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Application of the aza-Wittig reaction for the synthesis of carboranyl Schiff bases, benzothiazoles and benzoselenazolines†

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The aza-Wittig reaction was successfully applied to the synthesis of carboranyl-imines, which are difficult to obtain by classical methods. A variety of functionalized carboranyl Schiff bases was obtained proving the great scope of the methodology. All compounds were fully characterized, including the solid-state structures of six of them. The aza-Wittig reaction was modified to permit the synthesis in one step of carboranyl-benzothiazole and carboranyl-benzoselenazoline derivatives. The stability studies show that the carboranyl-imines and benzothiazole promote deboronation to the *nido*-derivatives, which is achieved by simple reaction with methanol or protic solvents. The structures of the *nido*-derivatives were also studied by X-ray diffraction. In contrast, the saturated derivatives, amine and benzoselenazoline, do not promote deboronation and are stable in protic solvents.

Introduction

Icosahedral *ortho*-*closo*-dodecaborane $C_2B_{10}H_{12}$ is the type of heteroborane cluster that has been most extensively studied due to its special electronic and chemical properties. Their functionalized derivatives have found several applications, mainly in the fields of material science,[1] catalysis[2] and medicine.[3] However, this uniqueness can affect the synthesis of different derivatives and impede progress in the study of some well-established functionalities. An example that stands out is the case of imine derivatives.

Imines, azomethines or Schiff bases, are compounds that have an imino group, $R_1HC{=}N–R_2$, *i.e.* a carbon-nitrogen double bond with the nitrogen atom attached to an alkyl or aryl group (not hydrogen).[4] Due to the presence of a donor nitrogen atom, Schiff bases can be used as ligands for the preparation of coordination compounds. In fact, Schiff base ligands are one of the most studied and used types of ligands, due to their ease of preparation and extensive coordination chemistry.[4] Schiff base ligands form metal complexes with virtually all metal ions. These compounds have many interesting applications, especially in biology and catalysis.[5] Thus, compounds derived from Schiff bases have been found with antibacterial, antifungal, anticancer, antioxidant, anti-inflammatory, antimalarial and antiviral activity.[5,6] In addition, many complexes with Schiff bases have high catalytic activity, for example in processes of olefin polymerization, hydrocarbon oxidation, alkene epoxidation, ketone reduction, and Heck reaction, among others.[5,7] The most common synthesis of Schiff bases is very simple and involves the condensation reaction between an aldehyde (or ketone) and a primary amine.

In the specific case of carboranes, we have to distinguish two types of derivatives: those in which the imino group is connected to the cluster through the nitrogen atom, carborane–N=C–R, and those in which it is connected through the carbon atom, carborane–C=N–R. In the case of derivatives of the first type, carborane–N=C–R, the usual synthesis method gives good results, and the small number of examples is due to the difficulty in obtaining the 1-amino-carborane precursors,[8] or 1,2-diamino-carborane,[9] whose syntheses have been perfected recently. In the case of derivatives of the second type, carborane–C=N–R, which are more relevant to this work, although the precursor aldehyde *C*-formyl-carborane can be easily obtained,[10] the low number of described examples is surprising. This is undoubtedly due to the difficulty in carrying out their synthesis, because the classical method of synthesis can give bad results. This usual method has been described for the synthesis of a few carboranyl-imines, although under inert gas conditions.[10–14] However, in the case of other derivatives the method needs especial conditions, such as the use of silica-alumina catalyst support grade 135,[15] which the authors consider crucial, stating that “other reaction conditions proceeded with very poor yields”. It seems that the success in the synthesis by the classical method depends greatly on the

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† Electronic supplementary information (ESI) available: Crystallographic details and selected bonds and angles for all crystal structures. Molecular structure of compound **IB3**. NMR spectra for all compounds. CCDC 2393159–2393168. For ESI and crystallographic data in CIF or other electronic format see DOI: **https://doi.org/10.1039/d4dt03378g**

desired final product. An alternative method has also been described for the synthesis of one imine-carborane, by reaction between carboranyl-lithium and imidoyl chloride,[16] but this is far from being a general method of synthesis for this type of compounds.

The lack of examples of carboranyl-imines should not be mistaken for a lack of potential applications of these compounds. They have been used as precursors of functionalized porphyrins with potential use in cancer therapies as boron neutron-capture therapy (BNCT) and photodynamic therapy (PDT).[11,17] The imine group has been used as a directing group for the *B*-functionalization of carboranes,[12–14] which coupled with the removable nature of the imine moiety can lead to the synthesis of carborane analogs of known drugs, which in some cases produces an improvement of their activity.[13] Besides, the few reported metal complexes with the *nido* form of these imine ligands were also active catalysts for the polymerization of ethylene.[15]

The aza-Wittig method is an alternative method for the synthesis of Schiff bases that, despite being well known,[18] has never been applied to the field of carboranes. This method involves the direct reaction between an aldehyde (or ketone) and an iminophosphorane, leading to imino bond formation under mild conditions. This process requires the preparation of the iminophosphorane precursors in a first step. These compounds, with the general formula $R_3P{=}NR'$, have a P═N double bond and can be easily obtained using the Staudinger reaction[19] or the Kirsanov reaction.[20] The aza-Wittig reaction is the nitrogen equivalent of the Wittig reaction, which has already been successfully tested for the production of alkenyl carboranes.[21] The aza-Wittig reaction proceeds through a tandem [2 + 2] cycloaddition-cycloreversion mechanism. The formation of C═N and O═P bonds occurs at the same time as the breaking of N═P and C═O bonds, producing the target imine and phosphine oxide as a by-product.[18] The nucleophilicity of the iminophosphorane and the electrophilicity of the aldehyde promote the aza-Wittig reaction. Considering the great electron-withdrawing character of the *C*-carboranyl group, the starting material *C*-formyl-carborane seems especially prone to this reaction. In the present work, the aza-Wittig method will be used to obtain carboranyl-imine compounds.

The aza-Wittig method can also be modified to access other types of important carboranyl derivatives as benzothiazole an benzoselenazoline (*vide infra*). Benzothiazoles are a very important class of compounds, due to their biological and pharmacological properties.[22] However, in the field of carboranes there are not many known examples of their derivatives. Literature examples of *ortho*-carboranyl-benzothiazoles include the direct connection of a *C*-*ortho*-carboranyl group to 2-benzothiazole,[23] the connection through a phenyl[24,25] or a sulfide spacer,[26] a B3-derivative[27] and the direct connection of a boron atom of a *o*-*nido*-carborane moiety to the nitrogen atom of the heterocycle.[28] Examples of *meta*-carborane derivatives include compounds with the connection of the benzothiazole carbon atom to a carbon of the cluster[29] and to the B9 position of the cluster.[30] In the case of carboranyl-benzoselenazolines (and benzoselenazoles) there are no reported examples of such compounds.

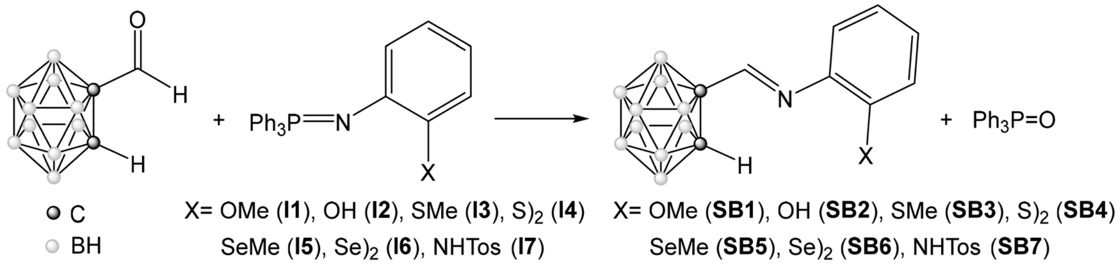
Results and discussion

Synthesis

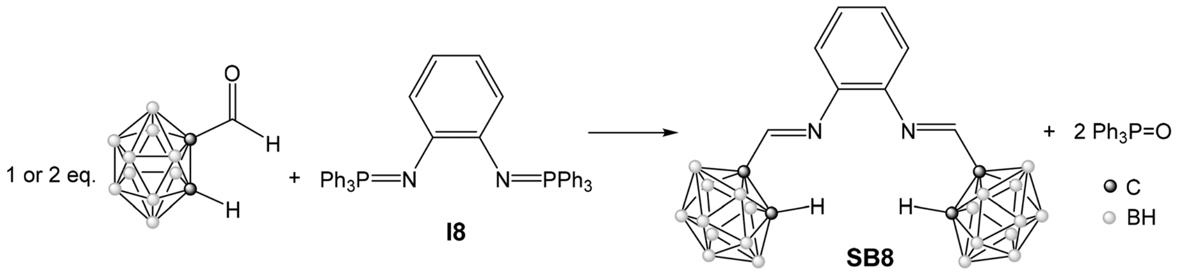
A variety of functionalized carboranyl Schiff Bases was obtained following the aza-Wittig methodology, *i.e.* by simply refluxing *C*-formyl-carborane[10] with the appropriate iminophosphorane precursor in commercial chloroform, as shown in Schemes 1 and 2.

The functionalized iminophosphorane precursors are non-commercial compounds that have to be previously obtained. Compounds **I1–4** and **I8** have been described in the literature[31–35] and the rest of them can be easily prepared using the Kirsanov method,[20] by direct reaction of commercial dibromotriphenylphosphine with the corresponding amine in the presence of dry triethylamine, in dry toluene at reflux (see Experimental section). The characterization of the compounds confirmed the formation of the expected iminophosphoranes. In particular, the IR spectra show a very intense band between 1346 and 1328 cm^{-1}, due to the stretching vibration of the P═N bond, and the $^{31}P\{^1H\}$ NMR spectra show a single signal between 6.9 and −0.3 ppm due to the presence of the iminophosphorane group in the compounds.

The aza-Wittig method used to produce the functionalized carboranyl Schiff bases **SB1–7** (Scheme 1) is experimentally very simple and requires the use of few precautions. It was very efficient in all cases, producing the desired products in very good yields (75–99%). The production of the bis-imine **SB8** was also possible (Scheme 2), although less efficiently (35%).



Scheme 1 Synthesis of functionalized carboranyl-imines using the aza-Wittig reaction.



Scheme 2 Synthesis of a bis(carboranyl-imine) using the aza-Wittig reaction.

The success in the synthesis of the bis(carboranyl-imine) derivative **SB8** also proves that this method can be used for the synthesis of compounds containing several imine-carborane groups. The only limitation is the fact that this reaction cannot be controlled by stoichiometry. Thus, when bis(iminophosphorane) **I8** is treated with one equivalent of *C*-formyl-carborane under the described conditions, only the bis(imine-carborane) **SB8** is obtained.

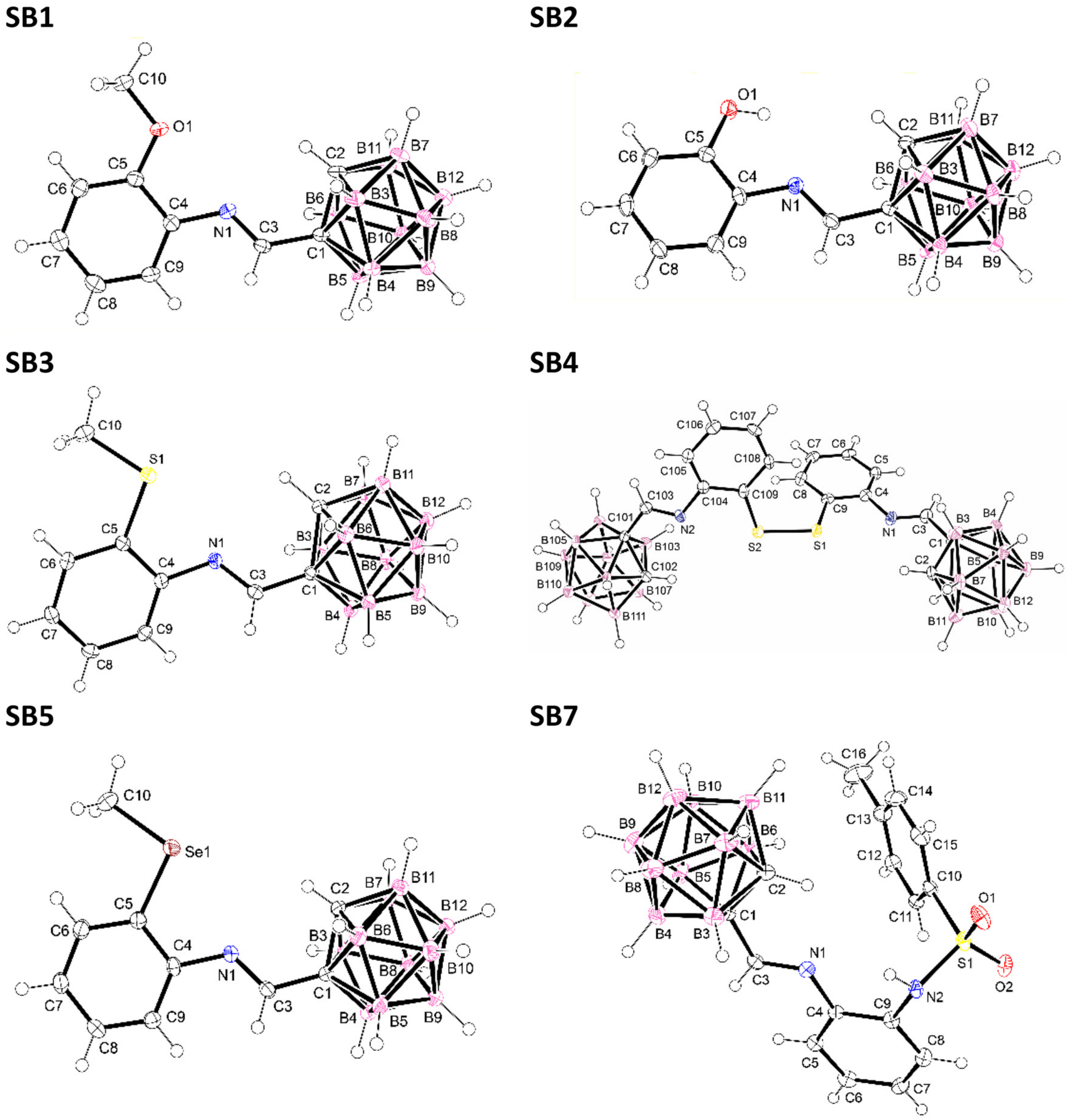
All compounds **SB1–8** were characterized by IR spectroscopy, ^{1}H, ^{13}C and ^{11}B NMR spectroscopy, mass spectrometry and elemental analysis. The IR spectra of these compounds show the B–H stretching between 2635 and 2565 cm^{-1}, which is compatible with the presence of a *closo*-carborane cluster, and a band associated with the imine bond, $\nu(C{=}N)$, between 1639 and 1634 cm^{-1}, due to the formation of the Schiff bases. The imine carbon also appears in the $^{13}C\{^{1}H\}$ NMR spectra, between 154.3 and 149.5 ppm. The ^{1}H NMR spectra show the resonance of the iminic proton between 8.01 and 7.65 ppm, which also confirms the success of the method. The $C_{cluster}$–H signal, between 4.56 and 4.29 ppm, indicates the formation of mono-substituted *ortho*-carboranyl derivatives. The range of the signals obtained in $^{11}B\{^{1}H\}$ NMR, between −1.8 and −14.8 ppm, also confirms the presence of the *closo*-carborane cluster in the final products.

Single crystals suitable for X-ray diffraction were obtained for all the Schiff bases, except for the diselenide derivative **SB6** and for the bis-imine derivative **SB8**. All crystals were obtained from solutions in a mixture of dichloromethane and hexane. The solid-state studies confirmed the expected molecular structures for all Schiff bases, shown in Fig. 1. The crystallographic data can be found in Table S1 (ESI†). Selected bond lengths and angles for these compounds are collected in Tables S2 and S3 (ESI†).

In all cases, the carborane substituents are distorted icosahedra with the expected order of bond lengths: C–C < C–B < B–B. The C–C distances of the clusters are all very similar, in the range 1.622(3)–1.637(2) Å, and very similar to the mean value of 1.631 Å found for the only 12 structures of carboranyl Schiff bases reported in the literature.[12–15] Likewise, the imine bond distances, in the range 1.248(5)–1.272(5) Å, are similar to the mean value of 1.253 Å found for the literature examples, and typical of a C=N double bond.

The synthesized imine-carboranes **SB1–7** present different potentially donating functional groups on the *ortho* position of the phenyl ring attached to the iminic nitrogen atom. The success of their synthesis shows the great scope of the aza-Wittig method and its compatibility with other functional groups. It is interesting to remember that the literature examples only present non-functionalized aromatic groups attached to the imine nitrogen atom, apart from two examples with an *ortho*-phenol group,[12,14] like the new compound **SB2**. In contrast, the synthesized compounds **SB1–7** have been designed to be potential bidentate chelating ligands (N, X) X = O, S, Se, N, capable of forming five-membered chelate rings by complexation with metal atoms. These ligands are also potential hemilabile ligands that could be exploited for homogeneous catalysis, a category with not many examples in carborane chemistry.[36]

We also checked the scope of the reaction by using carboranyl iminophosphoranes, due to the experience of the research group with these compounds.[34,37,38] Kennedy had already described the C_c-methyl and C_c-phenyl substituted *C*-triphenyliminophosphorane-carboranes as "unreactive substrates for the aza-Wittig reaction",[39] but we wanted to try the reaction with the activated *C*-formyl-iminophosphorane. Unfortunately, under our described conditions the unsubstituted 1-triphenyliminophosphorane-carborane[34] did not react with the carboranyl-aldehyde, and the reactants were recovered unchanged. We also checked if this unreactivity was due to the low basicity of the iminophosphorane caused by the electron-withdrawing character of the *C*-carboranyl group. Thus, we prepared and characterized the previously not reported B3-triphenyliminophosphorane-carborane (**IB3**), as the B3-carboranyl group is less electron-withdrawing than the *C*-carboranyl one.[38] This compound is easily obtained from 3-amino-carborane (see Experimental section), and shows the typical features of the other iminophosphoranes, *i.e.* a strong band at 1432 cm^{-1} in the IR spectrum due to the $\nu(P–N)$ stretching and a signal at 8.8 ppm in the $^{31}P\{^{1}H\}$ NMR spectrum. It also presents the signals associated with an *ortho*-carborane derivative, as the strong $\nu(B–H)$ band at 2578 cm^{-1} in the IR spectrum and the signal at 3.39 ppm in ^{1}H NMR due to the two equivalent CH protons of the cluster. The $^{11}B\{^{1}H\}$ NMR spectrum is the typical one associated with *closo*-B3-derivatives,[38] with signals in the range (2.6)–(−22.1) ppm, with the signal for the B3 substituted atom at low field, 2.6 ppm. It was also possible to study its solid-state structure using X-ray crystallography (see ESI, Fig. S1†). Unfortunately, the more donor character of



SB1 SB2 SB3 SB4 SB5 SB7

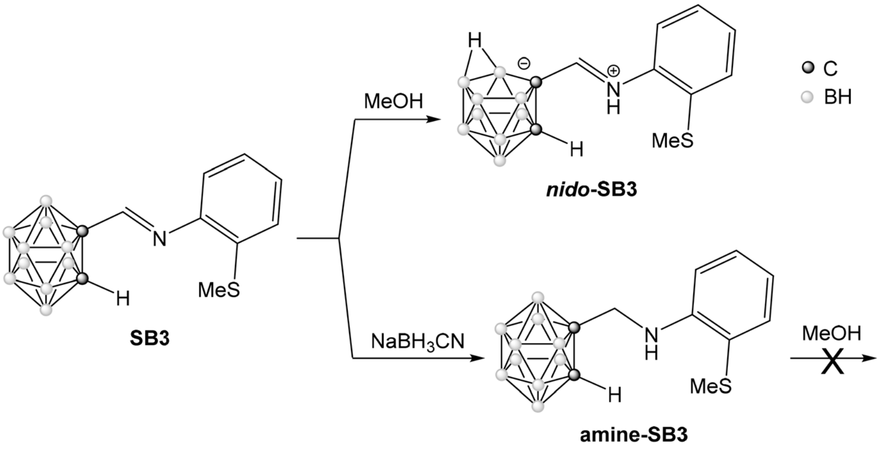
Fig. 1 Molecular structure of carboranyl Schiff bases **SB1–SB5** and **SB7**. Thermal ellipsoids are shown at the 40% probability level.

this iminophosphorane did not result in improved reactivity and, under the described conditions, it did not produce any amount of the expected carboranyl imine.

Stability and reactivity

All the *closo*-carboranyl Schiff bases **SB1–8** can also be used as precursors of other carboranyl derivatives, as the *nido* analogs or the corresponding *closo*-carboranyl amines (Scheme 3).

nido-Carboranes are usually obtained by treatment of the *closo* derivatives with a strong base or a nucleophile.[40] However, it has been shown that some substituents on carbon atoms strongly influence the tendency of carborane to undergo deboronation. Thus, electron-withdrawing substituents increase the electrophilicity of borons adjacent to carbons, which increases their reactivity. For example, ester, aldehyde, sulfoxide and electron-withdrawing aromatic rings are known to favor the evolution to the *nido* form in neutral media.[41] Xie and co-workers showed that the imine group is another one of these groups and that Schiff base derivatives of carborane evolve to *nido* derivatives simply by reaction with methanol, without the need for additional nucleophiles.[15] We have also observed this tendency with the functionalized Schiff bases **SB1–8**. Thus, during the recrystallization of the Schiff bases in air, it was observed that solutions of these compounds in alcohols and water-miscible solvents evolved over time, becoming darker. Analysis of these solutions by $^{11}B\{^1H\}$ NMR and IR spectroscopy revealed degradation to the *nido* derivatives. The solvents tested were methanol, ethanol, acetone, acetonitrile and THF. However, solutions of these compounds in water-immiscible solvents did not evolve over time in air. In this



Scheme 3 Synthesis of *nido*-carboranyl-imine and *closo*-carboranyl-amine using **SB3** as an example.

case, the solvents tested were ethyl ether, ethyl acetate, hexane, toluene, dichloromethane and chloroform. This means that special care must be taken in the choice of solvents when using these compounds.

As an example, Schiff base **SB3** was refluxed in dry methanol, which produced its total conversion to the *nido* analog, ***nido*-SB3** (Scheme 3). IR spectroscopy, as well as ^{1}H and ^{11}B{^{1}H} NMR spectroscopy, are techniques that clearly show the formation of the *nido* derivative. The shift to a lower wave number of about 50 cm^{-1} of the ν(B–H) band in the spectrum of the *nido* compound (2545 cm^{-1}) with respect to the *closo* compound (multiple band between 2635 and 2565 cm^{-1}) confirms the degradation. On the other hand, the ^{1}H NMR spectrum shows a broad signal at −2.27 ppm due to the hydrogen bridge in the open C_2B_3 face. The ^{11}B{^{1}H} NMR spectrum shows a greater number of signals with respect to the *closo* compound in a wider range (−5.2 to −31.3 ppm). The formation of ***nido*-SB3** was also confirmed by its crystal structure (see Fig. 2). The X-ray diffraction studies show that the compound presents a zwitterionic structure, with the imino group protonated and the negative charge located on the open C_2B_3 face.

The carboranyl Schiff bases **SB1–8** can also be transformed to the corresponding amines by reduction.[10,11] As an example, Schiff base **SB3** was treated with cyanoborohydride, affording the saturated **amine-SB3** (Scheme 3). The reduction of the imino group to the amino group is easily observed using techniques such as IR and NMR spectroscopy. Thus, the IR spectrum shows the disappearance of the imino group band, ν(C═N), and the appearance of the ν(N–H) band at 3366 cm^{-1}, due to the new amino group formed. The ^{1}H NMR spectrum shows the disappearance of the iminic proton and the appearance the new CH$_2$ and NH groups, at 3.97 and 4.80 ppm, respectively. In addition, the crystal structure of **amine-SB3** could be studied by single-crystal X-ray diffraction (Fig. 3). These studies confirmed that the compound obtained was the expected amine.

In contrast to the parent imine, **amine-SB3** is stable to the treatment in methanol and its *closo* cluster remains unaffected after 12 hours of reflux in dry methanol.

Apart from these two general transformations that can be performed with all carboranyl Shiff bases, the disulfide **SB4** and the diselenide **SB6** permit more specific reactions.

Treatment of the disulfide Schiff Base **SB4** with triphenylphosphine (Scheme 4) produces its transformation to the

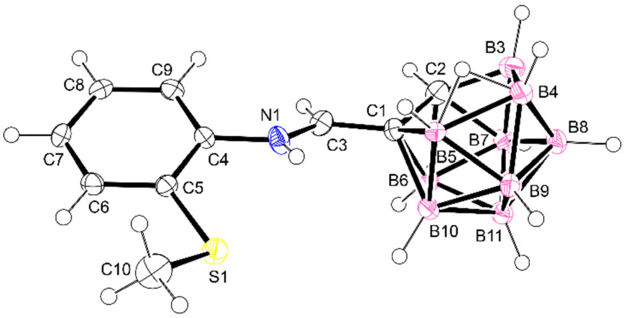


Fig. 2 Molecular structure of ***nido*-SB3**. Thermal ellipsoids are shown at the 40% probability level.

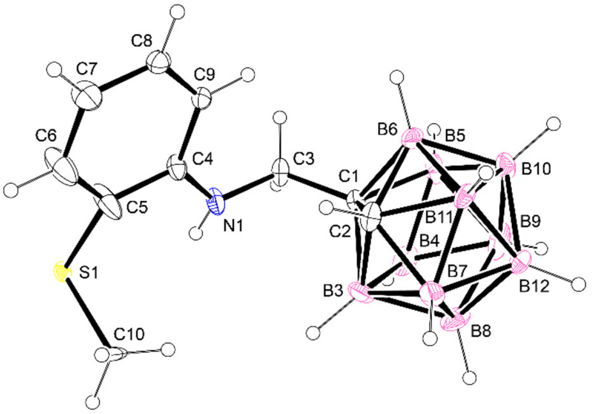
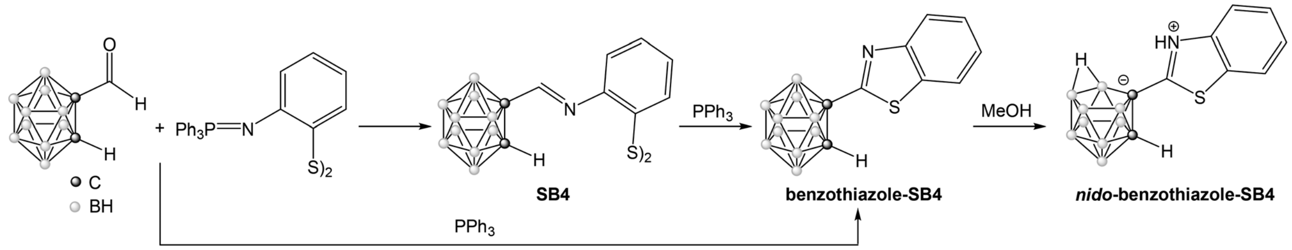


Fig. 3 Molecular structure of **amine-SB3**. Thermal ellipsoids are shown at the 40% probability level.



Scheme 4 Synthesis of **benzothiazole-SB4** and its evolution to ***nido*-(benzothiazole-SB4)**.

cyclic benzothiazole (**benzothiazole-SB4**), as described in the literature for organic analogues.[42] This reaction proceeds through the initial formation of the thiolate, intramolecular attack to the imine bond to form the benzothiazoline and subsequent aerial oxidation to the benzothiazole derivative. The general aza-Wittig protocol can be modified to include triphenylphosphine in the initial reaction mixture, as shown in Scheme 4, producing the benzothiazole in one step with good yield (73%). The ^{1}H NMR spectrum of **benzothiazole-SB4** shows the disappearance of the signal corresponding to the iminic proton of the parent Schiff base and the IR spectrum shows the C=N stretching vibration band shifted from 1639 cm^{-1} to 1504 cm^{-1}. These features indicate the formation of the cyclic benzothiazole. The range of signals found in ^{11}B{^{1}H} NMR spectrum indicates that the *closo* form of the cluster is retained after the reaction.

The **benzothiazole-SB4** with a C=N bond adjacent to the cluster carbon atom is also sensitive to the reaction with methanol, affording the *nido* derivative, as described before for the carboranyl Schiff bases. Thus, recrystallization from methanol produced the formation of ***nido*-(benzothiazole-SB4)**. This compound shows the typical features of a *nido* derivative, with a wider range of signals in ^{11}B{^{1}H} NMR (from −5.1 to −32.9 ppm) and a shift of the ν(B–H) band in the IR spectrum to lower wavenumbers (from 2575 cm^{-1} to 2527 cm^{-1}). The structure of this *nido* derivative was also confirmed by X-ray crystallography (Fig. 4). The compound exhibits a zwitterionic structure, with the nitrogen of the benzothiazole group protonated and the negative charge on the open face of the cluster, as discussed before for ***nido*-SB3**.

The synthesis of the same compound, **benzothiazole-SB4**, has been reported in the literature by condensation of *o*-carboryne and benzothiazole, although in smaller scale and yield.[23] The new aza-Wittig protocol can provide easy access to multigram quantities of this compound. It can also provide access to substituted carboranyl-2-benzothialzoles, starting from substituted amine-disulfides.

In contrast to the disulfide Schiff Base **SB4**, the reaction of the diselenide Schiff Base **SB6** with triphenylphosphine leads to the formation of the benzoselenazoline (Scheme 5). The same product (**benzoselenazoline-SB6**) can also be obtained in one step using the aza-Wittig reaction, including triphenylphosphine in the reaction mixture with the iminophosphorane diselenide **I6** and *C*-formyl-carborane (Scheme 5). The ^{1}H NMR spectrum of the final product shows the disappearance of the signal corresponding to the iminic proton of the Schiff base **SB6**, and the appearance of the signals of the CH group (5.89 ppm) and the NH group (4.74 ppm) formed after cyclization. The IR spectrum does not show an imine band, but a new band at 3370 cm^{-1} due to the NH group. These results indicate that the benzoselenazoline cycle has been formed. The range of signals found in ^{11}B{^{1}H} NMR indicates that the *closo* form of the cluster is retained after the reaction. The formation of this compound is due to the intramolecular attack on the imine bond by the selenolate formed *in situ*. However, in this case the cycle is not oxidized to the benzoselenazole, as found for the sulfur analog previously discussed. Although the result was unexpected, the difference in reactivity could be an effect of the different nature of the chalcogen, as the disulfide could aid in the second oxidation step. This is in line with recent literature, that indicates that the starting disulfide can photosensitize molecular oxygen and facilitate the dehydrogenation step that completes the formation of the benzothiazole.[43]

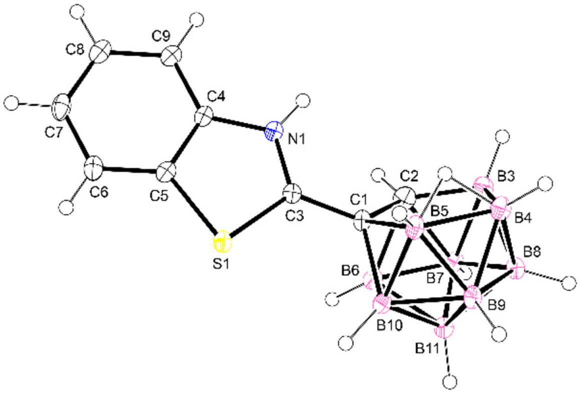
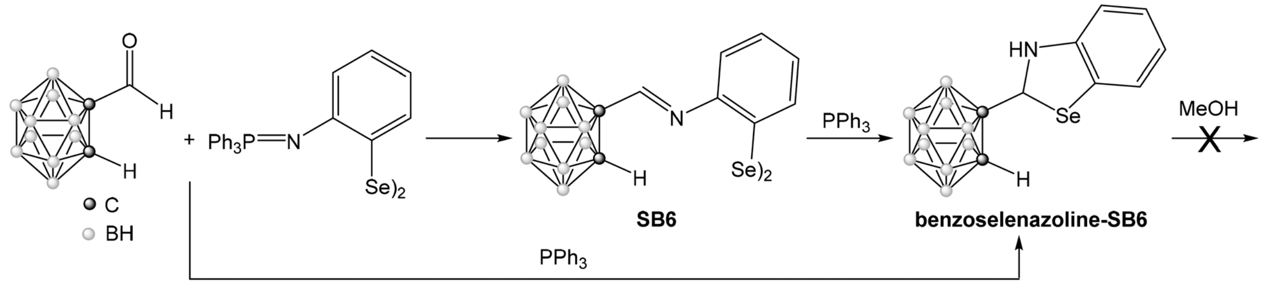


Fig. 4 Molecular structure of ***nido*-(benzothiazole-SB4)**. Thermal ellipsoids are shown at the 40% probability level.

Following our stability studies **benzoselenazoline-SB6** was refluxed with methanol. This compound was stable to this treatment, as observed for the **amine-SB3**, and the starting material was recovered after the reaction. Thus, only the derivatives with a –C(H)=N– bond attached to the carbon atom of the *ortho*-carborane cluster (Schiff base, benzothia-



Scheme 5 Synthesis of **benzoselenazoline-SB6**.

zole) promote the conversion to the *nido* derivative, while the derivatives with reduced version –C(H)$_2$–NH– (amine, benzoselenazoline) are more stable towards this conversion.

Conclusions

The aza-Wittig reaction was successfully used to synthesize carborane Schiff bases, by reaction of *C*-formyl-carborane and an aryl iminophosphorane. The method is experimentally very simple and very efficient, permitting the obtention of the otherwise difficult to obtain carboranyl-imines in multigram quantities. The method tolerates the presence of different functional groups, as shown by the preparation of a variety of compounds. All compounds were fully characterized including the solid-state.

The *closo*-carboranyl Schiff bases have been shown to promote the evolution to the *nido* derivatives. They can also be used as precursors of the corresponding *closo*-carboranyl-amines, more resistant to deboronation. Thus, the aza-Wittig methodology could provide BNCT researchers with a method to connect carborane clusters to carrier molecules through imine or amine groups, with a different tendency to evolve to their *nido* form or to retain their *closo* structure, respectively.

The aza-Wittig methodology has also been modified to generate in one step carboranyl-benzothiazole and carboranyl-benzoselenazoline, starting with the iminophosphorane disulfide or diselenide, respectively. Incidentally, this method has provided the first route to the previously unknown benzoselenazoline derivative. These compounds show a similar stability of the carborane cluster as the imine and amine derivatives, *i.e.*, a tendency to evolve to the *nido* derivative for the carboranyl-benzothiazole and a resistance to deboronation for the carboranyl-selenazolidine.

Experimental section

General

All manipulations of water-sensitive compounds were carried out under an atmosphere of dry argon using standard Schlenk techniques. Toluene and triethylamine were distilled from calcium hydride prior to use. Acetonitrile was distilled from P_4O_{10} prior to use. THF was distilled from sodium benzophenone prior to use. Methanol was dried by reaction with magnesium powder and distilled prior to use. The iminophosphoranes **I1**,[31] **I2**,[32] **I3**,[33] **I4**,[34] **I8**,[35] and the starting materials 2-(methylseleno)-aniline,[44] 2-aminophenyl diselenide,[45] *N*-tosyl-1,2-diaminobencene,[46] 3-amino-carborane,[47] and *C*-formyl-carborane,[10] are non-commercial products that were prepared using literature procedures. All further reagents were purchased from commercial sources and used as such without further purification.

Analytical methods

Elemental analyses were performed with a Thermo Finnigan Flash 1112 microanalyzer. IR spectra were recorded as KBr mulls with a Bruker IFS 66 V spectrophotometer. Mass spectra were determined using a Micromass Autospec instrument (positive electronic impact), except for compound **IB3** which was determined using a Bruker Microtof instrument in the ESI$^+$ mode. NMR spectra were recorded on a Varian Inova 500 (^{1}H 500 MHz; ^{13}C 126 MHz; ^{11}B 160 MHz, ^{31}P 202 MHz), Varian Inova 400 (^{1}H 400 MHz; ^{31}P 162 MHz); Varian Mercury 300 (^{1}H 300 MHz; ^{31}P 121 MHz) and Bruker DPX 250 (^{1}H 250 MHz). All NMR spectra were recorded in $CDCl_3$ solutions at 25 °C. Chemical shift values for ^{1}H and ^{13}C NMR were referenced to $SiMe_4$ (TMS), those for ^{31}P were referenced to 85% H_3PO_4 and those for ^{11}B NMR spectra were referenced to external $BF_3{\cdot}OEt_2$. Chemical shifts are reported in units of parts per million downfield from the reference, and all coupling constants are reported in Hertz.

Synthesis of iminophosphoranes I5–7

The iminophosphorane precursors not described in the literature were obtained following the Kirsanov reaction, using the same general procedure:

A 250 mL two-neck round-bottom flask is charged with commercial dibromotriphenylphosphine and placed under an inert argon atmosphere. A condenser equipped with a gas inlet is attached to the flask and the solid is suspended in 120 mL of dry toluene. The corresponding amine and dry triethylamine are added to the suspension. The reaction mixture is refluxed overnight (14 hours). Once reflux is complete the reaction mixture is allowed to cool and the salt formed (triethylammonium bromide, Et_3NHBr) is separated by filtration. The filtrate is concentrated to dryness using a rotary evaporator. The solid obtained is purified by recrystallization. The solid is isolated by filtration, washed with diethyl ether and dried under vacuum.

Iminophosphorane I5. Reaction mixture: dibromotriphenylphosphine (6.50 g, 15.40 mmol), 2-(methylseleno)-aniline (2.00 mL, 15.43 mmol) and dry triethylamine (4.30 mL, 30.85 mmol). Purified by recrystallization from a mixture of CH_2Cl_2/Et_2O (1 : 1). Brown solid, 4.51 g (77%).

^{1}H NMR (500 MHz, $CDCl_3$, ppm): 7.84 (m, 6H, *o*-P*Ph*$_3$), 7.52 (m, 3H, *p*-P*Ph*$_3$), 7.45 (m, 6H, *m*-P*Ph*$_3$), 7.09 (dd, 1H), 6.72 (m, 2H), 6.38 (m, 1H), 2.24 (s, 3H, SeC*H*$_3$, ^{77}Se satellites, $^2J_{\text{Se–H}}$ = 12 Hz). **^{31}P{^{1}H} NMR** (202 MHz, $CDCl_3$, ppm): −0.3. **IR** (KBr, ν/cm^{-1}): 1568m, 1482m, 1463vs, 1433s, 1328vs ν(P=N), 1286m, 1107s, 1066m, 1032m, 1016s, 741m, 715s, 690s, 588m, 528vs, 505m. **MS** (EI, *m*/*z*): 447.0 (94%) [M]$^+$, 431.9 (14%) [M − Me]$^+$, 366.0 (93%) [M − SeMe]$^+$, 261.8 (91%) [PPh$_3$]$^+$, 182.8 (100%) [PPh$_2$ − H]$^+$. **EA** (%): C 67.9, H 5.0, N 3.2. Calculated for $C_{25}H_{22}NPSe$: C 67.3, H 5.0, N 3.1.

Iminophosphorane I6. Reaction mixture: dibromotriphenylphosphine (6.80 g, 16.11 mmol), 2-aminophenyl diselenide (2.50 g, 7.30 mmol) and dry triethylamine (4.50 mL, 32.29 mmol). Purified by recrystallization from a mixture of CH_2Cl_2/Et_2O (1 : 1). Light brown solid, 2.82 g (45%).

^{1}H NMR (500 MHz, $CDCl_3$, ppm): 7.87 (m, 12H, *o*-P*Ph*$_3$), 7.50 (m, 20H: 18H *m*,*p*-P*Ph*$_3$ + 2H), 6.76 (m, 2H), 6.57 (m, 2H), 6.37 (m, 2H). **^{31}P{^{1}H} NMR** (202 MHz, $CDCl_3$, ppm): 0.7. **IR** (KBr, ν/cm^{-1}): 1569w, 1460s, 1434m, 1340m ν(P=N), 1107m, 1056w, 1015m, 745m, 717m, 694m, 526m. **MS** (EI, *m*/*z*): 860.5 (33%) [M − H]$^+$, 431.7 (72%) [M$_{1/2}$]$^+$, 349.8 (72%) [M$_{1/2}$ − Se]$^+$, 273.8 (66%) [M$_{1/2}$ − Se − Ph]$^+$, 182.8 (100%) [PPh$_2$ − H]$^+$. **EA** (%): C 65.7, H 4.6, N 3.2. Calculated for $C_{48}H_{38}N_2P_2Se_2$: C 66.8, H 4.4, N 3.2.

Iminophosphorane I7. Reaction mixture: dibromotriphenylphosphine (7.00 g, 16.58 mmol), *N*-tosyl-1,2-diaminobencene (4.00 g, 15.25 mmol) and dry triethylamine (4.62 mL, 33.19 mmol). Purified by recrystallization from a mixture of AcOEt/hexane (1 : 1). Brown solid, 4.59 g (58%).

^{1}H NMR (300 MHz, $CDCl_3$, ppm): 7.58 (m, 19H: 15H *o*,*p*,*m*-P*Ph*$_3$ + 4H SO$_2$*Ph*Me), 7.00 (m, 2H), 6.58 (m, 2H), 6.21 (d, 1H, N*H*), 2.27 (s, 3H, C*H*$_3$). **^{31}P{^{1}H} NMR** (121 MHz, $CDCl_3$, ppm): 6.9. **IR** (KBr, ν/cm^{-1}): 3182w, 3059w, 1593m, 1483vs, 1437s, 1400m, 1346vs ν(SO$_2$)$_a$ + ν(P=N), 1167vs ν(SO$_2$)$_s$, 1115s, 1047m, 1020m, 914w, 814w, 743s, 721s, 694s, 559s, 542s, 527s. **MS** (EI, *m*/*z*): 522.0 (13%) [M]$^+$, 367.2 (100%) [M − SO$_2$PhMe]$^+$, 277.2 (26%) [Ph$_3$P = NH]$^+$, 262.1 (8%) [PPh$_3$]$^+$, 182.9 (44%) [PPh$_2$ − H]$^+$. **EA** (%): C 70.2, H 5.3, N 5.2, S 5.9. Calculated for $C_{31}H_{27}N_2O_2PS$: C 71.2, H 5.2, N 5.4, S 6.1.

Iminophosphorane IB3. (Triphenylphosphinidene-B3-amino-carborane). A 50 mL Schlenk flask was charged with 3-amino-*o*-carborane (0.50 g, 3.14 mmol) and dissolved under argon in 10 mL of dry acetonitrile. The colorless solution was cooled to 0 °C with an ice bath and *tert*-butyl nitrite (0.62 mL, 5.24 mmol) was added dropwise, followed by trimethylsilyl azide (0.53 mL, 3.97 mmol). The yellow solution is stirred at room temperature for 1.5 h. After the time, a solution of PPh$_3$ (0.99 g, 3.78 mmol) in 10 mL of dry THF is added, and the reaction mixture is refluxed for 2 h. The reaction is left overnight under stirring at room temperature. The resulting solution is concentrated to give a white solid which is purified by column chromatography, using a mixture of ethyl acetate/hexane (3 : 97) as eluent. White solid, 1.11 g (84%).

^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.70 (dd, $^3J_{\text{P–H, H–H}}$ = 12.6, 7.2 Hz, 6H, *o*-P*Ph*$_3$), 7.54 (d, $^3J_{\text{H–H}}$ = 5.6 Hz, 3H, *p*-P*Ph*$_3$), 7.47 (td, $^3J_{\text{H–H}}$ = 7.6, 5.0 Hz, 6H, *m*-P*Ph*$_3$), 3.39 (s, 2H, C$_{\text{cage}}$–H), 2.77–1.08 (m, 9H, BH). **^{13}C{^{1}H} RMN** (126 MHz, $CDCl_3$, ppm): 131.2 (d, $^2J_{CP}$ = 10.4 Hz, *o*-P*Ph*$_3$), 130.8 (s, *p*-P*Ph*$_3$), 130.77 (s, $^1J_{CP}$ = 18.2 Hz, P–C), 127.5 (d, $^3J_{CP}$ = 12.3 Hz, *m*-P*Ph*$_3$), 56.2 (s, *C*$_{\text{cage}}$H). **^{11}B{^{1}H} RMN** (160 MHz, $CDCl_3$, ppm): 2.6, −6.3, −12.4, −14.1, −15.1, −15.9, −22.1. **^{31}P{^{1}H} NMR** (162 MHz, $CDCl_3$, ppm): 8.8. **IR** (KBr, ν/cm^{-1}): 3062m ν(C–H), 2578vs ν(B–H), 1432vs ν(P–N), 1110s, 719vs, 696vs, 528vs. **LR-ESI-MS** (*m*/*z*): 420.30 [M + H]$^+$. **EA** (%): C 57.4, H 6.4, N 3.3. Calculated for $C_{20}H_{26}B_{10}NP$: C 57.3, H 6.2, N 3.3.

Synthesis of schiff bases SB1–8

The Schiff Bases were obtained following the Aza-Wittig reaction, using the same general procedure:

A 100 mL one-neck round-bottom flask is charged with *C*-formyl-carborane and the corresponding iminophosphorane precursor. The solids are dissolved in 50 mL of commercial chloroform and the solution is heated at reflux for 16 hours. Once reflux is complete, the solution is concentrated to dryness using a rotary evaporator. The crude product is purified by column chromatography.

Schiff base SB1. Reaction mixture: *C*-formyl-carborane (0.50 g, 2.91 mmol) and iminophosphorane **I1** (1.17 g, 3.05 mmol). Column chromatography: ethyl acetate/hexane (1 : 4). Pale yellow solid, 0.75 g (94%).

^{1}H RMN (500 MHz, $CDCl_3$, ppm): 8.00 (s, 1H, *H*C=N), 7.23 (m, 1H), 6.94 (m, 3H), 4.51 (s, 1H, C$_{\text{cage}}$*H*), 3.84 (s, 3H, OC*H*$_3$), 3.00–1.50 (bm, 10H, B*H*). **^{13}C{^{1}H} RMN** (126 MHz, $CDCl_3$, ppm): 153.7 (H*C*=N), 151.9 (C), 136.6 (C), 128.5 (CH), 123.1 (CH), 121.0 (CH), 111.9 (CH), 73.1 (*C*$_{\text{cage}}$–[HC=N]), 56.2 (*C*$_{\text{cage}}$H), 55.8 (O*C*H$_3$). **^{11}B{^{1}H} RMN** (160 MHz, $CDCl_3$, ppm): −2.1, −3.3, −9.0, −10.8, −12.8. **IR** (KBr, ν/cm^{-1}): 3071 m ν(C$_{\text{cage}}$–H), 2595vs ν(B–H), 1634m ν(C=N), 1589m, 1495s, 1468m, 1254s, 1117m, 1026m, 750s. **MS** (EI, *m*/*z*): 277.2 (57%) [M]$^+$, 262.1 (6%) [M − Me]$^+$, 246.1 (6%) [M − OMe]$^+$, 134.0 (100%) [M − C$_2$B$_{10}$H$_{11}$]$^+$. **EA** (%): C 43.0, H 7.0, N 4.9. Calculated for $C_{10}H_{19}B_{10}NO$: C 43.3, H 6.9, N 5.0.

Schiff base SB2. Reaction mixture: *C*-formyl-carborane (0.75 g, 4.36 mmol) and iminophosphorane **I2** (1.63 g, 4.42 mmol). Column chromatography: ethyl acetate/hexane (1 : 4). Pale yellow solid, 1.14 g (99%).

^{1}H RMN (500 MHz, $CDCl_3$, ppm): 8.01 (s, 1H, *H*C=N), 7.26 (t, 1H), 7.12 (d, 1H), 7.00 (d, 1H), 6.89 (t, 1H), 6.50 (s, 1H, O*H*, *exchanges with* D$_2$O), 4.29 (s, 1H, C$_{\text{cage}}$*H*), 3.00–1.50 (bm, 10H, B*H*). **^{13}C{^{1}H} RMN** (126 MHz, $CDCl_3$, ppm): 152.2 (C), 149.5 (H*C*=N), 131.7 (C), 131.4 (CH), 120.5 (CH), 116.5 (CH), 116.2 (CH), 72.6 (*C*$_{\text{cage}}$–[HC=N]), 56.7 (*C*$_{\text{cage}}$H). **^{11}B{^{1}H} RMN** (160 MHz, $CDCl_3$, ppm): −2.8, −3.9, −9.8, −12.1, −13.6. **IR** (KBr, ν/cm^{-1}): 3470m ν(O–H), 3057w ν(C$_{\text{cage}}$–H), 2590vs ν(B–H), 1634m ν(C=N), 1589m, 1487s, 1357m, 1215s, 1018m, 748m. **MS** (EI, *m*/*z*): 263.2 (56%) $[\mathrm{M}]^+$, 121.1 (100%) $[\mathrm{M}-\mathrm{C_2B_{10}H_{11}}]^+$. **EA** (%): C 41.1, H 6.7, N 5.2. Calculated for $\mathrm{C_9H_{17}B_{10}NO}$: C 41.0, H 6.5, N 5.3.

Schiff base SB3. Reaction mixture: *C*-formyl-carborane (0.56 g, 3.26 mmol) and iminophosphorane **I3** (1.29 g, 3.23 mmol). Column chromatography: ethyl acetate/hexane (1 : 9). Yellow solid, 0.94 g (99%).

^{1}H RMN (500 MHz, CDCl$_3$, ppm): 7.78 (s, 1H, *H*C═N), 7.29 (m, 1H), 7.21 (dd, 1H), 7.15 (m, 1H), 6.85 (dd, 1H), 4.56 (s, 1H, C$_{\mathrm{cage}}$*H*), 2.46 (s, 3H, SC*H*$_3$), 3.20–1.60 (bm, 10H, B*H*). **^{13}C{^{1}H} RMN** (126 MHz, CDCl$_3$, ppm): 152.3 (H*C*═N), 144.7 (C), 134.6 (C), 128.3 (CH), 125.1 (CH), 124.7 (CH), 117.2 (CH), 72.6 (*C*$_{\mathrm{cage}}$–[HC═N]), 56.6 (*C*$_{\mathrm{cage}}$H), 14.5 (S*C*H$_3$). **^{11}B{^{1}H} RMN** (160 MHz, CDCl$_3$, ppm): −3.1, −4.2, −10.0, −11.8, −13.9. **IR** (KBr, ν/cm^{-1}): 3067m ν(C$_{\mathrm{cage}}$–H), 2635s, 2589vs, 2565vs ν(B–H), 1634m ν(C═N), 1468m, 1438m, 1124m, 1070m, 1016m, 750m, 725m. **MS** (EI, *m*/*z*): 293.0 (34%) $[\mathrm{M}]^+$, 149.9 (100%) $[\mathrm{M}-\mathrm{C_2B_{10}H_{11}}]^+$. **EA** (%): C 40.9, H 6.8, N 4.4, S 10.5. Calculated for $\mathrm{C_{10}H_{19}B_{10}NS}$: C 40.9, H 6.5, N 4.8, S 10.9.

Schiff base SB4. Reaction mixture: *C*-formyl-carborane (0.50 g, 2.91 mmol) and iminophosphorane **I4** (1.12 g, 1.46 mmol). Column chromatography: ethyl acetate/hexane (1 : 4). Yellow solid, 0.72 g (89%).

^{1}H RMN (500 MHz, CDCl$_3$, ppm): 7.83 (s, 2H, *H*C═N), 7.56 (m, 2H), 7.23 (m, 4H), 6.92 (m, 2H), 4.51 (s, 2H, C$_{\mathrm{cage}}$*H*), 3.20–1.30 (bm, 20H, B*H*). **^{13}C{^{1}H} RMN** (126 MHz, CDCl$_3$, ppm): 152.9 (2 H*C*═N), 145.2 (2 C), 132.1 (2 C), 128.8 (2 CH), 127.7 (2 CH), 127.0 (2 CH), 117.4 (2 CH), 72.5 (2 *C*$_{\mathrm{cage}}$–[HC═N]), 56.5 (2 *C*$_{\mathrm{cage}}$H). **^{11}B{^{1}H} RMN** (160 MHz, CDCl$_3$, ppm): −2.7, −3.9, −9.9, −11.7, −13.8. **IR** (KBr, ν/cm^{-1}): 3062m ν(C$_{\mathrm{cage}}$–H), 2592vs ν(B–H), 1639m ν(C═N), 1576m, 1462m, 1340w, 1197w, 1160m, 1126m, 1036m, 756m, 724m. **MS** (EI, *m*/*z*): 557.5 (2%) $[\mathrm{M}]^+$, 278.1 (100%) $[\mathrm{M_{1/2}}]^+$, 136.0 (97%) $[\mathrm{M_{1/2}}-\mathrm{C_2B_{10}H_{11}}]^+$. **EA** (%): C 39.1, H 5.8, N 5.1, S 11.7. Calculated for $\mathrm{C_{18}H_{32}B_{20}N_2S_2}$: C 38.8, H 5.8, N 5.0, S 11.5.

Schiff base SB5. Reaction mixture: *C*-formyl-carborane (0.50 g, 2.91 mmol) and iminophosphorane **I5** (1.30 g, 2.91 mmol). Column chromatography: ethyl acetate/hexane (1 : 4). Yellow solid, 0.98 g (99%).

^{1}H RMN (500 MHz, CDCl$_3$, ppm): 7.76 (s, 1H, *H*C═N), 7.27 (m, 2H), 7.17 (m, 1H), 6.84 (dd, 1H), 4.52 (s, 1H, C$_{\mathrm{cage}}$*H*), 2.28 (s, 3H, SeC*H*$_3$), 3.20–1.60 (bm, 20H, B*H*). **^{13}C{^{1}H} RMN** (126 MHz, CDCl$_3$, ppm): 152.1 (H*C*═N), 145.8 (C), 130.4 (C), 128.6 (CH), 127.6 (CH), 126.1 (CH), 117.1 (CH), 72.6 (*C*$_{\mathrm{cage}}$–[HC═N]), 56.6 (*C*$_{\mathrm{cage}}$H), 5.2 (Se*C*H$_3$). **^{11}B{^{1}H} RMN** (160 MHz, CDCl$_3$, ppm): −1.9, −3.0, −8.9, −10.7, −12.8. **IR** (KBr, ν/cm^{-1}): 3068m ν(C$_{\mathrm{cage}}$–H), 2622s, 2587vs, 2566vs ν(B–H), 1634m ν(C═N), 1574w, 1466m, 1427m, 1263m, 1123m, 1067m, 1035m, 1026m, 803m, 752m, 722m. **MS** (EI, *m*/*z*): 341.2 (43%) $[\mathrm{M}]^+$, 325.2 (7%) $[\mathrm{M}-\mathrm{Me}]^+$, 246.2 (64%) $[\mathrm{M}-\mathrm{SeMe}]^+$, 198.0 (100%) $[\mathrm{M}-\mathrm{C_2B_{10}H_{11}}]^+$. **EA** (%): C 36.0, H 5.8, N 4.1. Calculated for $\mathrm{C_{10}H_{19}B_{10}NSe}$: C 35.3, H 5.6, N 4.1.

Schiff base SB6. Reaction mixture: *C*-formyl-carborane (0.50 g, 2.91 mmol) and iminophosphorane **I6** (1.25 g, 1.45 mmol). Column chromatography: ethyl acetate/hexane (1 : 4). Pale yellow solid, 0.71 g (75%).

^{1}H RMN (250 MHz, CDCl$_3$, ppm): 7.88 (s, 2H, *H*C═N), 7.61 (d, 2H), 7.25 (m, 4H), 6.97 (d, 2H), 4.52 (s, 2H, C$_{\mathrm{cage}}$*H*), 3.20–1.60 (bm, 20H, B*H*). **^{13}C{^{1}H} RMN** (126 MHz, CDCl$_3$, ppm): 152.4 (2 H*C*═N), 145.6 (2 C), 130.2 (2 CH), 129.4 (2 CH), 128.1 (2 CH), 127.8 (2 C), 117.0 (2 CH), 72.5 (2 *C*$_{\mathrm{cage}}$–[HC═N]), 56.6 (2 *C*$_{\mathrm{cage}}$H). **^{11}B{^{1}H} RMN** (160 MHz, CDCl$_3$, ppm): −1.8, −2.6, −8.8, −10.7, −12.7. **IR** (KBr, ν/cm^{-1}): 3061m ν(C$_{\mathrm{cage}}$–H), 2589vs ν(B–H), 1638m ν(C═N), 1459m, 1262m, 1093m, 1065m, 1044m, 1028m, 1015m, 803m, 755m, 722m. **MS** (EI, *m*/*z*): 324.8 (13%) $[\mathrm{M_{1/2}}]^+$, 184.4 (100%) $[\mathrm{M_{1/2}}-\mathrm{C_2B_{10}H_{11}}]^+$. **EA** (%): C 33.4, H 4.8, N 4.1. Calculated for $\mathrm{C_{18}H_{32}B_{20}N_2Se_2}$: C 33.2, H 5.0, N 4.3.

Schiff base SB7. Reaction mixture: *C*-formyl-carborane (0.66 g, 3.84 mmol) and iminophosphorane **I7** (2.00 g, 3.83 mmol). Column chromatography: ethyl acetate/hexane (1.5 : 8.5). Yellow solid, 1.19 g (75%).

^{1}H RMN (500 MHz, CDCl$_3$, ppm): 7.70 (s, 1H, *H*C═N), 7.66 (dd, 1H), 7.57 (d, 2H), 7.36 (s, 1H, N*H*), 7.31 (m, 1H), 7.19 (d, 2H), 7.10 (m, 1H), 6.91 (dd, 1H), 4.22 (s, 1H, C$_{\mathrm{cage}}$*H*), 2.38 (s, 3H, C*H*$_3$), 3.20–1.60 (bm, 10H, B*H*). **^{13}C{^{1}H} RMN** (126 MHz, CDCl$_3$, ppm): 152.2 (H*C*═N), 144.2 (C), 137.0 (C), 136.2 (C), 132.6 (C), 130.0 (CH), 129.7 (2 CH), 126.9 (2 CH), 125.6 (CH), 122.5 (CH), 117.2 (CH), 72.2 (*C*$_{\mathrm{cage}}$–[HC═N]), 56.7 (*C*$_{\mathrm{cage}}$H), 21.5 (*C*H$_3$). **^{11}B{^{1}H} RMN** (160 MHz, CDCl$_3$, ppm): −1.8, −8.8, −11.2, −12.7, −13.7. **IR** (KBr, ν/cm^{-1}): 3281m ν(N–H), 3072m ν(C$_{\mathrm{cage}}$–H), 2590vs ν(B–H), 1634w ν(C═N), 1491m, 1393m, 1342m ν(SO$_2$)$_{\mathrm{a}}$, 1325m, 1261m, 1169vs ν(SO$_2$)$_{\mathrm{s}}$, 1094s, 1018m, 914w, 812s, 758m, 721m, 683m, 573m, 538m. **MS** (EI, *m*/*z*): 415.8 (1%) $[\mathrm{M}]^+$, 262.1 (100%) $[\mathrm{M}-\mathrm{SO_2PhMe}]^+$, 154.8 (17%) $[\mathrm{SO_2PhMe}]^+$. **EA** (%): C 45.6, H 5.9, N 6.4, S 7.2. Calculated for $\mathrm{C_{16}H_{24}B_{10}N_2O_2S}$: C 46.1, H 5.8, N 6.7, S 7.7.

Bis(schiff base) SB8. Reaction mixture: *C*-formyl-carborane (0.70 g, 4.07 mmol) and bis(iminophosphorane) **I8** (1.28 g, 2.03 mmol). Column chromatography: ethyl acetate/hexane (3 : 7). Pale yellow solid, 0.30 g (35%).

^{1}H RMN (300 MHz, CDCl$_3$, ppm): 7.65 (s, 2H, HC═N), 7.28 (d, 2H, *o*-P*Ph*$_3$), 6.98 (t, 2H, *m*-P*Ph*$_3$), 4.41 (s, 2H, C$_{\mathrm{cage}}$–H), 2.85–1.60 (bm, 10H, B–H).**^{13}C RMN** (126 MHz, CDCl$_3$, ppm): 154.3 (H*C*═N), 140.8 (C), 128.5 (CH), 120.7 (CH), 72.1 (*C*$_{\mathrm{cage}}$–[HC═N]), 56.9 (C$_{\mathrm{cage}}$–H). **^{11}B{^{1}H} RMN** (160 MHz, CDCl$_3$, ppm): −1.8, −2.8, −8.8, −10.9, −12.7, −13.6, −14.8. **IR** (IR-ATR, ν/cm^{-1}): 3074m, 2604s, 2577s ν(B–H), 1656m, 1634w ν(C═N), 1478w, 1340w, 1262w, 1198w, 1128m, 1109m, 1065w, 1039w, 1016m, 800w, 759m, 722m, 704w, 695w. **MS** (EI, *m*/*z*): 273.5 (100%) $[\mathrm{M}-(\mathrm{carboranil})]^+$, 416.7 (7.4%) $[\mathrm{M}]^+$. **EA** (%): C 34.1, H 6.5, N 6.4. Calculated for $\mathrm{C_{12}H_{28}B_{20}N_2}$: C 34.6, H 6.7, N 6.7.

Synthesis of *nido*-SB3. A 50 mL Schlenk was charged with Schiff Base **SB3** (0.20 g, 0.69 mmol) and dissolved in 25 mL of dry methanol under argon. The solution was refluxed 8 hours. The final solution was concentrated to dryness using a rotary evaporator and dried under vacuum. Orange solid, 0.19 g (96%).

^{1}H RMN (500 MHz, CDCl$_3$, ppm): 10.70 (bs, 1H, N*H*), 8.40 (d, 1H, *H*C═N, $^3J_{\mathrm{H-H}}$ = 16 Hz), 7.65 (m, 1H), 7.48 (m, 2H), 7.35 (m, 1H), 2.52 (s, 3H, SC*H*$_3$), 2.42 (s, 1H, C$_{\mathrm{cage}}$*H*), −2.27 (bs, 1H, B*H*B). **^{11}B{^{1}H} RMN** (160 MHz, CDCl$_3$, ppm): −5.2, −5.7, −11.3,

−12.7, −17.8, −24.0, −29.1, −31.3. **IR** (KBr, ν/cm^{-1}): 3423w, 3197w ν(N–H), 2927w $\nu(\mathrm{C_{cage}}$–H), 2545vs ν(B–H), 1637s ν(C═N), 1585m, 1475w, 1452w, 1435w, 1396w, 1385w, 1359w, 1322w, 1291m, 1211w, 1166m, 1064w, 1007m, 975w, 959w, 757m ν(C–S). **MS** (EI, *m*/*z*): 283.2 (32%) $[\mathrm{M}]^+$, 267.1 (21%) $[\mathrm{M-Me}]^+$, 139.0 (100%) $[\mathrm{1\text{-}NH_2-2\text{-}SMe-Ph}]^+$, 124.0 (96%) $[\mathrm{1\text{-}NH_2-2\text{-}S-Ph}]^+$. **EA** (%): C 42.1, H 7.3, N 4.7, S 10.7. Calculated for $\mathrm{C_{10}H_{20}B_9NS}$: C 42.3, H 7.1, N 4.9, S 11.3.

Synthesis of amine-SB3. A 100 mL round-bottom flask is charged with Schiff Base **SB3** (1.07 g, 3.66 mmol) and dissolved in 50 mL of a mixture of THF and acetic acid (1 : 1). The solution is cooled with an ice/water bath (0 °C) and sodium cyanoborohydride ($\mathrm{NaBH_3CN}$) (0.76 g, 12.10 mmol) is added in small portions, observing a loss of color from yellow to colorless. The cooling bath is removed and the reaction is stirred at room temperature overnight (16 h). The THF is removed in a rotary evaporator and the acetic acid is neutralized with a saturated solution of sodium bicarbonate ($\mathrm{NaHCO_3}$). The crude product is dissolved in 50 mL of dichloromethane and washed with water (2 × 30 mL). The organic phase is dried with anhydrous $\mathrm{Na_2SO_4}$, and concentrated in a rotary evaporator. The residue obtained is purified by column chromatography using a mixture of ethyl acetate and hexane (2 : 8), yielding a colorless oil that solidifies overnight in the refrigerator (1.08 g, 100%).

^{1}**H RMN** (500 MHz, $\mathrm{CDCl_3}$, ppm): 7.43 (dd, 1H), 7.21 (m, 1H), 6.79 (m, 1H), 6.65 (dd, 1H), 4.80 (bs, 1H, N*H*), 3.97 (s, 2H, C*H*$_2$), 3.77 (s, 1H, C$_{\mathrm{cage}}$*H*), 2.34 (s, 3H, SC*H*$_3$), 3.10–1.50 (bm, 10H, B*H*). ^{13}**C{^{1}H} RMN** (126 MHz, $\mathrm{CDCl_3}$, ppm): 145.8 (C), 134.6 (CH), 129.6 (CH), 121.0 (C), 119.4 (CH), 110.0(CH), 75.4 (*C*$_{\mathrm{cage}}$–C), 58.4 (*C*$_{\mathrm{cage}}$H), 49.3 (*C*H$_2$), 18.6 (S*C*H$_3$). ^{11}**B{^{1}H} RMN** (160 MHz, $\mathrm{CDCl_3}$, ppm): −3.2, −6.1, −10.2, −12.6, −14.1. **IR** (KBr, ν/cm^{-1}): 3366m ν(N–H), 3067w $\nu(\mathrm{C_{cage}}$–H), 2923w, 2585vs ν(B–H), 1587s, 1504vs, 1454m, 1361w, 1322m, 1284m, 1266m, 1165m, 1112m, 1042m, 1018m, 750s, 725m. **MS** (EI, *m*/*z*): 295.1 (100%) $[\mathrm{M}]^+$, 280.0 (10%) $[\mathrm{M-Me}]^+$, 247.0 (22%) $[\mathrm{M-SMe}]^+$, 151.8 (93%) $[\mathrm{M-(1,2\text{-}C_2B_{10}H_{11})}]^+$, 135.7 (62%) $[\mathrm{M-(1,2\text{-}C_2B_{10}H_{11})-Me}]^+$. **EA** (%): C 39.3, H 7.1, N 4.5, S 9.7. Calculated for $\mathrm{C_{10}H_{21}B_{10}NS}$: C 40.6, H 7.2, N 4.7, S 10.8.

Synthesis of benzothiazole-SB4. A 100 mL one-neck round-bottom flask is charged with *C*-formyl-carborane (0.93 g, 5.42 mmol), the iminophosphorane **I4** (2.08 g, 2.71 mmol) and triphenylphosphine (0.71 g, 2.71 mmol). The solids are dissolved in 50 mL of commercial chloroform and the solution is heated at reflux for 16 hours. Once reflux is complete, the solution is concentrated to dryness using a rotary evaporator. The residue obtained is purified by column chromatography using a mixture of ethyl acetate and hexane (1 : 4). Pale brown solid, 1.10 g (73%).

^{1}**H RMN** (500 MHz, $\mathrm{CDCl_3}$, ppm): 7.97 (m, 1H), 7.85 (m, 1H), 7.53 (m, 1H), 7.46 (m, 1H), 4.75 (s, 1H, C$_{\mathrm{cage}}$*H*), 3.20–1.70 (bm, 10H, B*H*). ^{13}**C{^{1}H} RMN** (126 MHz, $\mathrm{CDCl_3}$, ppm): 161.1 (*C*═N), 151.7 (C), 135.9 (C), 127.1 (CH), 126.6 (CH), 123.7 (CH), 121.6 (CH), 70.8 (*C*$_{\mathrm{cage}}$–C), 59.2 (*C*$_{\mathrm{cage}}$H). ^{11}**B{^{1}H} RMN** (160 MHz, $\mathrm{CDCl_3}$, ppm): −2.5, −3.2, −8.4, −10.4, −11.0, −12.8. **IR** (KBr, ν/cm^{-1}): 3071s $\nu(\mathrm{C_{cage}}$–H), 2594vs, 2575vs ν(B–H), 1504w $\nu(\mathrm{C{=}N})_{\mathrm{thiazole}}$, 1458m, 1433m, 1261m, 1153m, 1067m, 1016m, 804m, 754s, 725s. **MS** (EI, *m*/*z*): 277.2 (100%) $[\mathrm{M}]^+$, 135.9 (91%) $[\mathrm{M-(1,2\text{-}C_2B_{10}H_{11})}]^+$, 124.0 (74%) $[\mathrm{C_6H_6NS}]^+$. **EA** (%): C 38.8, H 5.4, N 4.9, S 10.5. Calculated for $\mathrm{C_9H_{15}B_{10}NS}$: C 39.0, H 5.5, N 5.1, S 11.6.

Recrystallization of a sample of **benzothiazole-SB4** in methanol produced the formation of single crystals of ***nido*-(benzothiazole-SB4)**.

^{11}**B{^{1}H} RMN** (160 MHz, $\mathrm{CDCl_3}$, ppm): −5.1, −7.7, −11.0, −15.3, −17.3, −21.9, −30.5, −32.9. **IR** (KBr, ν/cm^{-1}): 3538m ν(N–H), 2527vs ν(B–H), 1606w, 1584w, 1541m, 1443m, 1288w, 1252w, 1208w, 1159w, 1072w, 1004m, 761m.

Synthesis of benzoselenazoline-SB6. This compound was prepared following the same procedure used for **benzothiazole-SB4** starting with *C*-formyl-carborane (0.45 g, 2.62 mmol), the iminophosphorane **I6** (1.14 g, 1.32 mmol) and triphenylphosphine (0.34 g, 1.32 mmol). Purification by column chromatography using a mixture of ethyl acetate and hexane (1 : 4). Orange solid, 0.60 g (70%).

^{1}**H RMN** (500 MHz, $\mathrm{CDCl_3}$, ppm): 7.12 (dd, 1H), 7.06 (m, 1H), 6.82 (m, 1H), 6.70 (dd, 1H), 5.89 (d, 1H, *H*C–NH, $^3J_{\mathrm{H-H}} = 4$ Hz), 4.74 (bd, 1H, N*H*), 4.27 (s, 1H, C$_{\mathrm{cage}}$*H*), 3.20–1.00 (bm, 10H, B*H*). ^{13}**C{^{1}H} RMN** (126 MHz, $\mathrm{CDCl_3}$, ppm): 145.8 (C), 127.1 (CH), 124.8 (CH), 121.7 (CH), 119.5 (C), 111.0 (CH), 81.6 (*C*$_{\mathrm{cage}}$–C), 62.7 (H*C*–NH), 61.9 (*C*$_{\mathrm{cage}}$H). ^{11}**B{^{1}H} RMN** (160 MHz, $\mathrm{CDCl_3}$, ppm): −3.0, −4.5, −8.2, −9.0, −10.3, −12.7, −13.7. **IR** (KBr, ν/cm^{-1}): 3370m ν(N–H), 3067w $\nu(\mathrm{C_{cage}}$–H), 2572vs ν(B–H), 1579w, 1513w, 1469m, 1436w, 1411w, 1330w, 1293w, 1260m, 1187w, 1087m, 1040w, 1017m, 924w, 747m, 719m, 692w, 560w. **MS** (EI, *m*/*z*): 326.0 (8%) $[\mathrm{M-H}]^+$, 183.9 (100%) $[\mathrm{M-(1,2\text{-}C_2B_{10}H_{11})}]^+$. **EA** (%): C 33.3, H 5.4, N 4.1. Calculated for $\mathrm{C_9H_{17}B_{10}NSe}$: C 33.1, H 5.3, N 4.3.

Author contributions

P. C.: experimental work; I. V.-C.: experimental work and manuscript preparation; A. S.-P. research conception, research supervision, single crystal X-ray analysis and manuscript preparation.

Data availability

The data supporting this article have been included as part of the ESI.†

Crystallographic data for compounds **SB1–SB5**, **SB7**, ***nido*-SB3**, **amine-SB3**, ***nido*-benzothiazole-SB4** and **IB3** have been deposited at the Cambridge Crystallographic Data Centre under CCDC 2393159–2393168.†

Conflicts of interest

There are no conflicts to declare.

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