a \) (centre) and \( p-2a \) (right). ORTEP-type plots, 40% probability level. \( Cl^{-} \) or \( HCl^{-} \) anions and dichloromethane solvates are omitted for clarity. The 2,6-diisopropylphenyl groups are displayed as wireframes for clarity.
the position 2, which is in sharp contrast to the air-stable analo- 
gues published.47,48

Moreover, o-1b is a unique example of structurally char- 
acterised neutral heteroborane bearing an exoskeletal terminal double bond on a skeletal atom. Up to date, there are two 
structurally characterised anionic boranes with such a kind of bond, namely [endo-6(=S)-exo-6-R-arachno-6,7-PCB5H11] − and 
[1,2-O(Ph)C2B10H10] −, which again proves the high stabilisation 
potential of the carbene group. The 11B NMR spectra of o-1a 
and o-1b have revealed the same pattern with small differences in 
chemical shifts. The 31P NMR spectra of compounds o-1a, o-1b 
and o-2b always revealed one broad signal for the skeletal phosphorus atom. In the case of o-1a, the chemical shift (−82.5 
ppm) lies directly in the range of its published phosphacarborane analogues47,48,50 with the phosphorus atom in position 7 
(−67.7−(−104.0) ppm). The oxidation of the phosphorus atom by oxygen is usually tied to higher shielding and an upfield shift of the 31P NMR signal. On the contrary, o-1b (32.0 ppm) is 
strongly downfield shifted, which corresponds to the changes in the bonding pattern. Finally, o-2b (97.1 ppm) has no structural analogue (central B,PCl3 pattern), and thus it could not be compared.

The molecular structures (Fig. 5) of o-1a and o-1b are com- 
parable in terms of C−C, C−B, P−B and P−C separations, but the placement of the phosphorus atom and carbene ligand in the lower pentagon together with four boron atoms in o-1a is quite different from the situation found in o-1b. Formally, the nido-
type 11-vertex cluster o-1b has only three P−B bonds, and phosphorus is found in the upper open area. Moreover, the oxidation of the phosphorus atom has produced a very short P = O bond of 1.468(3) and 1.477(4) Å for two independent molecules.

Unexpectedly, the reaction of o-2 with phosphorus trichloride did not proceed as a condensation, unlike in the case with o-1. At first glance, it seemed that the carborane o-2 acted as a bidentate ligand coordinating the central phosphorus atom and forcing ionisation. The same side reaction has been observed as in cases of m-2 and p-2, where the addition of phosphorus trichloride produces hydrogen chloride and subsequently compound o-2a. However, o-2b could still be isolated in moderate yield (38%) thanks to its poor solubility in THF. The 11B NMR spectrum has a pattern very similar to o-2a, with differences in chemical shifts of B1 (22 ppm upfield) and B3 (15 ppm downfield). When the structure of o-2b was inspected for the second time (Fig. 5), the PCl3+ fragment did not have a shape typical of P(III), but it could be described as a cationic structure of pentavalent phosphorus. This suggestion could be supported not only by the shape of the slightly distorted tetrahedron on the P atom, but also by the very short P−B distances [P11−B7 1.859(4) Å, P11−B8 1.856(4) Å]. In addition, the B7 and B8 atoms are bound to the rest of the boron atoms in the cage in a non-standard way, where one short [B2−B7 1.683(6) Å, B4−B8 1.687(6) Å] bond has been found for each of the B7 and B8 atoms, and the remaining separations are much longer than expected (~2 Å). To explain these parameters, one could suggest that the phosphorus atom shares the electron density of the former lone electron pair to the formation of strong connections to the B7 and B8 atoms, while these are somehow expelled from the shape of the previous ten-vertex cluster. Stabi-
ilisation of an electron-deficient group of the main-group

Fig. 4 Computed (B3LYP/cc-pVTZ) ESP surface for p-2a. The colour range of the ESP is kcal/mol. The negative surface is located on HCl2−, the areas with the most positive ESP are the CH vertexes of the carborane cage and CH = CH fragment of the NHC.

Fig. 5 The molecular structures of o-1a (left), o-1b (centre) and o-2b (right). ORTEP-type plots, 40% probability level. Chloride anion and dichloromethane solvates are omitted for clarity in o-2b. The 2,6-disopropylphenyl groups are displayed as wireframes for clarity.
element in o-2b is a rare example of nucleophilic reactivity of a boron cluster and it would definitely not be possible without strong electron donation from the NHCs, which supports the C2B3H5 fragment interacting with the (BH)3P2Cl- part. The cationic character of the central heteroborane cage in o-2b was proved by the IBO and AIM analysis of bonding orbitals and the atomic charges, which revealed similar results when compared to o/m/p-2a (0.659 e, for more details, see Supplementary Table 12). By the same approach, the bonding pattern in the area of B6, P11 and B8 atoms was explored and estimated to be a shared interaction.

In this work, the involvement of NHCs in the chemistry of closo-ten-vertex carboranes leads surprisingly to the opening of closo types with no deprotonation or the loss of a boron vertex. Paradoxically, the introduction of adjacent-electron density into these structures by NHCs provides, after protonation by HCl, thermally robust cationic carboranes, which could potentially resolve the solubility and stability problems that often hamper the further applicability of this class of compounds. In addition, the reactivity of these NHC adducts with PCl3 results in uncommon cage patterns and redox activity.

**Data availability**
The crystallographic data for structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 2062928-2062936. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EY, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk). The NMR data have been deposited at Figshare.com and are available at [https://doi.org/10.6084/m9.figshare.1505943#v3].

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Author contributions
J.V. and A.R. designed the study. J.V. and J.H. synthesised the compounds and measured NMR spectra. A.R., M.A.S. and Z.R. determined and refined the structures by scXRD. J.C. measured and analysed compounds by MS techniques. M.A.S., J.F., M.L.M. and D.H. performed the computations. J.V. and A.R. wrote the paper with input from all authors.

Competing interests
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